

Article

Study of Hydrogen Interactions with Nd₂Fe₁₇ and Nd₂Fe₁₄B by Means of Calorimetric Method

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Received: 30 January 2018; Accepted: 27 March 2018; Published: 9 April 2018



Abstract: Hydrogen interactions with Nd₂Fe₁₇ and Nd₂Fe₁₄B was investigated by means of the calorimetric method with application of differential heat-conducting calorimeters that were of the Tean-Calvet type. The reaction of hydrogen absorption and desorption was carried out at 250 and 300 °C for Nd₂Fe₁₇, while the pressure-composition-isotherms (P-C-T) and enthalpy change with hydrogen concentration in the intermetallic compound (IMC) were obtained. The Nd₂Fe₁₄B-H₂ system was studied at 50 °C and the dependence of the enthalpy change with hydrogen concentration in the intermetallic compound was also obtained. Based on the measured data, the assumption about the order of filling the interstitial sites by hydrogen atoms was made.

Keywords: Nd₂Fe₁₇-H₂; Nd₂Fe₁₄B-H₂; calorimetry; thermodynamics; enthalpy

1. Introduction

It is well known that in the production of the magnetic materials of the Nd-Fe-B and Re₂Fe₁₇-type (Re = rare earth metals), the process of hydrogenation–dehydrogenation (HD) was used. However, this process was not studied completely until now.

Generally, scientists studied magnetic properties [1–3] and the influence of hydrogen on the structure of alloys. To better understand how hydrogen insertion influences physical and magnetic properties of alloys, it is necessary to know the thermodynamic parameters of the process of hydrogen interaction with magnet materials. Unfortunately, the studies in which the thermodynamic properties of HD processes are studied directly by means of calorimetric method are practically negligible. The authors in a previous study [4] studied hydrogen desorption from R₂Fe₁₇H_x (R = Nd and Dy) compounds with $x \leq 5$ using differential scanning calorimetry (DSC). In previous works [5,6], the thermodynamic parameters of hydrogen interactions with Sm₂Fe₁₇ (the partial molar enthalpy and the partial molar entropy) were determined from pressure-composition isotherms. Ram et al. [7] investigated the hydrogen desorption from Nd₂Fe₁₄BH_x (X~5) by means of differential scanning calorimetry.

In the present work, we continue our research of hydrogen interaction with the systems of R₂Fe₁₇ and Nd₂Fe₁₄B [8–10] and summarize the obtained results.

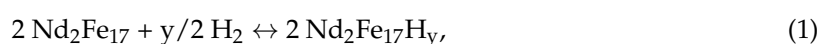
2. Materials and Methods

The initial sample of Nd₂Fe₁₇ was prepared by the arc melting of a stoichiometric mixture of constituent metals of 2–17 (23.3 mas. % Nd and 76.7 mas. % Fe) in a furnace with a non-consumable tungsten electrode on a water-cooled boat in a purified argon atmosphere under a pressure of 2 atm. The purity grade of starting metals was 99.999% for Fe and 99.98% for Nd. Following this, the sample was annealed in a quartz tube at 1100 °C for 40 h to ensure homogeneity.

The details of the synthesis of the materials and results of X-ray Diffraction analysis (XRD) were described elsewhere [8,9]. According to XRD data [8], the synthesized $\text{Nd}_2\text{Fe}_{17}$ sample has the $\text{Th}_2\text{Zn}_{17}$ type structure. The X-ray analysis of $\text{Nd}_2\text{Fe}_{17}\text{H}_{4.6}$ showed that the hydrogenation of the crystal structure of the initial compound was retained, while the anisotropic distortion of the unit cell in the base plane occurs. That agrees with literary data [11] Lattice parameters of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and its hydride coincided with reference data too [12–15]. The chemical composition of the initial samples of $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ was checked by the roentgen-fluorescent analysis on the spectrometer Rigaku Primus II. According to the obtained data, the initial sample of $\text{Nd}_2\text{Fe}_{17}$ contained 76.69 mas. % Fe and 22.92 mas. % Nd, while the initial sample of $\text{Nd}_2\text{Fe}_{14}\text{B}$ contained 28.7 mas. % Nd, 70.1 mas. % Fe and 1 mas. % B [9].

The investigation of hydrogen interactions with $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{14}\text{B}$ was carried out by means of the calorimetric method with application of the differential heat-conducting calorimeter DAK-12, which was connected with Sievert's-type volumetric installation for gas-dose feeding to measure the quantity of absorbed or evolved hydrogen by means of the volumetric method. The apparatus scheme, experimental procedure and analysis of collected data were described in a previous study [9,16]. The use of such complex apparatus permits us to measure P-C-T and $\Delta\text{H-C-T}$ (where P is the equilibrium hydrogen pressure, C is the hydrogen concentration in the intermetallic compound (IMC), $C = \text{H}/\text{IMC}$, T is the experimental temperature and ΔH is the reaction enthalpy), simultaneously. The purity of hydrogen was 99.9999%.

