Formation of $Nd_2Fe_{14}B$ hydride by milling of anhydride particles in toluene in a closed reactor

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Abstract. When milling micrometer thin $Nd_2Fe_{14}B$ platelets, of an average 1–2 mm diameter, in toluene in a closed reactor, part of the toluene decomposes at the surface of the platelets and yields nascent hydrogen and carbon/low hydrocarbons. The hydrogen diffuses into the $Nd_2Fe_{14}B$ platelets and the carbon forms a thin surface passivation layer of the platelets, forming the stable $Nd_2Fe_{14}BH_x$, $x \leqslant 5$, hydride at room temperature. On heating in a calorimeter, the hydrogen desorbs off the sample with a well-defined endotherm between 370 and 425 K. An N_2 gas atmosphere, if used during the heating, facilitates the H-desorption process with the modified kinetic parameters. For example, the enthalpy of the H-desorption ΔH and the related activation energy E_a have the measured values $\Delta H \approx 153$ J/g and $E_a = 58\cdot2$ kJ/mol in argon and $\Delta H = 256$ J/g and $E_a = 41\cdot6$ kJ/mol in N_2. It is argued that N_2 gas has a fast reaction with the H atoms desorbing off the thin sample platelets and forms NH_3 gas with an instantaneous decrease of the total external gas pressure at the sample. This supports the fast desorption of H atoms in the sample with the modified desorption kinetics in N_2 gas.

Keywords. $Nd_2Fe_{14}BH_x$, $x \leqslant 5$; hydrides; hydrogen intercalation; hydrogen desorption; stable metal hydride; thermal desorption; mechanical attrition.

1. Introduction

The $Nd_2Fe_{14}BH_x$, $x \leqslant 5$, hydrides form an important series of magnetic materials of considerably modified properties of the anhydride (Buschow 1988; Ram 1994; Ram et al 1995a, 1997). For example, the hydride with $x \sim 5$ H atoms per formula unit has a dramatically decreased magnetocrystalline anisotropy (H_a) of anhydride from 82·5 kOe to 17·6 kOe (Pareti et al 1988) along with an increased saturation magnetization (M_s) from 168 emu/g to 195 emu/g as measured at room temperature (Ram et al 1995b). It also has an increased Curie temperature $T_c = 642$ K in comparison to 593 K for the anhydride (Cadogan and Coey 1986; Fruchart and Miraglia 1991).

The hydrides of Nd–Fe–B alloys are generally obtained with the intercalation of H atoms by heating the sample with H_2 gas at elevated temperature (Rupp et al 1988; Zhang et al 1988; Williams et al 1990). This method yields the hydride of oxide free nascent–grain–surfaces, which are highly susceptible to oxidation in an ambient atmosphere. As a result, a significant part of the interstitial H atoms in the hydride sample automatically desorb off the sample if it is stored in an ambient atmosphere. This causes an unwanted oxidation of the sample in an ambient atmosphere. These hydride samples are stable only in an inert atmosphere.

In this article, we report a new method to synthesize stable $Nd_2Fe_{14}B$ hydride particles (with a thin stable grain–surface–passivation) by milling the anhydride sample in a hydrocarbon liquid such as toluene in a closed confined volume. These hydrided particles are

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stable at room temperature in an ambient atmosphere. The hydrogen desorb off the sample only on heating it at reasonably high temperatures 370–425 K. The results are discussed with thermal analysis, thermogravimetric analysis, X-ray diffractometry, and microstructure of the selected samples measured before and after the milling.

2. Experimental

The $Nd_2Fe_{14}B$ ingots were prepared by induction melting of pure (99·9%) iron, boron and neodymium metal at ~ 1473 K in a boron nitride crucible in a pure argon atmosphere. Since Nd metal is significantly volatile at this temperature, a sufficiently 10–20% excess of Nd than in the stoichiometric $Nd_2Fe_{14}B$ composition, was used. The obtained ingots were melt-spun as 15–30 µm thin ribbons by ejecting the molten alloy on the circumferential surface of a rapidly spinning copper wheel under a pure argon atmosphere. The ribbons were cut and crushed into thin $Nd_2Fe_{14}B$ platelets of 1–2 mm size. These platelets were finally ball-milled under toluene, in a closed reactor, for a short period of 20 min to perform the hydrogenation and to stabilize the platelets with a thin grain–surface–passivation without a severe distortion or decomposition of the lattice by the milling. In this process, part of the toluene decomposes at the surface of the alloy particles during the milling and yields nascent hydrogen, which vigorously reacts with the thin $Nd_2Fe_{14}B$ platelets of refreshed surfaces created during the milling and forms the hydrided $Nd_2Fe_{14}BH_x$, $x \leqslant 5$, platelets.

