

**INTERNATIONAL ASSOCIATION FOR HYDROGEN  
ENERGY**

**Permanent Working International Scientific Committee  
on Hydrogen Treatment of Materials**

**PROGRESS  
IN HYDROGEN TREATMENT  
OF MATERIALS**

**Edited by V.A. Goltsov**



**Donetsk – 2001 – Coral Gables**

# **Progress In Hydrogen Treatment Of Materials**

Edited by V.A. Goltsov

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A successful entering into the life of an ecologically clean hydrogen economy and an expected transition to hydrogen civilization in the future require the creation of new and new hydrogen-stable structural materials, new and new advanced functional ones, new special technologies of their production and treatment.

In response to these modern day requirements the world-renowned scientists and experts from ten countries have contributed to this book – the first book reviewing the origination and development of a novel field of Materials Science and Engineering now referred to as “Hydrogen Treatment of Materials” (HTM).

The book generalizes the knowledge related to the HTM-theory and the HTM-technology. There are considered structures and properties of material–hydrogen (MH) systems, their surface and subsurface layers, thin films and multilayers. A diffusive–cooperative synergetic nature of MH-systems is generalized, their thermodynamic and kinetic peculiarities are analyzed, and related phenomena are described. For the first time there are systematically considered hydrogen-induced phase transformations: their nature, classification, mechanisms, kinetics, morphology, influence on structure and properties and use in the HTM. The present day knowledge is summarized as it relates to the HTM-technologies for deformed, cast and synthesized materials, such as palladium, niobium, vanadium, alloys on the base of Al, Ti, Fe, intermetallics, nonmetallic materials; the achievements of the HTM-technologies, improving their structures, mechanical, physical and catalytic properties are described. Some attention is also given to hydrogen degradation of metals, alloys and steels.

The book is intended for Materials Science scientists, physicists, chemists, engineers and other active members of the world hydrogen movement. It will be highly useful for students, post-graduates and young scientists who are interested in the structure, properties and applications of material–hydrogen systems.

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*Mankind is not only discovering something new, unknown, nonunderstandable in the nature, but at the same time it is discovering in its own history a lot of forgotten flashes of understanding by some individuals of these phenomena which seemed to be new. Advancing is conditioned by a long imperceptible unrealizable spade-work of many generations. Having reached something new and unknown, we are always surprised to find precursors in the past.*

V.I. Vernadsky, 1911

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## *P R E F A C E*

It was just a little over a quarter of a century ago, during the first International Conference on Hydrogen Energy (the Hydrogen Economy Miami Energy Conference, 18-20 March 1974, Miami Beach, FL, U.S.A.) when a small group of “Hydrogen Romantics” got together. It was agreed that the Hydrogen Energy System was an idea whose time had arrived. It was the permanent solution to the global environmental problems.

So International Association for Hydrogen Energy (IAHE) was established by the end of that year, and started working in earnest. One of the first activities of IAHE was establishing (1975) *The International Journal of Hydrogen Energy (IJHE)* – the official journal of IAHE and then organizing the biennial World Hydrogen Energy Conferences (WHEC) to provide a platform for forming Hydrogen Energy Community: the scientists, energy engineers, environmentalists, decision makers, and the thinkers of the future of humankind and Planet Earth. Since 1976 WHEC was held in Miami, Zürich, Tokyo, Pasadena, Toronto, Vienna, Moscow, Honolulu, Paris, Cocoa Beach, Stuttgart, Buenos Aires and Beijing.

In the quarter of the century hydrogen has made significant progress and inroads in all the directions in the energy field, due to its unmatched superior properties and characteristics as an energy carrier, on the one hand, and due to the unrelenting work of all those who took part in the Hydrogen Movement, on the other hand.

Historically in parallel with Hydrogen Energy Community Hydrogen–Materials one was successfully developing in the world. As materials problem forms a very important part of any global vector of human development, more and more close cooperation of the above mentioned communities was necessary for the future Hydrogen Economy entering into the life. This cooperation has already its own long history, and its development was very successful thanks to the activity of many outstanding scientists and well-known scientific groups. Among them it is necessary to emphasize the Donetsk group, headed by Professor V.A. Goltsov – the Editor of this Book, a scientist awarded now (June 2000) with IAHE Rudolf E. Erren Award “for Outstanding Contribution to Hydrogen Energy in General and to Hydrogen Treatment of Materials in Particular”.