The partial molar enthalpy $\Delta\text{H}_{\text{abs}}$. (des) was determined from the heat effect of the reaction for $\text{Nd}_2\text{Fe}_{17}$:



or from the heat effect of the reaction for $\text{Nd}_2\text{Fe}_{14}\text{B}$:



The heat effect of the reaction was calculated according to the following equation [17]:

$$Q = S \bullet A / \Delta n \quad (3)$$

where S is the area of voltage–time plot; A is the receptiveness, determined from an electrical calibration; and Δn is the number of absorbed/desorbed H_2 molecules.

In a previous study [18], it was shown that the measured heats corresponded to the enthalpies of reaction when H_2 or $1/2 \text{H}_2$ is expressed per mole.

The measurement error in the present work is reflected in Tables 1 and 2. It was determined in accordance with recommendation of International Union of Pure and Applied Chemistry (IUPAC) [19] as a standard deviation of the mean value:

$$\delta = \sqrt{\Sigma \Delta^2 [m(m - 1)]^{-1}} \quad (4)$$

where Δ is the deviation from the mean value and m is the number of data points.

3. Results and Discussion

3.1. P-C Measurements

The reaction of hydrogen interactions with the $\text{Nd}_2\text{Fe}_{17}$ sample was studied in the present work at 250 and 300 °C. Absorption and desorption processes were carried out. In the Figure 1, P-C (P- equilibrium hydrogen pressure, $C = \text{H}/\text{IMC}$) isotherms are shown for these processes.

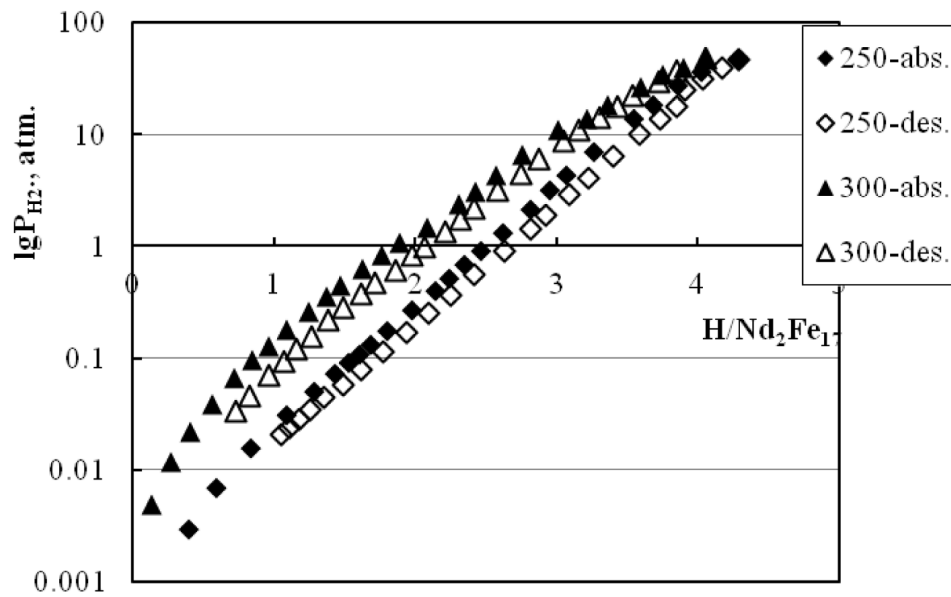
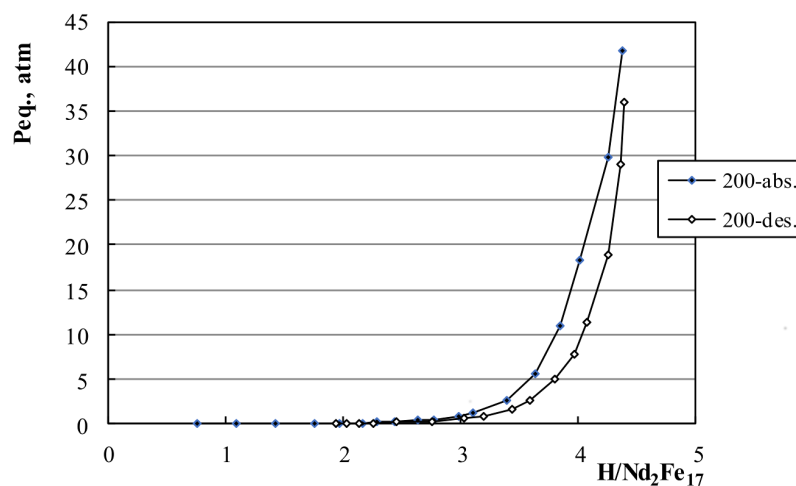


Figure 1. Absorption and desorption isotherms for $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ at 250 and 300 °C.