The incorporation of hydrogen in the alloy by milling in toluene was analysed using the change in the mass of the sample. A value of $\Delta m \sim 0.2$ wt%, i.e. equivalent to $x \sim 2$ H atoms per $Nd_2Fe_{14}B$ formula unit, was analysed using thermal desorption of the H atoms by heating the hydride sample over 300–500 K, i.e. just above the H-desorption peak in the thermal measurement described below. The thermal desorption of the H atoms in this example results in a well-defined endothermic signal during heating a 15–50 mg sample (in a prescribed aluminium pan for the DSC measurements as described earlier (Ram et al 1997)) in a pure argon and/or N_2 gas in a differential scanning calorimeter (Perkin–Elmer DSC-7). To confirm the reproducibility of the results and to perform a detailed study and to evaluate the activation energy E_a of the process of desorption of the interstitial H atoms, the sample was measured at selected heating rates β, usually in the range 20–40 K/min. A fresh sample was used in each case.

A JEOL model 840 scanning electron microscope together with an electron microprobe analyser was used to study the microstructure and also to perform an *in situ* chemical analysis of the composition of the selected samples. The chemical analysis of the representative particles of the sample before and after the milling presents the nominal composition of the $Nd_2Fe_{14}B$ alloy. The results were further confirmed with the X-ray diffractograms, which were studied with a D 5000 Siemens X-ray diffractometer using a filtered CoK_{α} radiation of wavelength $\lambda = 0.17903$ nm.

3. Results and discussion
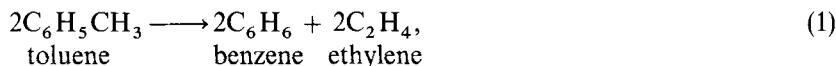
3.1 *Microstructure and chemical analysis*

Figure 1a portrays the SEM micrograph of the $Nd_2Fe_{14}B$ particles before milling. A coarse microstructure of these particles obtained after a controlled milling in toluene
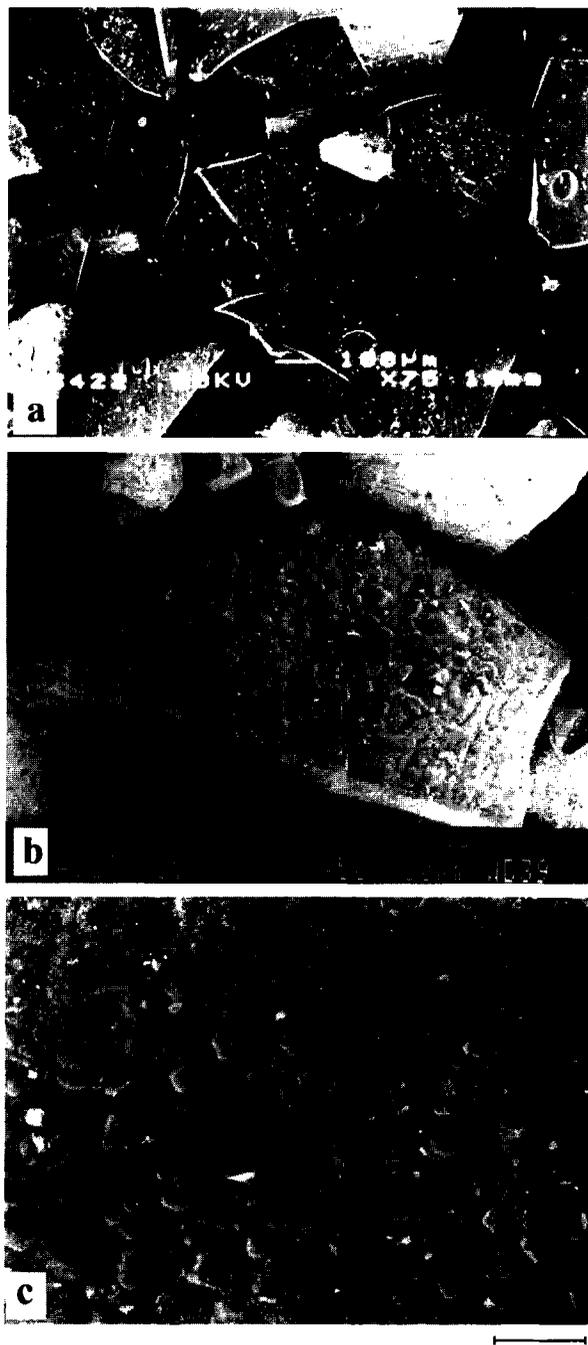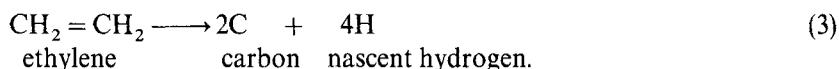
Figure 1. SEM images of $Nd_2Fe_{14}B$ particles (a) before and (b) after milling in toluene. A close up of a typical particle in (b) is reproduced in (c). The scale bar refers to (a) 100 μm, (b) 10 μm, and (c) 20 μm.

