

# Investigation of Hydrogen Interaction with Magnetic Materials of Nd–Fe–B Type by Calorimetry Method

E. Yu. Anikina<sup>a</sup>, V. N. Verbetskiy<sup>a</sup>, A. G. Savchenko<sup>b</sup>, V. P. Menushenkov<sup>b</sup>, and I. V. Shchetinin<sup>b</sup>

<sup>a</sup>Moscow State University, Moscow, Russia

<sup>b</sup>National University of Science and Technology MISIS, Moscow, Russia

e-mail: Verbetsky@hydride.chem.msu.ru

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**Abstract**—The interaction of hydrogen with the Nd–Fe–B system is studied via calorimetry with use of a Tian–Calvet differential calorimeter and reconstruction of the pressure–composition isotherms ( $P$ – $C$ – $T$ , where  $P$  is the equilibrium pressure of hydrogen,  $C = H/\text{Nd}_2\text{Fe}_{14}\text{B}$ , and  $T$  is the reaction temperature). No hybrid phase coexistence is found on the  $P$ – $C$  hydrogen sorption/desorption isotherms or on plots of the dependence of the enthalpy on the hydrogen concentration in the metallic matrix. Nevertheless, several segments with constant enthalpy values can be distinguished in the reaction enthalpy on the hydrogen content plot.

**Keywords:** calorimetry, absorption, desorption, Nd–Fe–B material, enthalpy

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## INTRODUCTION

Since Japanese and American scientists discovered in 1983 the high coercive force in intermetallic  $\text{Nd}_2\text{Fe}_{14}\text{B}$  magnetic materials [1, 2], the systems on the basis of  $\text{R}_2\text{Fe}_{14}\text{B}$  stoichiometry (where  $R$  is a rare-earth element) have been of great interest in terms of their fundamental characteristics and for the prospects of their use in high-energy permanent magnets. As 30 years ago, one can distinguish the compound  $\text{Nd}_2\text{Fe}_{14}\text{B}$  among the above systems, which possesses high magnetocrystalline anisotropy and saturation induction, as well as a high Curie temperature.

Despite numerous works dedicated to the investigation of hydrogen with  $\text{R}_2\text{Fe}_{14}\text{B}$  compounds, the effect of hydrogenation on the magnetic properties of these intermetallic compounds is a particular focus of attention. The most modern and high-technology method of the synthesis of Nd–Fe–B-based magneto-anisotropic alloy powder is the so-called HDDR process, which is the optimized complex of subsequent thermal treatments in hydrogen and vacuum, resulting in hydrogen-induced phase transformations. It is based on four main stages, which are hydrogenation–decomposition (disproportion)–desorption–recombination, whose fundamental aspects define the phenomenology of this extremely interest phenomenon based on hydrogen and its unique properties. Numerous works are devoted to the study and description of the HDDR process, which are reviewed in detail in [3].

For better understanding of the effect of hydrogen on the physical and magnetic properties of Nd–Fe–B alloys, it is necessary to know the thermodynamic parameters of the interaction between hydrogen and  $\text{Nd}_2\text{Fe}_{14}\text{B}$ . There are, however, several works to date [4, 5] which report the  $P$ – $C$ – $T$  dependences (here,  $P$  is the equilibrium pressure of hydrogen in the  $\text{Nd}_2\text{Fe}_{14}\text{B}$ –hydrogen system;  $C$  is the hydrogen concentration in  $\text{Nd}_2\text{Fe}_{14}\text{B}$ ,  $C = H/\text{Nd}_2\text{Fe}_{14}\text{B}$ ; and  $T$  is the temperature of experiment). In [4], the hydrogen absorption is reported at temperatures of 370, 470, and 570 K. No horizontal segments were observed on the obtained isotherms, which means the lack of some stoichiometric phases. However, the hydrogen concentration in  $\text{Nd}_2\text{Fe}_{14}\text{B}$  at 370 K and the hydrogen pressure of  $10^2$  Mbar was  $\sim 0.11$  H/M, which corresponds to  $\text{Nd}_2\text{Fe}_{14}\text{B}$  stoichiometry.