As one can see on the obtained plots of the $P = f(C)$ dependence, there is no plateau region, which is the characteristic feature of the formation of metal and IMC hydrides. We obtained the same result as a previous study [8] for the hydrogen reaction with $\text{Nd}_2\text{Fe}_{17}$ at 200 °C, which are consistent with results shown in references [20,21].

However, Figure 2a,b shows the absorption and desorption isotherms collected at 200 and 250 °C, which do not coincide with the region of $1.8 < C < 4.3$, while the absorption and desorption isotherms measured at 300 °C coincide completely (see Figure 2c).



(a)

Figure 2. Cont.

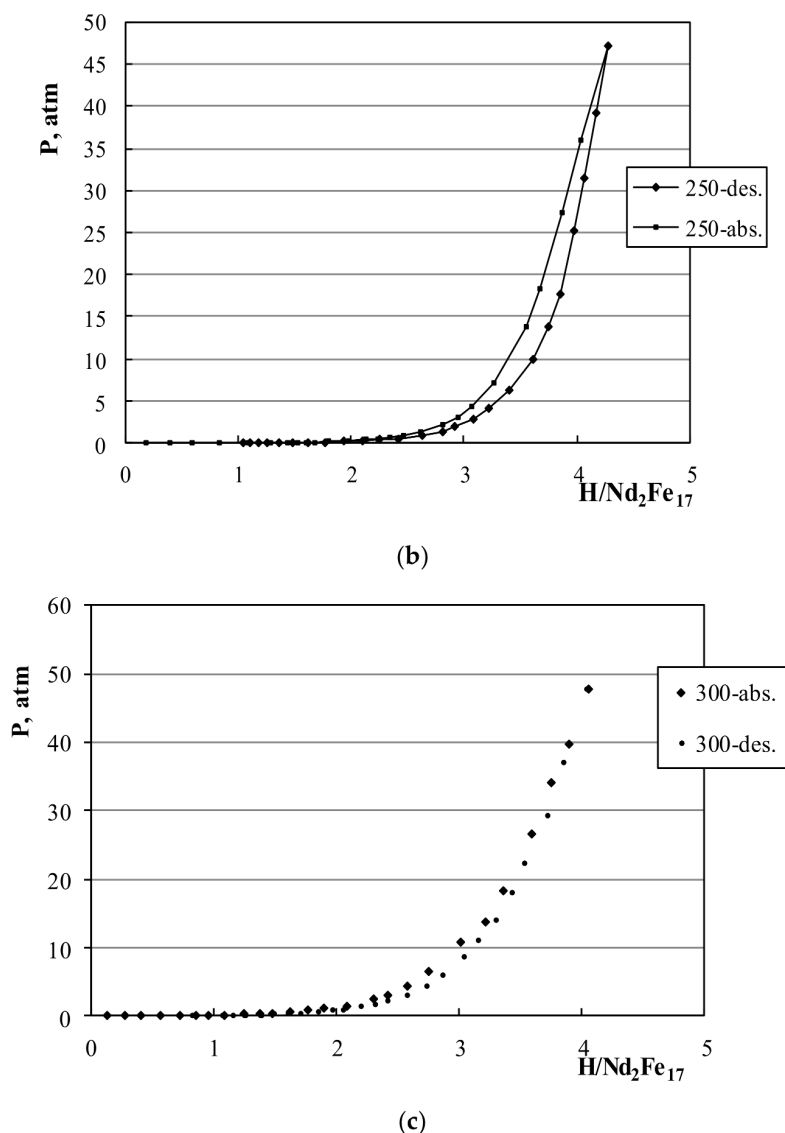


Figure 2. (a) Absorption and desorption isotherms for the $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ system at 200 °C according to reference [8]; (b) absorption and desorption isotherms for the $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ system at 250 °C; and (c) absorption and desorption isotherms for the $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ system at 300 °C.

In other words, in the $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ system, there is a small pressure hysteresis. Previously, we observed such hysteresis in the $\text{Sm}_2\text{Fe}_{17}\text{-H}_2$ system at 250 °C [10] and $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ system at 200 °C [8]. We obtained the following values of hysteresis for the $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ system at 200 and 250 °C at a hydrogen concentration $C \sim 3.6 \ln(10/4.9) = 0.84$ and $\ln(13/10) = 0.60$, respectively.