for 20 min is reproduced in the micrograph in figure 1b. It does not show a significant change in the apparent shape or size of the particles by the milling for the short period of 20 min. A closer observation of the microstructure of a typical particle in figure 1b at

a higher resolution, however, reveals local subdivisions of the particle at a submi-crometer scale. This is reproduced in figure 1c. During the milling part the toluene decomposes at the surface of $Nd_2Fe_{14}B$ particles and yields nascent hydrogen along with carbon and low hydrocarbons of decomposed toluene. The $Nd_2Fe_{14}B$ particles of refined surfaces, obtained by collisions between the particles during the milling, function as a strong catalyst in this decomposition reaction of the toluene, which probably proceeds via the following three steps:

$$2C_6H_5CH_3 \longrightarrow 2C_6H_6 + 2C_2H_4, \tag{1}$$
$$\text{toluene} \qquad\qquad \text{benzene} \quad \text{ethylene}$$

$$C_2H_4 \longrightarrow C_2H_2 + 2H, \tag{2}$$
$$\text{acetylene}$$

or

$$CH_2=CH_2 \longrightarrow 2C \quad + \quad 4H \tag{3}$$
$$\text{ethylene} \qquad\qquad \text{carbon} \quad \text{nascent hydrogen.}$$

The thermal decomposition transformation of toluene into benzene and ethylene at $Nd_2Fe_{14}B$ metal surfaces at an elevated temperature T_1 is feasible thermodynamically with a negative value of the enthalpy of the reaction, i.e.

$$\Delta H = [(\Delta H_B^f + \Delta H_C^f) - \Delta H_A^f] + \Delta H'_{BC-A}$$
$$= \Delta H^f_{BC-A} + \Delta H'_{BC-A}$$
$$\cong -24\cdot8\,\text{kJ/mol}, \tag{4}$$

at room temperature (298 K), with $\Delta H^f_{BC-A} \cong -17\cdot6\,\text{kJ/mol}$ and $\Delta H'_{BC-A} \cong -7\cdot2\,\text{kJ/mol}$. Here, $\Delta H_A^f = -6\cdot85\,\text{kJ/mol}$ and $\Delta H_B^f = -9\cdot95\,\text{kJ/mol}$ are the standard enthalpies of formation of toluene (melting point $T_m = 178\,\text{K}$) and benzene ($T_m = 279\,\text{K}$), respective-ly, in the liquid state at T_m, whereas $\Delta H_C^f = -14\cdot47\,\text{kJ/mol}$ is the total sum of the standard enthalpy of formation of C_2H_4 at $T_m = 91\,\text{K}$ and the heat of vaporization of it at the boiling point $T_b = 169\,\text{K}$.