In [5], there was absorption and desorption of hydrogen at 323, 363, 423, and 453 K at the pressures of  $3 \times 10^{-3} < p < 1200$  mbar. No features of the plateau existence typical of stable hydrides were detected in [5], and there was no difference between the  $P$ – $C$  absorption and desorption isotherm plots. On this basis, no stable hydrides were concluded to exist in the studied pressure range. Unfortunately, there are almost no works reporting calorimetric studies of the hydrogenation–dehydrogenation dynamic parameters. However, in [5], the hydrogenation enthalpy was calculated. The conducted isobaric DTA/TG measurements allowed establishing that  $\Delta H_R = -57.2(8)$  kJ/mol  $\text{H}_2$ . Moreover, the hydrogen sorption was found to proceed in

two stages: here, the first peak in the diagram is attributed to the hydrogenation of a tetragonal hard magnetic phase, whereas the second peak is associated with the irreversible exothermal decomposition of the tetragonal hard magnetic phase [6] (corresponding to  $\Delta H_R = -53.3(6)$  kJ/mol  $H_2$ ). Besides these data in [6], there is also an interesting observation on the temperature rise to 350°C on the sample surface in the hydrogenation depending on the weight of the hydrogenated alloy.

Hydrogen desorption from Nd–Fe–B alloys was investigated in [7] via mass spectrometry. The obtained mass spectrometry diagram allowed one to conclude the two-stage hydrogen desorption from the hydrogen-containing  $Nd_2Fe_{14}B$  phase, where the first stage in the diagram is manifested as a sharp peak at 150°C, while the second stage is observed at a maximum near 250°C. Since the  $Nd_2Fe_{14}B$  sample is a single-phase, this evident two-stage desorption behavior can be explained by hydrogen desorption from various interstitials in the  $Nd_2Fe_{14}B$  phase and/or different microcrystalline effects, such as separated hydrogen desorption from the grain boundaries and the matrix. The similar double peak was observed in [4] in hydrogen desorption from a  $Nd_2Fe_{14}BH_3$  sample.

According to [8], the enthalpy of hydrogenation of the  $Nd_2Fe_{14}B$  system is  $\Delta H = -13$  kcal/mol  $H_2$  (or  $\Delta H = -54.4$  kJ/mol  $H_2$ ). Study of the kinetics of hydrogen desorption from  $Nd_2Fe_{14}BH_x$  ( $x \leq 5$ ) via isothermal heating in [9] revealed that there are four maxima of the hydrogen desorption rate ( $H_1$ ,  $H_2$ ,  $H_3$ , and  $H_4$ ) on the hydrogen desorption isotherms ( $dP/dt$ ) during the heating of  $Nd_2Fe_{14}BH_x$  ( $x \sim 4.5$ ) system as a function of the time at various temperatures. This is explained by the fact the hydrogen desorption originates from four different interstitials and is characterized by four different activation energies. The average activation energy in the non-isothermal mode is  $E_a = 39.2$  kJ/mol. In the isothermal mode, this value is  $E_a = 38.2$  kJ/mol.

Dehydrogenation of  $Nd_2Fe_{14}BH_x$  ( $x \sim 5$ ) was also studied in [10] via differential scanning calorimetry. Six maxima were found on the decomposition curve (hydrogen desorption from  $Nd_2Fe_{14}BH_x$ , where  $x \sim 5$ ) in the temperature range of 325–800 K, which were attributed to hydrogen desorption phenomena from  $4c$ ,  $16k_1$ ,  $16k_2$ ,  $4e$ ,  $8j_2$ , and  $8j_1$  interstitials. The corresponding values of activation energy (from 48 to 123 kJ/mol) and enthalpy (from 23 to 78 J/g), as well as the value of total enthalpy of 249 J/g, were reported in [10]. These results are in some disagreement with the neutron diffraction data [11], which revealed only four interstitials filled with the hydrogen atoms in the  $Nd_2Fe_{14}B$  crystal lattice ( $8j$ ,  $16k_1$ ,  $16k_2$ , and  $4e$ ), and the order of their filling with the hydrogen atoms was determined. This mismatch in the results in [10] is nevertheless explained by the fact that the method used in [11] is