Similar phenomena were observed previously in references [22–25] for $\text{AB}_2\text{-H}_2$ systems, including $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2\text{-H}_2$, ZrCrV-H_2 , $\text{ZrCrFe}_{1.2}\text{-H}_2$ and $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.3}\text{V}_{0.7}\text{-H}_2$ systems. The authors explained this phenomenon by the formation of hydride phases.

Thus, the presented data permit us to suggest that in the $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ system at 200 and 250 °C, the existence of hydride phases is possible.

3.2. Calorimetric Results

The calorimetric investigation of the hydrogen interactions with $\text{Nd}_2\text{Fe}_{17}$ in the present work was carried out at 250 and 300 °C. As a result, we obtained the dependences of the change in the partial

molar enthalpy of absorption and desorption with hydrogen concentration C ($C = H/ Nd_2Fe_{17}$) in the intermetallic compound $\Delta H_{abs. (des.)} = f(C)$ (see Figure 3a–c and Table 1).

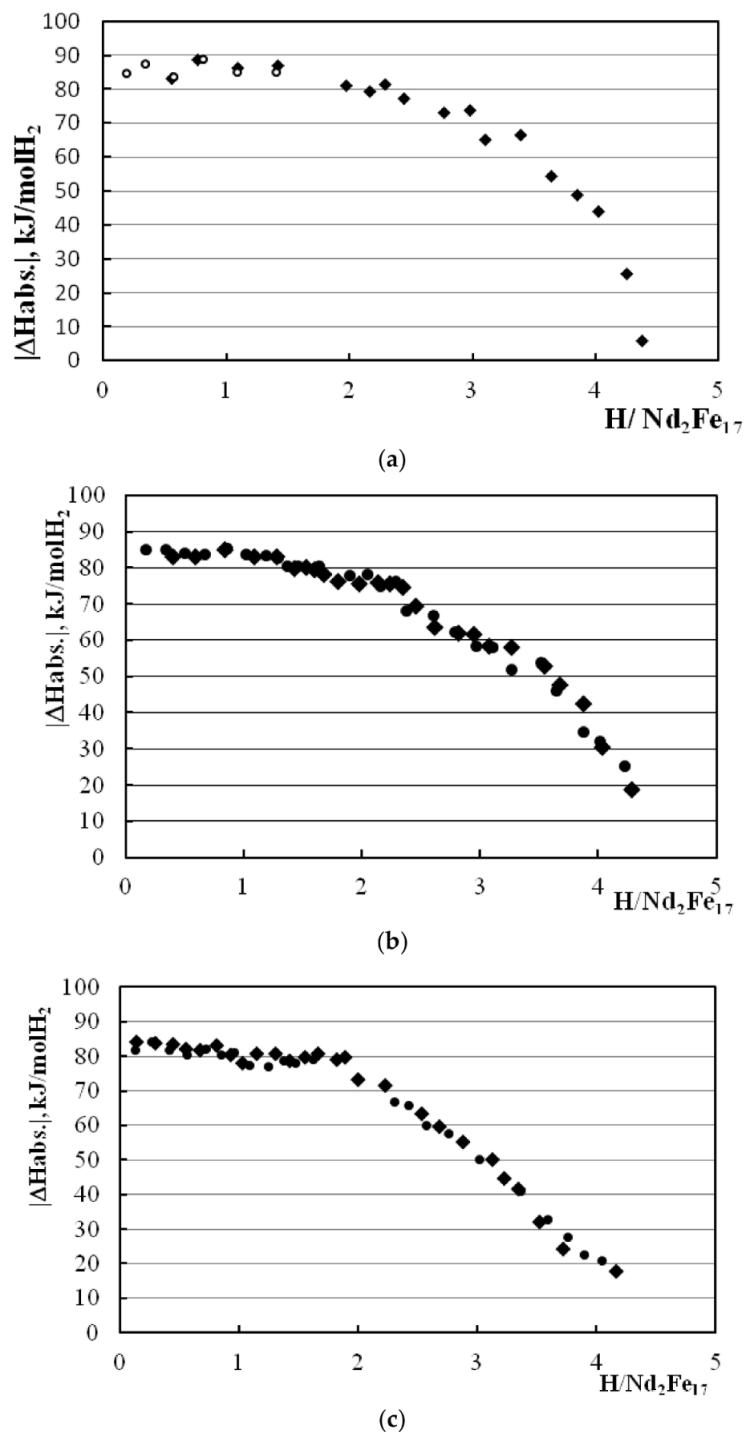


Figure 3. (a) Absorption enthalpy vs. composition at 200 °C for the Nd_2Fe_{17} - H_2 system. The different symbols refer to different runs of determination [8]; and (b) Absorption enthalpy vs. composition at 250 °C for the Nd_2Fe_{17} - H_2 system. The different symbols refer to different runs of determination. (c) Absorption enthalpy vs. composition at 300 °C for the Nd_2Fe_{17} - H_2 system. The different symbols refer to different runs of determination.