In the above relation (4),

$$\Delta H'_{BC-A} = [\Delta H'_B + \Delta H'_C] - \Delta H'_A, \tag{5}$$

is the contribution to the total ΔH due to the heat capacities C_{PA}, C_{PB} and C_{PC} of the reaction species $C_6H_5CH_3$, C_6H_6 and C_2H_4, respectively. The values of the individual $\Delta H'$s are calculated through the C_p's as follows (Swalin 1962):

$$\Delta H'_B = \int_{T_m}^{T_1} C_{PB}\,dT,$$

$$\Delta H'_C = \int_{T_m}^{T_b} C_{PC}\,dT + \int_{T_b}^{T_1} C'_{PC}\,dT,$$

and

$$\Delta H'_A = \int_{T_m}^{T_1} C_{PA}\,dT. \tag{6}$$

Assuming the constant values for $C_{PA} = 157\cdot6\,\text{Jmol}^{-1}\,\text{K}^{-1}$ (liquid), $C_{PB} = 136\cdot6\,\text{Jmol}^{-1}\,\text{K}^{-1}$ (liquid) and $C'_{PC} = 43\cdot6\,\text{Jmol}^{-1}\,\text{K}^{-1}$ (gas) throughout the prescribed temperatures in (6), it yields a value for the $\Delta H'_{BC-A} \cong -7\cdot2\,\text{kJ/mol}$ with $\Delta H'_A \cong 18\cdot79\,\text{kJ/mol}$,
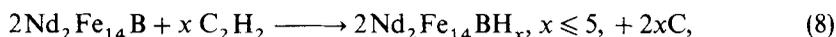
$\Delta H'_B \cong 2.60$ kJ/mol and $\Delta H'_C \cong 9.03$ kJ/mol at temperature $T_1 = 298$ K, which is far lower than $T_b = 384$ K for toluene or 353 K for benzene. At this temperature, the intermediate by-product reaction species C_2H_4 exists in the gas state with $T_b = 169$ K ($T_m = 91$ K). Since it exists in the gas state over a wide range of temperature of present interest, the same value of $C'_{PC} = C_{PC}$ is assumed in the calculation of $\Delta H'_C$ for the gas and liquid C_2H_4 as well. The substitution of the resultant value of the three contributions of $\Delta H'_{BC-A}$ in (4) yields a resultant value of $\Delta H \cong -24.8$ kJ/mol at $T_1 = 298$ K, as mentioned above. The standard values of the ΔH^f's and C_ps used in these calculations are taken from the CRC Handbook of Chemistry and Physics edited by Lide (1996).

It is found that the heat produced by collisions in the milling and in the subsequent reactions between the alloy and the toluene or its decomposed species in this example raises up the average temperature of the system to 325–340 K. The local temperatures of the reaction species may be reasonably higher than the average value. At this temperature, the benzene ($T_b = 353$ K) and other decomposed species of toluene ($T_b = 384$ K) essentially exist in a non equilibrium mixed liquid–gas state with toluene. They have lower partial vapour pressures than toluene, which promotes its decomposition transformation to nascent hydrogen/low hydrocarbons according to reactions (2) and (3). The intermediate by-product reaction species $C_2H_4(T_b = 169$ K) and $C_2H_2(T_b = 198$ K) produced in these reactions are highly combustible with oxygen impurities, if any, in the sample. They refine the $Nd_2Fe_{14}B$ particle surfaces to the oxide-free pure metallic surfaces.