not sensitive enough to detect small hydrogen or deuterium contents, whereas differential scanning calorimetry allows better understanding of the interaction between hydrogen and  $Nd_2Fe_{14}B$ .

In the present work, we have studied the interaction of hydrogen with  $Nd_2Fe_{14}B$  (desorption and absorption processes) via calorimetry with using a differential heat-conducting Tian–Calvet calorimeter connected to a Siverts setup. First, this complex allows determining the reaction enthalpy in the single-phase and double-phase area with a high accuracy in comparison with the enthalpies calculated from the Van–Hoff equation from the  $P$ – $C$  isotherms, because in this case the pressure hysteresis exerts no influence on the enthalpy values. Second, studying the behavior of the material at the interface and calculating the entropy values for all compounds is the scope here [12, 13].

## EXPERIMENTAL

The  $Nd_2Fe_{14}B$  sample was melted in a vacuum induction oven in a purified argon environment with subsequent pouring of the melt into a metal mold. The in-cast alloy was characterized by an inhomogeneous multiphase structure which was formed during cooling after the incomplete subsequent peritectic transformations. To remove the inhomogeneities, the ingot was subjected to homogenizing annealing in a vacuum resistance oven at a temperature of 1100°C for 30–40 h. The phase analysis was implemented on a Rigaku Ultima IV diffractometer in the Bragg–Brentano mode with using  $CoK_\alpha$  radiation and a graphite monochromator on a diffracted beam. The lattice periods were evaluated via extrapolation. The spectrum processing and determination of the lattice periods were implemented in the PDXL platform. The X-ray diffraction revealed that the homogenizing annealing led to almost complete dissolution of the primary  $\alpha$ -Fe phase releases present in the ingot alloy structure, and the content of the main hard magnetic  $Nd_2Fe_{14}B$  phase increased to 99%. The lattice periods are determined for the  $Nd_2Fe_{14}B$  phase:  $a = 8.802$  Å,  $c = 12.192$  Å. These values are in a good agreement with the published data [1, 10, 14–17].

The chemical composition was determined via X-ray fluorescence on a Rigaku Primus II spectrometer and micro-X-ray spectral analysis on a JEOL JSM-6610LV scanning electron microscope. The X-ray fluorescence and micro-X-ray spectral analysis data match also in the main components, giving Nd = 28.7%, Fe = 70.1%, and B = 1%.

The interaction of hydrogen with intermetallic  $Nd_2Fe_{14}B$  compound was studied on a calorimetric setup equipped with a differential heat-conductive DAK12 calorimeter connected to a volumetric Siverts system serving for metering (or selection) of gaseous hydrogen. The working range of the Siverts setup is from  $5.0 \times 10^{-5}$  to 60 atm. This system was developed

and constructed at the Laboratory of Energy and Catalytically Active Substances of the Faculty of Chemistry, Moscow State University. The calorimeter operates in the temperature range of 20 to 400°C. Two identical calorimetric stainless steel cells developed for investigating the interaction of hydrogen with a substance are connected to the Siverts setup. The calorimetric cells and all volumes of the Siverts setup were calibrated. LaNi<sub>5</sub>-based hydride was used as a highly pure hydrogen (99.999%) source, which was stored in a special steel reservoir.