Really, since the middle of the 1970s special national and international conferences on the Hydrogen Energy and Hydrogen–Materials problems were held in Donetsk every two–three years. It was just Professor V.A. Goltsov who discovered in the 1970s a new fundamental hydrogen property: hydrogen is not only an excellent universal energy carrier, but it is a fundamental, unique agent for hydrogen treatment of materials permitting to improve their structure and properties, to create new advanced materials needed for Hydrogen Economy. Since that time this new paradigm of Materials Science has attracted new and new adherents.

In 1997 under the auspices of IAHE the Permanent Working International Scientific Committee on Hydrogen Treatment of Materials (PWISC HTM) was established (Chairperson is Professor V.A. Goltsov, Co-Chairperson is Dr. F. Lewis). One of the general aims and tasks of the created Committee is to support permanently the cooperation of the Hydrogen Energy Community and Hydrogen-Materials one. For this purpose IAHE and PWISC HTM organized triennial international conferences “Hydrogen Treatment of Materials”. Proceedings of the selected papers of these conferences are published in *IJHE*.

This Book is also a result of PWISC HTM activity and of a long scientific work of all its authors. Being the first review of the topic the book “Progress in Hydrogen Treatment of Materials” generalizes the achievements of this new field of Materials Science and Engineering during its starting period of time. Without any doubt it will be very useful for moving forward on all fronts of Hydrogen Treatment of Materials and other Hydrogen – Materials problems.

My colleagues, authors of this Book, being members of World Hydrogen Movement you can be very proud of the results of your unrelenting work making a great contribution to the development of Hydrogen Economy, the only one known to be clean, efficient, sustainable, abundant, hospitable to life on the Planet Earth. I am sure the readers of this Book will positively estimate your scientific achievements.



*T. Nejat Veziroglu*  
President,  
International Association for Hydrogen Energy

# KINETICS AND SOME GENERAL FEATURES OF HYDROGEN INDUCED DIFFUSIVE PHASE TRANSFORMATIONS IN $\text{Nd}_2\text{Fe}_{14}\text{B}$ TYPE ALLOYS

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## Abstract

In this review there are generalized experimental data on the kinetics of direct and reverse hydrogen-induced diffusive phase (HIDP) transformations in alloys of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type being the basis of the HDDR technology. There are discussed general regularities of these transformations: their most general mechanisms, types of isothermal kinetic diagrams of both direct and reverse HIDP transformations, mechanisms of temperature and hydrogen pressure influence on the kinetics. There is made a conclusion that hydrogen is not only a necessary thermodynamic condition, but the most important kinetic factor characterizing general features of HIDP transformations.

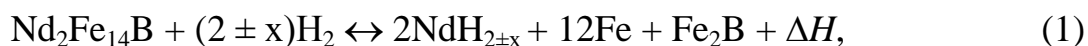
## 1. Introduction

Hydrogen treatment of materials [1,2] is based on the specific peculiarities of hydrogen and hydrogen induced phase transformations [3]. For example, a recently developed [4,5] HDDR process (Hydrogenation–Disproportionation–Decomposition–Recombination) is based on hydrogen induced direct and reverse phase transformations in intermetallic compounds of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type. The intermetallic compounds of this type are high-coercive ferromagnetic materials currently used in the production of power compact magnets [6–11]. A characteristic feature of these alloys is the fact that upon hydrogenation they lose their thermodynamical stability and at elevated temperatures undergo a phase transformation, namely, decomposition into a hydride of a rare-earth component

(NdH<sub>x</sub>), an  $\alpha$ -phase of Fe, and the iron boride Fe<sub>2</sub>B [9–11]. Hydrogen evacuation causes a reverse phase transformation with the formation of an initial Nd<sub>2</sub>Fe<sub>14</sub>B phase. This hydrogen treatment results in a significant structure refinement and an increase in the coercive force of the intermetallic compound. This type of hydrogen treatment called the HDDR process enables to obtain high-coercive materials with  $H_c$  up to 1.3 MA/m [9–11]. Isotropic bonded magnets produced by this technique exhibit a maximum energy product  $(BH)_{\max}$  of about 180 kJ/m<sup>3</sup> [11].

Phenomena taking place upon hydrogen influence in intermetallics containing rare-earth and transition metals can be studied within different sciences, *vis.* general chemistry and chemistry of solids, solid state physics, materials science, metal science, *etc.*

From the viewpoint of chemistry hydrogen induced reform of the Nd<sub>2</sub>Fe<sub>14</sub>B type alloys are described by the following solid state reactions [11]:



where  $\Delta H$  is the reaction enthalpy.