The data which we obtained earlier for the $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ system at 200 °C [10] are presented in Table 1.

Table 1. The values of hydrogen absorption and desorption enthalpy in the $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ system.

T, °C	H/IMC	$\Delta\text{Habs.} \pm \delta, \text{ kJ/mol H}_2$	H/IMC	$\Delta\text{Hdes.} \pm \delta, \text{ kJ/mol H}_2$	Ref.
300	0–2.0	-80.5 ± 0.9	0.7–1.9	81.8 ± 1.3	This work
250	0–1.3	-84.2 ± 0.3	0.8–2.0	80.0 ± 0.2	This work
250	1.4–1.8	-79.8 ± 1.3			This work
200	0–2.0	-85.95 ± 0.65			[8]
200	2.0–2.7	-80.64 ± 1.0	1.9–2.7	76.48 ± 0.85	[8]

Analyzing the data presented in the Table 1 and Figure 3a–c, it should be noted that in the $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ system, there are two regions with constant values of $\Delta\text{Habs.}$ at 200 and 250 °C. The increase in reaction temperature results in shrinkage of a length of the part with the constant values of $\Delta\text{Habs.}$ At 300 °C, there is only one region with constant values of $\Delta\text{Habs.}$ (des.). Furthermore, it should be noted that an increase in the reaction temperature of hydrogen interaction with $\text{Nd}_2\text{Fe}_{17}$ results in the decrease in values of partial molar enthalpy in terms of absolute magnitude.

Previously, Isnard et al. [26,27] investigated the hydride phases of R_2Fe_{17} , where R is the light rare-earth element with rhombohedral structure R-3m, by means of neutron diffraction analysis and determined that hydrogen atoms in these intermetallic compounds occupied octahedral 9e and tetrahedral 18g sites. It was determined that 9e sites were filled completely and 18g sites were occupied partially.

In a previous study [4], authors studied the hydrogen desorption from $\text{Nd}_2\text{Fe}_{17}\text{H}_x$ by means of differential scanning calorimetry (DSC) and they determined that for the $\text{Nd}_2\text{Fe}_{17}\text{H}_x$ sample, the DSC curve at a high hydrogen concentration ($X = 5$) had two peaks, which were namely high-temperature (HT) and low-temperature (LT). At the smaller hydrogen concentrations in metallic matrix ($X = 1, 2, 3$), there was one high-temperature peak in the DSC curve. The authors theorized that hydrogen atoms occupied one type of interstitial site in this case.

At $X = 3$ on the DSC curve, the clear shoulder appears. Based on these data, the authors concluded that hydrogen H_1 occupied the pseudo-octahedral interstitial 9e site and hydrogen H_2 occupies the tetrahedral 18g site. In addition, the authors noted that 9e sites that occupied hydrogen H_1 possibly consisted of two energy non-equivalent interstitial sites, which experimentally verified the existence of the clear shoulder in the plots (see Figure 2 (top) and refer to a previous study [4]).

The calorimetric results that we obtained in the present work and in previous studies [8,10] are consistent with the data obtained in reference [4]. We may assume that hydrogen atoms fill 9e sites during absorption at 200 and 250 °C at the range of hydrogen concentration of $0 < C < 2.0$ ($\Delta\text{Habs.} = -85.05 \pm 0.65 \text{ kJ/mol H}_2$ at 200 °C). Furthermore, at $C > 2.0$, the occupancy of 9e sites by hydrogen atoms results in less heat evolution ($\Delta\text{Habs.} = -80.64 \pm 1.00 \text{ kJ/mol H}_2$ at 200 °C). In other words, we may conclude that the 9e position consists of two non-equivalent energy sites. The increase in experimental temperature up to 300 °C results in the appearance of one region with the constant enthalpy values. In this case, we may assume that smoothing of two energy levels in the 9e site takes place at 300 °C.

At the hydrogen concentration $C > 2.7$ in the intermetallic compound, the values of partial molar enthalpy of hydrogen absorption decrease sharply in absolute magnitude when hydrogen atoms start to occupy 18g site (see Figure 3 and Table 1). In the plots $\Delta\text{Habs.} = f(C)$, there are no regions with constant enthalpy values. It is difficult to assume that we deal with the formation of stable hydride in this case as suggested by a previous study [4]. However, the P-C isotherms in Figure 2a,b show some hysteresis in the range of $1.8 < C < 4.3$.