The fresh metallic surfaces of $Nd_2Fe_{14}B$ particles are possibly as highly reactive with the by-product reaction species C_2H_4 or C_2H_2 gas as the nascent hydrogen. A high affinity of H atoms to recombine with $Nd_2Fe_{14}B$ to form $Nd_2Fe_{14}BH_x$, $x \leqslant 5$, hydrides with the enthalpy of formation of $\Delta H = 100$–300 kJ/mol, according to the experimental conditions of the sample (Ram *et al* 1997), leads to the following:

$$4Nd_2Fe_{14}B + x\,C_2H_4 \longrightarrow 4Nd_2Fe_{14}BH_x, x \leqslant 5, + 2xC, \qquad (7)$$

or,

$$2Nd_2Fe_{14}B + x\,C_2H_2 \longrightarrow 2Nd_2Fe_{14}BH_x, x \leqslant 5, + 2xC, \qquad (8)$$
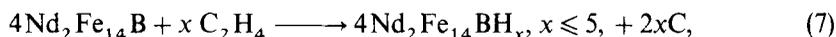
highly exothermic reaction with the alloy, forming the stable $Nd_2Fe_{14}BH_x$, $x \leqslant 5$, hydrides. Note that the 1–2 mm big particles of $Nd_2Fe_{14}B$ shown in the micrographs a and b in figure 1 comprise of several submicrometer-sized grains intimately adhering to one another. During milling, the non-interrupted inelastic collisions of H atoms (or other high energy mobile gas species C_2H_4 or C_2H_2, produced according to reactions (2) and (3)) with the $Nd_2Fe_{14}B$ particles fragment the latter into the individual separated grains. These high energy gas species develop a dynamic pressure gradient between the grains that leads to separate them apart in the milling in a closed reactor. As a result, separated $Nd_2Fe_{14}B$ grains are clearly visualized in the micrograph shown in figure 1c. They have well-resolved grain boundaries developed on the milling. The sample which is obtained has the same X-ray diffraction pattern as the starting sample with an $\sim 1\%$ expansion in the lattice volume due to the hydrogen intercalation that occurred during milling. This expansion of the lattice is not large but it is in the proportionate ratio to a maximum of 4.2% expansion observed for the saturated $Nd_2Fe_{14}BH_x$ hydride, with $x \sim 5$H atoms per formula unit, prepared by other methods (Fruchart *et al* 1988; Fruchart and Miraglia 1991; Ram and Joubert 1992; Ram *et al* 1995a).
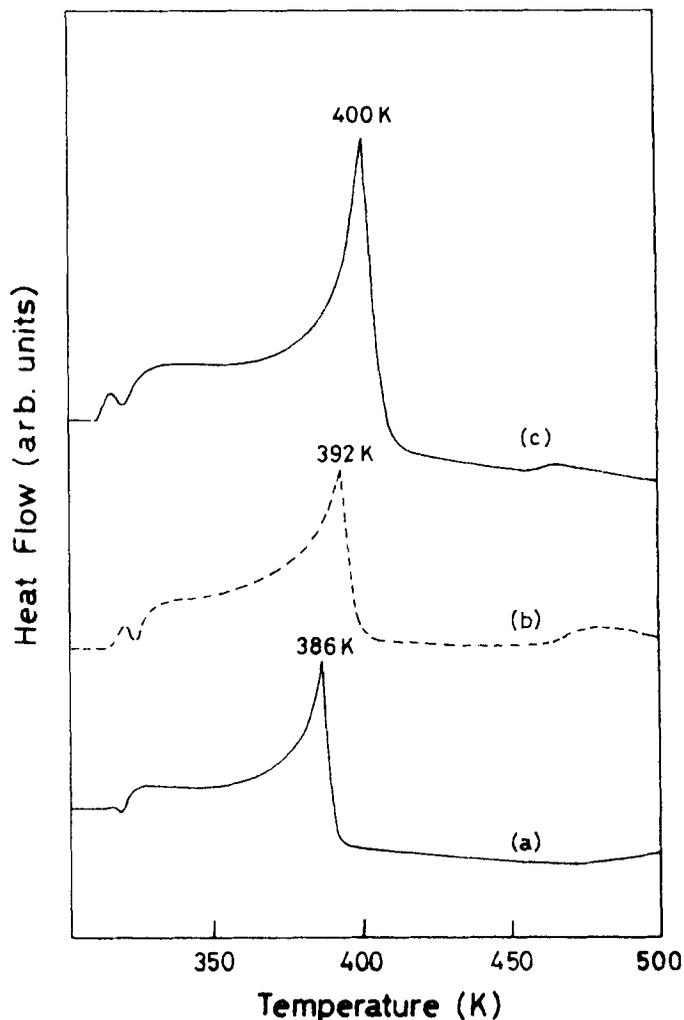
Figure 2. The DSC thermograms of the $Nd_2Fe_{14}B$ hydride sample (mass ~ 15 mg) recorded during heating at the heating rate (a) 20 K/min, (b) 30 K/min, and (c) 40 K/min in a pure argon atmosphere.

