

Mechanically activated disproportionation of NdFeB alloy by ball milling in hydrogen^①

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Abstract: Mechanically activated disproportionation of Nd₁₂Fe₈₂B₆ alloy by ball milling in hydrogen atmosphere was experimentally investigated. The aspects of thermodynamics and kinetics for the mechanically activated disproportionation of the NdFeB alloy were discussed. Both the evolution of the disproportionation reaction and the corresponding microstructure change of the alloy during milling were characterized by X-ray diffraction (XRD) analysis. The results show that the matrix phase Nd₂Fe₁₄B of the as-cast Nd₁₂Fe₈₂B₆ alloy can be disproportionated into a mixture of Nd hydride (H₃Nd₂), FeB/Fe₂B, and α -Fe, by ball milling under hydrogen pressure of 0.2 MPa. The as-disproportionated phases are of the size about 20 nm, suggesting that ball milling in hydrogen is an effective route for low-temperature disproportionation processing of the NdFeB alloy to ensure a full nanostructured as-disproportionated microstructure. This is the basis for synthesizing Nd₂Fe₁₄B/ α -Fe nano composites with magnetic exchange coupling effect by subsequent desorption-recombination processing.

Key words: mechanically activated disproportionation; NdFeB alloy; nanostructured phases; ball milling

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1 INTRODUCTION

Since the discovery of the uniaxial Nd₂Fe₁₄B compound in 1983^[1,2], the NdFeB alloys have been widely used for permanent magnet applications owing to their excellent magnetic properties, such as high coercivity, high-energy products^[3,4]. In these rare earth permanent magnets, a further exciting recent development is the suggestion of nano-composite exchange magnets combining the large coercivities in hard magnets with large inductions found in softer transition metal magnets^[5,6]. Indeed, the nano-composite magnets have been the topic of many recent researches^[7-10].

Hydrogenation, disproportionation, desorption, and recombination (HDDR) has been reported as a very promising technique to produce highly coercive and high energy product NdFeB powders with submicron Nd₂Fe₁₄B grains (about 0.3 μ m), directly from the as-cast ingot alloy^[11,12]. However, it is very difficult or impossible to produce nanocrystalline Nd₂Fe₁₄B grains by the conventional HDDR process, owing to the fact that the typical processing temperature is as high as 800 °C, thus leading to significant grain growth which occurs simultaneously with the progress of new phase nucleation during both the disproportionation and the recombination reaction.

To prepare nanostructured NdFeB alloy powders based on the principle of HDDR processing, we propose a new disproportionation route, i. e., the low-temperature disproportionation process activated by ball milling of the alloy powders in hydrogen. The new process is found to be an effective route to obtain nanostructured as-disproportionated microstructure, which is the very important precursor for further synthesis of Nd₂Fe₁₄B/ α -Fe nano-composites by subsequent desorption-recombination processing at temperature much lower than that used for the conventional HDDR process. The present paper reports an experimental investigation, and also some theoretical discussion with respect to the aspects of thermodynamics and kinetics, on the mechanically activated disproportionation by ball milling of the NdFeB alloy in hydrogen.

2 EXPERIMENTAL

The commercially available as-cast Nd₁₂Fe₈₂B₆ (atomic ratio) alloy, with impurities in total less than 0.5%, was used as the starting material. Before milling, the as-cast ingot alloy was crushed into powders by a mechanical hammer. The powders were then loaded into a planetary ball-mill and mechanically milled in hydrogen atmosphere. The milling vials were made of stainless steel. The milling balls were 6

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8 mm in diameter and made of hardened high-strength chromium steel.

To investigate the effect of milling intensity on the disproportionation reaction of the alloy, different ball to powder mass ratios (10:1 and 20:1) and mill rotation velocities (280 and 360 r/min) were used, respectively. For all runs of milling experiments, the hydrogen pressure in the milling vial was kept at 0.2 MPa, and the milled powders in each batch was 20 g.

For the purpose of preventing from oxidation, the alloy powders were kept in an argon-filled glove box, and the charging and discharging of the alloy powders and the milling balls were performed in the glove box. Before milling operation, the charged vial was evacuated and then filled with hydrogen until a pressure of 0.2 MPa was reached. This procedure was repeated for any subsequent discharging operation to take sample powders during milling. The sample powders obtained under different milling conditions were characterized by X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation. The crystallite size of the phases of the milled powders was calculated on the basis of the half-width of the most intensive diffraction peaks of the XRD patterns.