An exothermal reaction in the forward direction is called ‘disproportionation’, and this emphasizes that a chemical formula of the initial compound is disturbed. An endothermal reaction in the return direction taking place upon degassing is called ‘recombination’ which means a recovery of the compound assumption formula. This approach has taken shape historically [4–8], it is a productive one and allows to store information and to analyze it by the methods of chemistry. First, in the 1970s and 1980s the ‘disproportionation’ was classified as a reaction of ‘hydrogenolysis of chemical compounds’. This term means a thermodynamic instability of intermetallics as chemical compounds upon their interaction with hydrogen. It’s obvious that just on the base of reaction (1) there can be an assumption thermodynamic analysis (without regarding structural factors) assessing the directivity of the processes and the equilibrium finite products in these conditions ( $T$  и  $P_{\text{H}_2}$ ).

In this paper we’ll consider these very phenomena from the viewpoint of physics of solids [12] and physical metallurgy [13] in which corresponding theoretical approaches have been developed and a great experimental experience of studying phase transformations and their influence on the structure and properties of metals and alloys have been stored. Such an approach is the most adequate when considering kinetic and structural aspects of the HDDR process and phase transformations being its base.

So, the first aim of this paper is to summarize the knowledge of the kinetics of hydrogen induced diffusive phase transformations in the  $R_2\text{Fe}_{14}\text{B}$  type alloys (where  $R$  is Nd, Pr and other rare-earth elements), and the second one is to discuss some general features of these transformations from the physical metallurgy and solid state physics viewpoint.

## 2. Direct HIDP-Transformations

The kinetics of direct HIDP-transformations was systematically studied in works [14–18] by Sadikov's magnetometrical method [19]. The idea of this method is based on the following fact. Within experimental temperatures (610–760°C) the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type alloys are paramagnetic ( $T_c=312^\circ\text{C}$ ), but the phases of decomposition ( $\alpha\text{-Fe}$  and  $\text{Fe}_2\text{B}$ ) are ferromagnetic. A  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type alloy sample was placed into an alternating magnetic field of about 15 kA/m. The bifilar measuring coil was placed around the reaction chamber cooled by water. A sample put into the chamber was undergoing hydrogen action, and an electromotive force was induced. Values of the electromotive force were proportional to the quantity of the ferromagnetic phases in the sample ( $\alpha\text{-Fe}$  and  $\text{Fe}_2\text{B}$ ).

The following procedure was used to investigate direct HIDP-transformations in the temperature range of 600–760°C. Samples of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type alloys were placed into the working chamber, which was evacuated up to  $10^{-2}$  Torr. The samples were heated under a continuous evacuation at an average rate of 20 K/min to a desired temperature chosen from the range of 600 to 760°C. After establishing isothermal conditions in the working chamber it was filled with hydrogen. The direct HIDP transformations during the isothermal annealing were monitored by an increase in the amount of the ferromagnetic phases ( $\alpha\text{-Fe}$  and  $\text{Fe}_2\text{B}$ ). The data obtained were used to plot the kinetic curves and isothermal transformation diagrams of the direct HIDP transformations in the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type alloys. The kinetic data in a paramagnetic field of  $\alpha\text{-Fe}$  ( $T > T_c = 770^\circ\text{C}$ ) were obtained by a special method. This method is as follows. The sample undergoes a direct HIDP-transformation at temperatures higher than the Curie point of  $\alpha\text{-Fe}$  (800, 830 and 860°C) during some time. Then, it is rapidly cooled up to 600°C (it is the temperature where a HIDP transformation doesn't develop) in equal intervals of time (as a rule, it is 2.5–5 min). After this it is rapidly heated again to the previous isothermal temperature (800, 830 and 860°C). So, kinetic data for plotting the kinetic curves were obtained from magnetic measurements in the ferromagnetic field of  $\alpha\text{-Fe}$  and  $\text{Fe}_2\text{B}$  phases. In all cases the transformation degree was confirmed by the results of the X-ray powder diffraction and by magnetic measurements of Curie points of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  and  $\alpha\text{-Fe}$  phases.