The important feature of the differential heat-conductive Tian–Calvet calorimeter is the presence of two calorimetric cells. One of them serves as the working cell, while the second one is the comparative cell. This calorimeter construction thus makes it possible to exclude the corrections to the heat effect of the gas injected into the system and the changes in the environment at long duration of the experiment. The measured heat effect corresponds to the molar enthalpy of reaction [18]. Before starting the measurements, the Nd<sub>2</sub>Fe<sub>14</sub>B sample was crushed and placed in one of the calorimetric cells. The second cell remained empty. The cells were attached to the Siverts setup and were evacuated for 1 h at room temperature to the residual pressure of  $5.0 \times 10^{-5}$  atm. The hydrogen desorption was studied from the intermetallic compounds by saturating the sample with hydrogen at a pressure of 40 atm and room temperature. Next, the calorimetric cells were put into the calorimetric chambers. The calorimetric experiment was initiated when the studied sample was heated to the calorimeter temperature and the equilibrium was stabilized in the studied sample.

During the absorption process, small portions of hydrogen were added to the calorimetric cells. In the study of desorption, hydrogen was bled in small portions into the calibrated volume. The amount of absorbed or desorbed hydrogen was around  $100\text{--}200 \times 10^{-6}$  mol H<sub>2</sub>. The end of hydrogen absorption or release was determined from the heat release curve achieving the zero line and from the constancy of the pressure gauge readings for 0.5–1 h depending on the duration of the experiment. The calorimeter was calibrated by the electric method twice a day in accordance with the Joule effect. The scheme of the setup and the details of the experiment and data processing are described in [19]. The measurements were made with use of the CRWDAQ software package [21, 22]. Absorption and desorption were conducted at 150°C. The differential molar enthalpies of hydrogen absorption or desorption were evaluated from the heat effect of the reaction



The heat effect of the reaction was calculated from the equation

$$Q = SA/\Delta n,$$

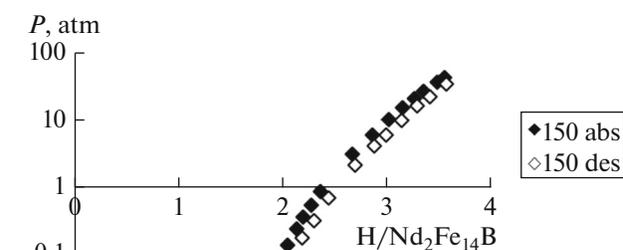


Fig. 1. Pressure–composition isotherms for hydrogen absorption and desorption in the Nd<sub>2</sub>Fe<sub>14</sub>B–H<sub>2</sub> system at 150°C.

where  $S$  is the area under the heat release (heat absorption) curve, mm<sup>2</sup>;  $A$  is the sensitivity of the device, determined from the electric calibration for each experiment (mJ/mm<sup>2</sup>); and  $\Delta n$  is the number of moles of released (absorbed) hydrogen. The measurement error in this work was expressed as the quadratic error of the average result with respect to the recommendation of the IUPAC chemical thermodynamics committee [22]:

$$\delta = \sqrt{\Sigma \Delta^2 / n(n-1)},$$

where  $\Delta$  is the deviation of the results from the mean value and  $n$  is the number of measurements.

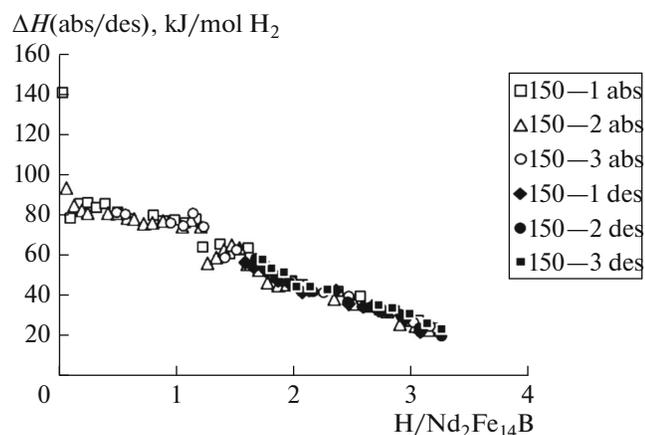
## RESULTS AND DISCUSSION

### Pressure–Composition Isotherms

The absorption and desorption of hydrogen were conducted at 150°C and the  $P$ – $C$  dependences were obtained. Before the desorption process, the studied sample was saturated with hydrogen at room temperature and a pressure of 50 atm, which allowed obtaining the compound Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>4.1</sub>. Figure 1 displays the  $P$ – $C$  dependences obtained at 150°C.