3 RESULTS AND DISCUSSION

3.1 Effect of milling intensity on disproportionation

Fig. 1 shows the XRD patterns of the $\text{Nd}_{12}\text{Fe}_{82}\text{B}_6$ alloy powders milled for various times by using relatively lower milling intensity parameters, with the ball to powder mass ratio being 10:1 and the mill rotation velocity 280 r/min respectively. As it can be seen from the XRD patterns, the starting alloy powders (denoted by 0 h) are characterized in structure as a dominant tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, i. e., the magnetic matrix phase of the NdFeB alloy, and a small portion of $\alpha\text{-Fe}$. After milling for 3 h, new phases H_5Nd_2 , Fe_2B , and FeB , which are not found in the starting alloy powders, are observed, while the diffraction peaks of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase become weaker, suggesting that a portion of the tetragonal $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase has disproportionated during milling. With the increase of the milling time, more and more $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase becomes disproportionated. Meanwhile, the diffraction peaks of both the original and the as-disproportionated phases broaden gradually with increasing milling time, suggesting a corresponding decrease in crystallite size. However, it is noted that even after milling for 20 h, some non-disproportionated $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is still observed.

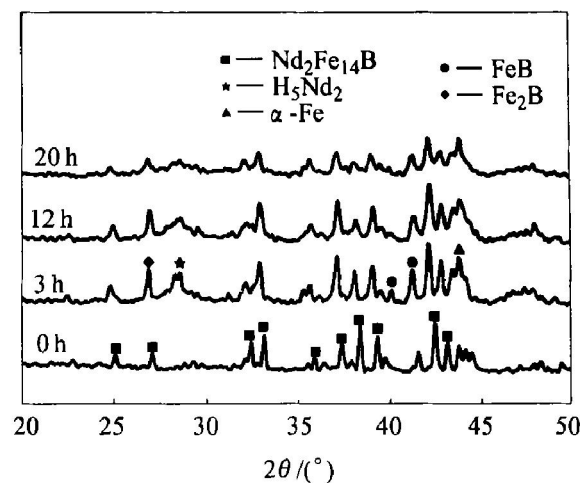


Fig. 1 XRD patterns of $\text{Nd}_{12}\text{Fe}_{82}\text{B}_6$ powders milled using low-intensity parameters

Fig. 2 shows the XRD patterns of the $\text{Nd}_{12}\text{-Fe}_{82}\text{B}_6$ alloy powders milled continuously and intermittently respectively for 12 h by using higher milling intensity parameters (ball to powder mass ratio of 20:1, and mill rotation velocity of 360 r/min), in comparison with the original starting powders. It is noted that milling continuously for 12 h results in the full disproportionation of the alloy powders. In contrast, non-disproportionated $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is observed in the powders milled for the same time when the intermittent milling route is used. The results shown in Figs. 1 and 2 suggest that low-temperature disproportionation of the NdFeB alloy can be activated by milling the alloy powders in hydrogen atmosphere, and this process can be accelerated significantly by providing the system with a higher milling energy input per unit time.

3.2 Thermodynamics and kinetics analysis

When exposed to the hydrogen environment, the NdFeB alloy absorbs hydrogen and the matrix $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase combines with hydrogen to form,

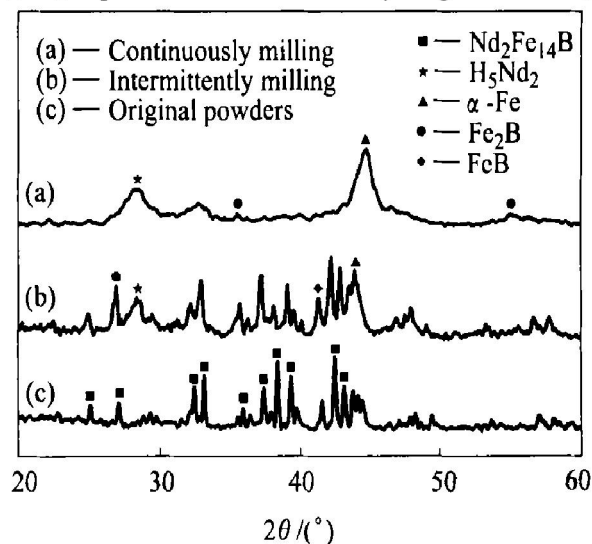
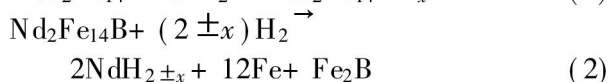
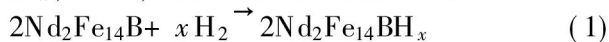


Fig. 2 XRD patterns of $\text{Nd}_{12}\text{Fe}_{82}\text{B}_6$ powders milled using high-intensity parameters

depending on the environmental conditions, either a solid solution $\text{Nd}_2\text{Fe}_{14}\text{BH}_x$ or an intimate mixture of $\text{NdH}_{2\pm x}$, $\alpha\text{-Fe}$, and Fe_2B as follows^[13]:



where the first reaction is interpreted as hydrogenation, and the second disproportionation. It is well known that the hydrogenation reaction is much easier to take place than the disproportionation reaction, owing to the fact that the latter demands a structural reform to decompose the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase into the new as-disproportionated phases. Since the disproportionation reaction is the main concern of the present study, here our discussion will be focused on this topic.