Comparing results of the calorimetric study for the $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ and for $\text{Sm}_2\text{Fe}_{17}\text{-H}_2$ systems (presented in Table 2 made on the basis of the results in reference [10]), one can notice that the

values of $\Delta H_{\text{abs.}}(\text{des.})$ for the $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ system are higher in absolute value compared to the $\text{Sm}_2\text{Fe}_{17}\text{-H}_2$ system.

Table 2. The values of hydrogen absorption and desorption enthalpy in the $\text{Sm}_2\text{Fe}_{17}\text{-H}_2$ system.

T, °C	H/IMC	$\Delta H_{\text{abs.}} \pm \delta, \text{kJ/mol H}_2$	H/IMC	$\Delta H_{\text{des.}} \pm \delta \text{ kJ/mol H}_2$
250	0.3–2.0	-81.7 ± 0.5	0.5–0.7	81.6 ± 0.5
250	2.1–3.0	-75.6 ± 1.0	1.0–2.3	76.8 ± 0.8
200	0.8–1.6	-80.2 ± 0.8	1.2–1.6	~81
200	1.8–2.6	-74.9 ± 2.2	1.6–2.6	73.0 ± 1.1

This phenomenon may be explained by the fact that the samarium radius is less than the neodymium radius due to lanthanum contraction, which leads to a decrease in the volume of the hole available for filling by hydrogen. In other words, the stability of ternary hydrides in the range of $0 < C < 3.0$ depends on the unit cell volume of the alloy. This suggestion was obtained from reference [21].

Cuevas et al. [4] investigated hydrogen desorption from $\text{Nd}_2\text{Fe}_{17}\text{H}_x$ and $\text{Dy}_2\text{Fe}_{17}\text{H}_x$ hydrides by the DSC method. It was determined that the heat of reaction of hydrogen desorption was equal to $29.2 \pm 0.8 \text{ kJ/mol H}_2$ for both $\text{R}_2\text{Fe}_{17}\text{H}_x$ compounds. However, our results show that values of enthalpy absorption and desorption differ for the $\text{Nd}_2\text{Fe}_{17}\text{-H}_2$ and $\text{Sm}_2\text{Fe}_{17}\text{-H}_2$ systems and the enthalpy values change depending on reaction temperature and hydrogen concentration in the metallic matrix.

In a previous study [26], the authors noted that both sites exhibit different behavior depending on the temperature. The structure analysis shows that D1 is the most thermally stable and the most occupied site at higher hydrogen concentrations.

The study of hydrogen with $\text{Nd}_2\text{Fe}_{14}\text{B}$ was carried out in the present work at 50°C . The results of calorimetric study of hydrogen interaction with $\text{Nd}_2\text{Fe}_{14}\text{B}$ are presented in Figure 4 and in Table 3.

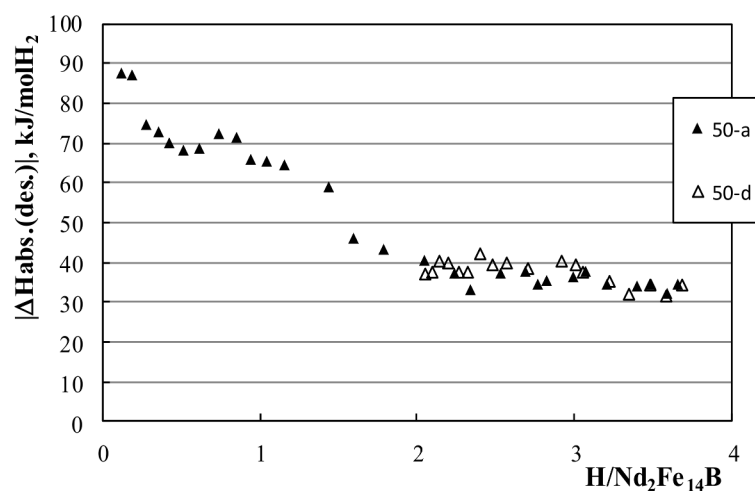


Figure 4. Absorption and desorption of enthalpy vs. composition at 50°C for the $\text{Nd}_2\text{Fe}_{14}\text{B-H}_2$ system. The different symbols refer to different runs of determination. Filled symbols refer to absorption of H, while the open symbols refer to the desorption.

As seen in Figure 4 in the plot of $\Delta H_{\text{abs./des.}} = f(C)$ dependence, it is possible to mark three parts with constant values of enthalpy absorption and two parts with constant values of enthalpy desorption. The values of absorption and desorption enthalpy in these regions are presented in Table 3.