3.2 *Thermal analysis*

Figure 2 shows the DSC thermograms of the $Nd_2Fe_{14}B$ sample (milled in toluene) recorded during heating between 300 and 500 K at three diffferent heating rates (β); (i) 20 K/min, (ii) 30 K/min, and (iii) 40 K/min. All the three thermograms exhibit a well-defined endothermic peak between 370 and 425 K in desorption of the hydrogen atoms in the hydrided $Nd_2Fe_{14}B$ particles formed during milling in toluene. The position of the peak, marked at temperature T_p in figure 2, shifts to increasingly higher temperatures at regular intervals with increasing value of β in the range 20–40 K/min. It proves that the process of desorption of H atoms in this example is a kinetic process
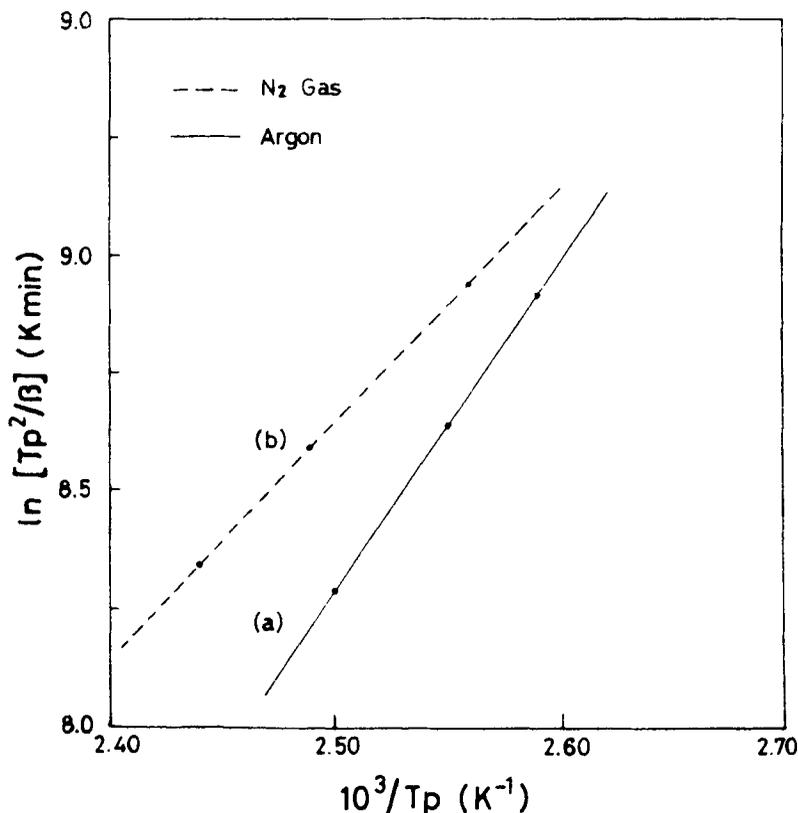
Figure 3. Kissinger plot of the peak in the H-desorption thermogram measured by heating the $Nd_2Fe_{14}B$ hydride sample in (**a**) argon and (**b**) N_2 gas.

with an activation energy E_a. The value of E_a is calculated with the variation of T_p with β using the Kissinger (1957) relation,

$$\ln\left\{\frac{T_p^2}{\beta}\right\} = \left\{\frac{E_a}{R}\right\} T_p^{-1} + \text{const.},\qquad(9)$$

with $R = 8\cdot314\,\mathrm{Jmol^{-1}\,K^{-1}}$ the universal gas constant, assuming a single activation process of desorption of the H atoms.