As is obvious, no plateau typical of the hydride formation reactions is observed on the acquired curves. There is also no difference between the  $P$ – $C$  dependences for hydrogen absorption and desorption. This enables us to conclude that there is no Nd<sub>2</sub>Fe<sub>14</sub>B hydride formation in the studied pressure range and at the given temperature.

The data in our work coincide with those acquired in [4, 5]. The  $P$ – $C$  dependence for desorption was investigated for the hydrogen pressures of 0.025 atm <  $P$  < 43.2 atm; in this case, the hydrogen concentration varies from 3.4 to 1.7 H/Nd<sub>2</sub>Fe<sub>14</sub>B, whereas for absorption the hydrogen pressure range is 0.003 atm <  $P$  < 43 atm with the hydrogen concentration in the studied composite of 0 to 3.2 H/Nd<sub>2</sub>Fe<sub>14</sub>B. The study



**Fig. 2.** Partial molar absorption and desorption enthalpy as a function of hydrogen concentration in the  $\text{Nd}_2\text{Fe}_{14}\text{B}-\text{H}_2$  system at  $150^\circ\text{C}$ . Various symbols are attributed to different series of experiments.

at lower hydrogen pressure is difficult because of the long time needed for attaining equilibrium in the system.

#### Calorimetric Measurement Results

The calorimetric measurement results in the form of the enthalpy change during the reaction of hydrogen with the intermetallic  $\text{Nd}_2\text{Fe}_{14}\text{B}$  compound as a function of the hydrogen concentration  $\Delta H(\text{abs/des}) = f(C)$  for hydrogen absorption and desorption are shown in Fig. 2 and in the table. As is evident from the acquired  $\Delta(\text{abs/des}) = f(C)$  dependences, the enthalpy for the absorption and desorption processes matches in absolute value at the hydrogen concentrations of  $1.7 < C < 3.4$ . For the absorption process, the  $\Delta H(\text{abs/des}) = f(C)$  dependence was obtained for the hydrogen concentrations of 0 to 3.4.

As is seen in Fig. 2, several areas can be distinguished in the  $|\Delta H(\text{abs/des})| = f(C)$  dependence with various enthalpy values, namely,  $0.3 < C < 0.5$ ,  $0.6 < C < 1.2$ ,  $1.2 < C < 1.6$ , and  $2.0 < C < 2.5$ . It is known from the neutron diffraction studies of hydrogen-containing  $\text{Nd}_2\text{Fe}_{14}\text{BH}_x$  phases [11, 23] that the hydrogen atoms fill four nonequivalent tetrahedral vacancies as follows: H(1) occupies vacancy  $8j$  formed by three Nd

atoms and one Fe atom; H(2) fills vacancy  $16k_1$  formed by two Nd atoms and two Fe atoms; vacancy  $16k_2$  formed by two Nd atoms and two Fe atoms is taken by the H(3) atom; and vacancy  $4e$  formed by two Nd and two Fe atoms is occupied by H(4).