As one can see from these data, the enthalpy values of absorption and desorption coincide at absolute values on the regions of $2.0 < C < 3.0$ and $3.2 < C < 3.7$.

Table 3. The values of hydrogen absorption and desorption enthalpy in the Nd₂Fe₁₄B-H₂ system.

T, °C	H/IMC	ΔHabs. ± δ, kJ/mol H ₂	H/IMC	ΔHdes. ± δ, kJ/mol H ₂
50	0.3–0.9	−69.3 ± 1.3		
50	2.0–3.0	−36.6 ± 1.6	2.0–3.0	38.7 ± 0.8
50	3.2–3.7	−34.0 ± 1.3	3.2–3.7	33.5 ± 1.8

4. Conclusions

The reaction of hydrogen interactions with Nd₂Fe₁₇ and Nd₂Fe₁₄B was investigated by means of the calorimetric method at different temperatures. It was shown that the values of enthalpy absorption and desorption changed with reaction temperature and hydrogen concentration in the intermetallic compounds.

It was demonstrated that the character of the change of the enthalpy values correlated with the extent of filling of crystallographic holes.

The observed pressure hysteresis might be the evidence of the beginning of hydride phase formation, which requires further study.

The role of enthalpy in the occupation of crystallographic holes and hydride phase formation needs further research to be completely characterized.

Author Contributions: Elena Anikina and Victor Verbetsky conceived and designed the experiments; Elena Anikina performed the experiments; Elena Anikina and Victor Verbetsky analyzed the data; Alexander Savchenko contributed reagents, materials and analysis tools; Elena Anikina and Victor Verbetsky wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Isnard, O.; Miraglia, S.; Guillot, M.; Fruchart, D.; Buschow, K.H.J. High field magnetization measurements of Sm₂Fe₁₇, Sm₂Fe₁₇C_x and Sm₂Fe₁₇C_xH_{5-x}. *J. Appl. Phys.* **1994**, *76*, 6035–6937. [[CrossRef](#)]
- Isnard, O.; Miraglia, S.; Soubeyroux, J.L.; Fruchart, D.; L'Hétiier, P. A structural analysis and some magnetic properties of the R₂Fe₁₇H_x series. *J. Magn. Magn. Mater.* **1994**, *137*, 151–156. [[CrossRef](#)]
- Cristodoulou, C.N.; Takeshita, T. Preparation, structural and magnetic properties and stability of interstitial Sm₂Fe₁₇—Carbonitrides. *J. Alloys Compd.* **1993**, *198*, 1–24. [[CrossRef](#)]
- Cuevas, F.; Isnard, O.; Villeroy, B. An investigation of hydrogen desorption from Nd₂Fe₁₇H_x and Dy₂Fe₁₇H_x compounds by differential scanning calorimetry. *Thermochim. Acta* **2013**, *561*, 14–18. [[CrossRef](#)]
- Koeninger, V.; Koike, U.; Kamata, K.; Matsumura, Y.; Noguchi, T.; Kurino, T.; Kaneko, H.; Yanagisawa, T.; Uchida, H.H.; Uchida, H. Hydrogen absorption characteristics of Sm₂Fe₁₇ alloy. *J. Phys. Chem.* **1993**, *181*, 299–304.
- Kuji, T.; Uchida, H.; Kinoshita, K.; Yamamuro, M.; Komatsu, A. Dual site occupancy of hydrogen in Sm₂Fe₁₇. *J. Alloys Compd.* **2002**, *330–332*, 187–201. [[CrossRef](#)]
- Ram, S.; Fecht, H.J.; Haldar, S.; Ramachandrarao, P.; Banerjee, H.D. Calorimetric study of the desorption of the interstitial hydrogen atoms in ferromagnetic Nd₂Fe₁₄BH_x (X~5) microcrystals. *Phys. Rev. B Condens. Matter* **1997**, *56*, 726–737. [[CrossRef](#)]
- Anikina, E.Y.; Verbetsky, V.N.; Savchenko, A.G.; Menushenkov, V.P.; Shchetinin, I.V. Investigation of hydrogen interaction with intermetallic compound Nd₂Fe₁₇ by means of calorimetric method. *Inorg. Mater.* **2017**, *53*, 8–11. [[CrossRef](#)]
- Anikina, E.Y.; Verbetsky, V.N.; Savchenko, A.G.; Menushenkov, V.P.; Shchetinin, I.V. Investigation of Hydrogen Interaction with Magnetic Materials of Nd–Fe–B Type by Calorimetry Method. *Inorg. Mater. Appl. Res.* **2016**, *7*, 497–501. [[CrossRef](#)]
- Anikina, E.Y.; Verbetsky, V.N.; Savchenko, A.G.; Menushenkov, V.P.; Shchetinin, I.V. Calorimetric study of hydrogen interaction with Sm₂Fe₁₇. *J. Alloys Compd.* **2015**, *645*, S257–S260. [[CrossRef](#)]
- Sagawa, M.M.; Fujirama, S.; Togawa, M.; Yamamoto, H.; Matsuura, Y. New materials for permanent magnets on a base of Nd and Fe. *J. Appl. Phys.* **1984**, *55*, 2083–2087. [[CrossRef](#)]
- Oesterreicher, H. Structure and magnetic properties of Nd₂Fe₁₄BH_{2.7}. *J. Phys. Status Solidi* **1984**, *85*, K61–K64. [[CrossRef](#)]