The experimental data is best represented by a straight line in the $\ln[T_p^2/\beta]$ vs T_p^{-1} plot shown in figure 3a. The slope (E_a/R) of the straight line yields the value of $E_a = 58\cdot2\,\mathrm{kJmol^{-1}}$. The saturated $Nd_2Fe_{14}BH_x$, $x \sim 5$, hydride, obtained by other methods (Ram 1994), desorbs over similar temperatures with a significantly lower $E_a = 37\,\mathrm{kJmol^{-1}}$ value. In fact, the kinetics of H-desorption process is a function of the total H content in the sample. The larger the H content faster is the thermal desorption of the H atoms with a smaller value for E_a at a given temperature, irrespective of other experimental parameters.

Figure 4 portrays the DSC thermograms, similar to those shown in figure 2, measured in a pure N_2 gas atmosphere. These thermograms present a significantly
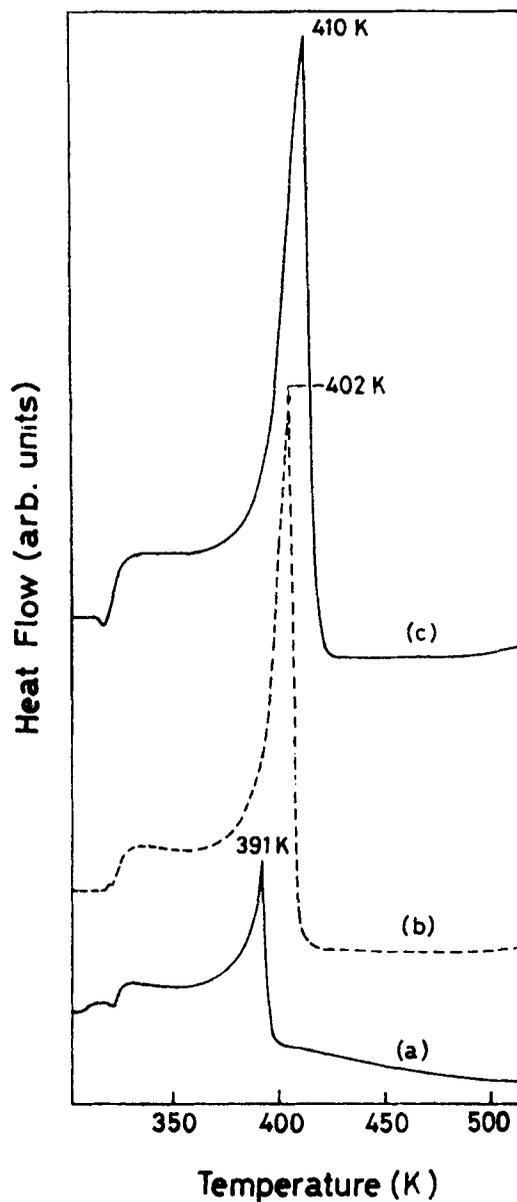
Figure 4. The DSC thermograms of the $Nd_2Fe_{14}B$ hydride sample (mass $\sim 15\,mg$) recorded during heating at the heating rate (a) $20\,K/min$, (b) $30\,K/min$, and (c) $40\,K/min$ in a pure N_2 gas atmosphere.

modified kinetics of desorption of the H atoms. For example, at $\beta = 20\,K/min$, the T_p and the enthalpy (ΔH) of the H desorption have modified from $T_p = 386\,K$ and $\Delta H = 153\,J/g$ measured in argon to $T_p = 391\,K$ and $\Delta H = 256\,J/g$ in N_2 gas. A value of $E_a = 41\cdot6\,kJmol^{-1}$ is obtained from the Kissinger plot of $\ln[T_p^2/\beta]$ vs T_p^{-1} shown in figure 3b. The present value of E_a is considerably lower than that determined above for the H desorption of the sample under the argon atmosphere. All these results

Table 1. Kinetic parameters of the desorption of interstitial H atoms in $Nd_2Fe_{14}BH_x$, $x \leqslant 5$, hydrides by DSC and other measurements.