The sequence of filling of these vacancies with hydrogen atoms was studied in [11]. As was found, at its initial concentration  $C \leq 1$ , hydrogen H(1) is located at the interstitial  $8j$  and fills it by 50%, whereas other interstitials remain vacant. This can be explained by two causes: first, this tetrahedron is formed by the largest number of Nd atoms, and, second, this vacancy ( $8j$ ) is much larger in the size (with the inner radius  $R_{\text{inn}} = 0.45 \text{ \AA}$ ). We can attribute this to our reaction enthalpy data measured via calorimetry on the hydrogen concentration in the metal matrix and assume the heat effect of  $-84 \text{ kJ/mol H}_2$  upon the penetration of hydrogen into vacancy  $8j$ . In accordance with [11], at the hydrogen concentration  $C = 2$  in the  $\text{Nd}_2\text{Fe}_{14}\text{B}-\text{H}_2$  system, there is a redistribution of hydrogen between vacancies  $8j$  and  $16k_1$ , and a part of the hydrogen passes from the interstitial  $8j$  to  $16k_1$ . One can assume that this transition in the  $|\Delta H(\text{abs})| = f(C)$  dependence is manifested in the second segment of the constant enthalpy values ( $\Delta H(\text{abs}) \sim -78 \text{ kJ/mol H}_2$ ). Evidently, the enthalpy values in the first two segments are slightly different. At its content  $C = 3$ , hydrogen fills all four interstitials  $8j$ ,  $16k_1$ ,  $16k_2$ , and  $4e$  in a different manner. This situation corresponds to the third segment with the constant enthalpy values of  $\Delta H(\text{abs}) \sim -62 \text{ kJ/mol H}_2$ . At a further increase in the hydrogen concentration in the metal matrix ( $C = 4$ ), hydrogen is also located at these interstitials, but is distributed over them differently. As is seen from Fig. 2, in both absorption and desorption of hydrogen, the reaction enthalpy values (at  $C > 2.6$ ) monotonically decrease with rising hydrogen content in the metal matrix. This result is in agreement with the data [24] on the isotropic enlargement of the crystal lattice in  $\text{Nd}_2\text{Fe}_{14}\text{B}$  in this concentration range. It was mentioned in [24] that, regardless of the solid solution behavior of the studied material ( $\text{Nd}_2\text{Fe}_{14}\text{B}$ ) in the reaction with hydrogen (no plateau is observed in the  $P-C$  plot), the lattice parameters do not exhibit a linear dependence over the whole hydrogen concentration in IMC.

It is also worth mentioning that, even at a high hydrogen content, interstitial  $4e$  remains poorly filled obviously because of its small size in comparison with other vacancies [11].

Our disagreements on the filling of vacancies with the results in [11] are explained by the fact the neutron diffraction study in [11] was conducted at room temperature, whereas we conducted the measurements at  $150^\circ\text{C}$ .

Hydrogen absorption and desorption enthalpies in  $\text{Nd}_2\text{Fe}_{14}\text{B}$

$\text{H}/\text{Nd}_2\text{Fe}_{14}\text{B}$	$\Delta H(\text{abs})$ , kJ/mol $\text{H}_2$	$\Delta H(\text{des})$ , kJ/mol $\text{H}_2$
0.3–0.6	$-82.8 + 1.5$	–
0.6–1.2	$-77.7 + 1.2$	–
1.2–1.6	$-62.1 + 1.8$	–
2–2.5	$-42.7 + 2.1$	$44.2 + 1.3$

## CONCLUSIONS

(1) The interaction of hydrogen with hard magnetic intermetallic compound  $\text{Nd}_2\text{Fe}_{14}\text{B}$  was studied for the first time via calorimetry.

(2) The introduction of hydrogen into  $\text{Nd}_2\text{Fe}_{14}\text{B}$  was shown to occur in several stages with various reaction enthalpy values.

(3) The maximum reaction enthalpy was achieved when the  $8j$  ( $[\text{Nd}_3\text{Fe}]$ ) tetrahedral interstitials were filled with hydrogen.

(4) The enthalpies of the absorption/desorption reactions of hydrogen with  $\text{Nd}_2\text{Fe}_{14}\text{B}$  obtained in this study are of practical interest for specialists working in the field of development of powders of magnetic materials.

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