13. Givord, D.; Li, H.S.; Moreau, J.M. Magnetic properties and crystal structure of Nd₂Fe₁₄B. *Solid State Commun.* **1984**, *50*, 497–499. [[CrossRef](#)]
14. Herbst, J.F.; Croat, J.J.; Pinkerton, E.F.; Yelon, W.B. Relationships between crystal structure and magnetic properties in Nd₂Fe₁₄B. *J. Phys. Rev. B* **1984**, *29*, 4176–4178. [[CrossRef](#)]
15. Buschow, K.H.J.; De Mooij, D.B.; Daams, J.L.C.; van Noort, H.M. Phase relationships, magnetic and crystallographic properties of Nd-Fe-B alloys. *J. Less Common Met.* **1986**, *115*, 357–366. [[CrossRef](#)]
16. Anikina, E.Y.; Verbetsky, V.N. Calorimetric investigation of the hydrogen interaction with Ti_{0.9}Zr_{0.1}Mn_{1.1}V_{0.1}. *J. Alloys Compd.* **2002**, *330–332*, 45–47. [[CrossRef](#)]
17. Calvet, E.; Prat, H. Microcalorimétrie: Applications physico-chimiques et biologiques. *J. Am. Chem. Soc.* **1957**, *79*, 3614–3615.
18. Boureau, G.; Kleppa, O. Significance of thermal effects associated with solid-gas reaction in the Tian-Calvet calorimeter. *J. Chem. Thermodyn.* **1977**, *9*, 543–548. [[CrossRef](#)]
19. Currier, L.A.; Svehla, G. Nomenclature for the presentation of results of chemical analysis. (IUPAC Recommendations). *J. Pure Appl. Chem.* **1994**, *66*, 595–608. [[CrossRef](#)]
20. Rupp, B.; Wiesinger, G. Magnetic and structural properties of a novel ternary hydride Nd₂Fe₁₇H_X (0 < X < 5). *J. Magn. Magn. Mater.* **1988**, *71*, 269–278.
21. Isnard, O.; Miraglia, S.; Fruchart, D.; Akiba, E.; Nomura, K. Hydrogen absorption in R₂Fe₁₇ alloys (R = rare earth metals) thermodynamics, structural and magnetic properties. *J. Alloys Compd.* **1997**, *231*, 150–155. [[CrossRef](#)]
22. Grant, D.M.; Murray, J.J.; Post, M.L. The Thermodynamics of the System Zr(Fe_{0.75}Cr_{0.25})₂-H₂ Using Heat Conduction Calorimetry. *J. Solid State Chem.* **1990**, *87*, 415–422. [[CrossRef](#)]
23. Sirotina, R.A.; Umerenko, E.A.; Verbetsky, V.N. Calorimetric Study of Interaction in the ZrCrFe-H₂ System. *Inorg. Mater.* **1996**, *32*, 629–632.
24. Ivanova, T.V.; Verbetsky, V.N. Calorimetric investigation of the hydrogen interaction with ZrCrFe_{1.2}. *J. Alloys Compd.* **1999**, *293–295*, 34–37. [[CrossRef](#)]
25. Anikina, E.Y.; Verbetsky, V.N. Investigation of the hydrogen interaction with Ti_{0.9}Zr_{0.1}Mn_{1.3}V_{0.7} by means of the calorimetric method. *Int. J. Hydrog. Energy* **2016**, *41*, 11520–11525. [[CrossRef](#)]
26. Isnard, O.; Soubeyroux, J.L.; Miraglia, S.; Fruchart, D.; Garcia, L.M.; Bartolome, J. Neutron powder diffraction study of the desorption of deuterium in R₂Fe₁₇D~X. *Phys. B* **1992**, *180–181*, 620–631.
27. Isnard, O.; Miraglia, S.; Soubeyroux, J.L.; Fruchart, D. Neutron powder diffraction study of R₂Fe₁₇H_X compounds with R = Pr and Nd. *Solid State Commun.* **1992**, *81*, 13–19. [[CrossRef](#)]



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