Sample	Peak temp. $T_p(K)^*$	Activation energy $E_a(kJmol^{-1})$	Enthalpy $\Delta H(J/g)^*$	Reference
I. DSC measurements				
A. $Nd_2Fe_{14}BH_x$, $x \sim 2$				
(i) in argon gas	386	58·2	153	Present work
(ii) in N_2 gas	391	41·6	256	Present work
B. $Nd_2Fe_{14}BH_x$, $x \sim 5^{**}$	439	49·0	140	Ram *et al* (1997)
II. Analysis of the partial gas pressure in the desorption of the H atoms				
$Nd_2Fe_{14}BH_x$, $x \sim 5^{**}$	533	37·0	—	(Ram 1994)

*The values of T_p and ΔH are reported for the thermograms measured at the heating rate of 20 K/min in A, 15 K/min in B, and 3 K/min in II.
**These samples had a strong grain–surface–passivation which prevents the H-desorption at lower temperatures.

demonstrate the fact that the presence of the N_2 gas facilitates the thermal desorption of H atoms in $Nd_2Fe_{14}BH_x$, $x \leqslant 5$, at an elevated temperature.

3.3 *Mechanism of the enhanced thermal desorption of H atoms in* $Nd_2Fe_{14}BH_x$, $x \leqslant 5$, *in the flowing* N_2 *gas*

During heating the powder sample of $Nd_2Fe_{14}B$ hydride in a steadily flowing N_2 gas at $\sim 1{\cdot}3$ bar total gas pressure in the calorimeter, the separated particles of the sample have an intimate contact with the N_2 gas, which reacts instantaneously with the nascent hydrogen desorbing off the sample at elevated temperature and forms ammonia gas

$$N_2 + 3H_2 \longrightarrow 2NH_3, \tag{10}$$

at the surface of the particles. Here, the combination of a total of four moles of the two gases N_2 and H_2 results in a total of only two moles of NH_3 gas, i.e. the final gas has a partial pressure (or volume) reduced by a factor of 2 and that results in an instantaneous decrease in the total external gas pressure at the sample. This, in turn, therefore induces a faster desorption of the H atoms in the $Nd_2Fe_{14}BH_x$, $x \leqslant 5$, sample through the surface of the individual particles in process to attain an equilibrium pressure with the internal gas pressure at elevated temperatures.

The catalytic effect of $Nd_2Fe_{14}B$ in this example can be used to recombine two gases N_2 and H_2 together to perform a mass-scale production of ammonia gas at a moderate pressure. This gas is usually produced by the Haber process (as described elsewhere, e.g. see the book of Physical Chemistry by Maron and Prutton (1972)). In this process, an appropriate mixture of the two gases is reacted at the surface of a catalyst of iron metal at 10–50 atm pressure. In the case of the use of $Nd_2Fe_{14}B$, this reaction occurs at moderate pressure of the order of 1 atm. only. Also are known several other metallic catalysts, e.g. tungsten, molybdenum, osmium, or platinum, which support an adverse

effect to decompose NH_3 into N_2 and H_2 gases at high temperatures of 1100–1400 K (Maron and Prutton 1972). In all these examples, the material used as a catalyst has a strong tendency of adsorption of these gases at its surface. The surface adsorption of the reaction species causes a change of their chemical equilibrium so that it supports an activated spontaneous reaction at the expense of the reactants or at the decomposition of the product according to the instantaneous flow of the heat of the reaction and other experimental conditions.

4. Conclusions

Separated fine $Nd_2Fe_{14}B$ particles, with highly reactive fresh surfaces, could be stabilized by surface passivation by milling in an organic liquid as toluene in a closed reactor. Part of the toluene decomposes during milling and yields nascent hydrogen and carbon/low hydrocarbons. The H atoms hydrogenate the $Nd_2Fe_{14}B$ sample while the carbon adheres to the sample forming a thin grain–surface–passivation layer with the surface atoms. This layer, when dried, becomes rigidly hard and stands against atmospheric corrosion of the sample in an ambient atmosphere at room temperature or lower. When heated in a pure argon and/or N_2 gas in a calorimeter, the hydrogen atoms desorb off the sample showing up in a well-defined H-desorption endotherm between 370 and 425 K. The H desorption in this example is a kinetic process whose kinetic parameters significantly depend on the experimental conditions of the measurement of the thermal signal.

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