Referring to Ref. [14], we list in Table 1 the standard formation free energy data of the individual $\text{Nd}_2\text{Fe}_{14}\text{B}$, $\text{NdH}_{2\pm x}$, and Fe_2B phases, denoted by $\Delta G_{\text{Nd}_2\text{Fe}_{14}\text{B}}$, $\Delta G_{\text{NdH}_{2\pm x}}$, $\Delta G_{\text{Fe}_2\text{B}}$ respectively, and the free energy change of disproportionation reaction of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, denoted by ΔG . Thermodynamically, the disproportionation reaction can occur more easily with the decrease of temperature, because the free energy change for the disproportionation reaction became more negative at a lower temperature. That is to say, it is reasonably possible for the disproportionation reaction to take place even at a very low temperature. However, thermal processing of the NdFeB alloy in hydrogen reveals that the actual temperature for the disproportionation of the alloy needs to be as high as 650 °C because of the kinetic energy barrier due to the element rearrangement and structure reform associated with disproportionation. Therefore, a certain amount of energy must be provided by either raising the temperature of the system, as seen in conventional HDDR processing, or other means to conquer this energy barrier.

Recently, mechanical milling has been reported as an effective means of activation in solid-gas

reactions^[15,16]. During milling, the external kinetic energy of the colliding balls is passed to the milled powders, resulting in an accumulative increase in stored internal energy of the milled powders with increasing milling time. It is the increased store energy due to ball milling that acts as the driving force of the mechanically activated solid-gas reactions. Therefore, it is very important to evaluate the energy transferred in a given time to the milled powders during milling, so as to relate the reaction kinetics to the milling parameters.

For the milling process with the use of a planetary mill, the total energy (E_t) transferred to per unit mass of powders (W_p) in a given milling time (t) can be estimated by the model proposed by Magini et al^[17,18], as given below:

$$E_t = \frac{vE'_b n_b t}{W_p} \quad (3)$$

$$E'_b = \frac{1}{2} m_b v_b^2, \quad v_b = \frac{2\pi w_p (R_p + R_v)}{60} \quad (4)$$

where v is the frequency of colliding impacts^[19]; E'_b is the kinetic energy of an individual ball; n_b is the number of balls; W_p is the mass of powders; R_p is the distance between mill center and vial center; R_v is the radius of vial; m_b is the mass of an individual ball; w_p is the angular velocity of mill, r/min; v_b is the ball velocity.

Making use of the milling parameters, the kinetic energy transferred to the NdFeB powders can be calculated for either milling case chosen in the present study, as listed in Table 2. It is noted that the energy transferred to the powders for a certain milling time can be enhanced significantly by using high-intensity milling parameters, owing to the fact that both the energy transferred by an individual colliding impact and the total colliding events in a given milling time increases remarkably. In the case that high-intensity milling parameters (ball to powder mass ratio 20: 1, and mill rotation velocity 360 r/min) are used, the energy transferred by an individual colliding impact is as high as 1.37×10^{-2} J/g, and the total energy transferred to the powders milled continuously for 12 h reaches 481.6 kJ/g. In contrast, the energy transferred by an individual colliding impact is 0.85×10^{-2} J/g, and the total energy transferred to the powders milled for 20 h reaches only 192 kJ/g when low-intensity milling parameters (ball to powder mass ratio 10: 1, and mill rotation velocity 280 r/min) are used. Taking it for granted that the more the energy transferred to the powders during milling, the greater the kinetic driving force to the disproportionation reaction, we expect that the mechanically activated disproportionation reaction of the NdFeB

Table 1 Free energy change of $\text{Nd}_2\text{Fe}_{14}\text{B}$ disproportionation reaction

T/K	$\Delta G_{\text{Nd}_2\text{Fe}_{14}\text{B}}/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta G_{\text{NdH}_{2\pm x}}/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta G_{\text{Fe}_2\text{B}}/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta G/(\text{kJ} \cdot \text{mol}^{-1})$
298	-178.0	-167.5	-75.7	-232.7
400	-173.2	-152.9	-74.6	-207.2
600	-163.6	-123.7	-72.5	-156.3
800	-154.0	-94.5	-70.5	-105.5
1 000	-144.5	-65.3	-68.4	-54.5
1 200	-134.9	-36.1	-66.3	-3.6
1 400	-125.4	-6.9	-64.2	+47.7

Table 2 Energy transferred to powders milled by using different parameters

Milling intensity	v / s^{-1}	$w / (\text{r} \cdot \text{min}^{-1})$	Ball diameter/mm	$E'_{\text{b}} / (\text{J} \cdot \text{g}^{-1})$	$E_{\text{t}} / (\text{kJ} \cdot \text{g}^{-1})$			
					3 h	8 h	12 h	20 h
High intensity	83	360	8	1.37×10^{-2}	120.4	320.9	481.6	802.7
Low intensity	64	280	6	0.85×10^{-2}	28.8	76.7	115.2	192

alloy will be accelerated remarkably when high-intensity milling parameters are used. Obviously, this is in good accordance with the experimental results as shown in Figs. 1 and 2.

3.3 Change of crystallite size during milling

Fig. 3 shows the changes of crystallite sizes of the non-disproportionated matrix $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and the as-disproportionated phases Fe_2B , FeB , and H_5Nd_2 during milling with the use of low-intensity parameters. In general, crystallite refinement due to milling is observed. However, difference is obvious between the non-disproportionated matrix phase, $\text{Nd}_2\text{Fe}_{14}\text{B}$, and the as-disproportionated phases Fe_2B , FeB , and H_5Nd_2 . The as-disproportionated phases are found to possess a nano-structure, with the average crystallite size being in the range of 20–25 nm depending on milling time. In contrast, the simultaneously milled but non-disproportionated matrix $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase is much coarser, with its crystallite size being still above 300 nm even after milling for 20 h. This suggests that the peculiar nano-structure featured by the as-disproportionated phases Fe_2B , FeB , and H_5Nd_2 is attributed mainly to the low-temperature disproportionation reaction rather than the effect of mere milling, and that the very importance of mechanical milling lies in that it provides the system with sufficient energy to activate the reaction.

Table 3 shows the crystallite sizes of the as-

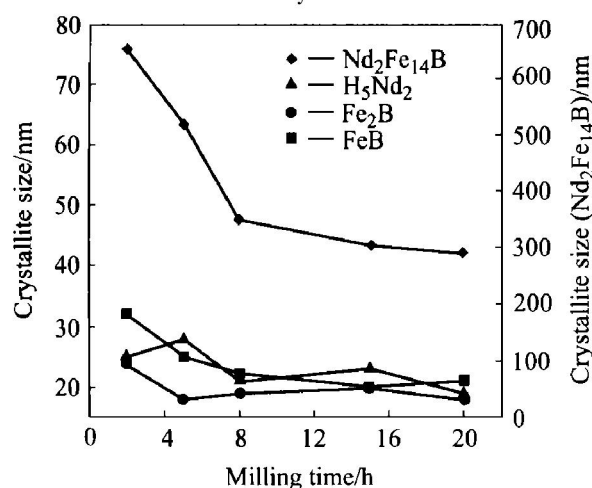


Fig. 3 Curves of crystallite size vs milling time for low-intensity milling

disproportionated phases Fe_2B , FeB , and H_5Nd_2 prepared using different milling intensities for 12 h. It is noted that the effect of milling intensity on the crystallite size is minor, though a higher milling intensity gives somewhat finer as-disproportionated phases, again suggesting a mechanism that the disproportionation reaction plays a dominant role in the crystallite refining of the as-disproportionated phases.

Table 3 Crystallite sizes of as-disproportionated phases (nm)

Milling intensity	H_5Nd_2	Fe_2B	FeB
High intensity	21.71	18.07	16.72
Low intensity	24.37	22.62	17.13

4 CONCLUSIONS

1) The low-temperature disproportionation of the $\text{Nd}_{12}\text{Fe}_{82}\text{B}_6$ alloy can be activated by ball milling of the alloy powders in hydrogen, with the reaction kinetics strongly depending on the rate of energy input during milling. The disproportionation process can be significantly accelerated, and the milling time needed for full disproportionation of the alloy correspondingly can be shortened, by using high-intensity milling parameters.

2) The as-disproportionated $\text{Nd}_{12}\text{Fe}_{82}\text{B}_6$ alloy obtained by ball milling in hydrogen consists of a mixture of phases Fe_2B / FeB , H_5Nd_2 , and $\alpha\text{-Fe}$, with crystallite size about 20 nm. This nano-sized as-disproportionated structure is attributed mainly to the fact that the mechanically activated disproportionation reaction is performed at low-temperature, with mechanical energy serving as the driving force.

3) The effect of milling intensity on the crystallite size of the disproportionated phases is much less than that on the disproportionation rate of the alloy. That is to say, the disproportionation reaction plays a dominant role in crystallite refining of the disproportionated phases, while the milling intensity controls the progress of the disproportionation reaction.

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