### 2.1. Influence Of Temperature

The investigation of a direct HIDP-transformation in a commercial  $R_2\text{Fe}_{14}\text{B}$  alloy (where  $R$  is Nd, Pr and others rare-earth elements) in the temperature range of 610–760°C and hydrogen pressure of 0.15 MPa was studied in [15]. Figure 1 shows the isothermal kinetic curves of this transformation. As can be seen in Figure 1, at isothermal temperature  $T = 610^\circ\text{C}$  (curve 1) a direct HIDP-transformation does not develop in 360 min of an experimental time. Increasing the isothermal temperature to 640°C (curve 2) and 670°C (curve 3) induces a slow

evolution of the phase transformation. Now it reaches 18 and 59% degree of transformation, respectively. A further increasing of temperature makes transformation much more rapid. So, at 690°C (curve 4) the phase transformation is fully completed in 340 *min*. And finally, in the temperature range of 710–760°C (curves 5–8) this transformation is developed with a maximal rate. So, at 760°C (curve 8) it is finished in 65 *min*.

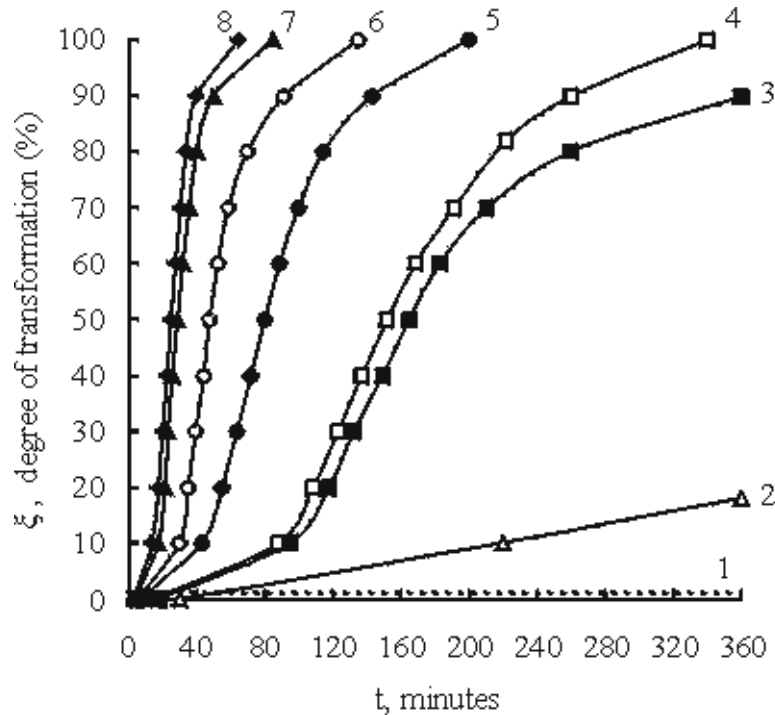


Fig. 1. A direct HIDP transformation in a commercial  $R_2Fe_{14}B$  alloy at hydrogen pressure of 0.15 MPa and various isothermal temperatures: 1–610°C; 2–640°C; 3–670°C; 4–690°C; 5–710°C; 6–730°C; 7–750°C; 8–760°C.

At all temperatures there is a noticeable incubation period of a phase transformation (from 35 *min* at 640°C to 1.25 *min* at 760°C).

Influence of the isothermal temperature exposure on the kinetics of a direct HIDP-transformation in  $Nd_{15}Fe_{77}B_8$  (analog of  $Nd_2Fe_{14}B$  alloy) was studied in [18].

Figure 2a shows the isothermal kinetic curves of direct HIDP-transformations in the  $Nd_{15}Fe_{77}B_8$  (at.%) alloy obtained in the temperature range of 610–750°C and hydrogen pressures of 0.1 MPa. As can be seen from this figure at 610°C (curve 1), 640°C (curve 2) and 670°C (curve 3) the direct transformation reaches only 28%, 46% and 62%, respectively. At  $T = 690^\circ\text{C}$  (curve 4) the phase transformation is over in 345 *min*. Increasing the isothermal temperature to 710°C (curve 5) induces an acceleration of the direct HIDP-transformation. At this temperature, a full transformation is accomplished in 175 *min*. At temperatures 730°C (curve 6) and 750°C (curve 7) a direct phase transition is completed in 115 and 85 *min*, respectively.

So, as can be seen in Fig. 2a, at an increase of temperature from 610°C up to 750°C a transformation rate increases quickly by analogous with the above-described commercial alloy of the  $R_2Fe_{14}B$  type (Fig. 1).

In principle analogous data were obtained when studying kinetics of decomposition in the  $Nd_{16}Fe_{76}B_8$  alloy at hydrogen pressure of 0.1 MPa by the magnetometrical method [20]. It was shown that at an increase of temperature from 600°C up to 720°C the rate of decomposition accelerates.

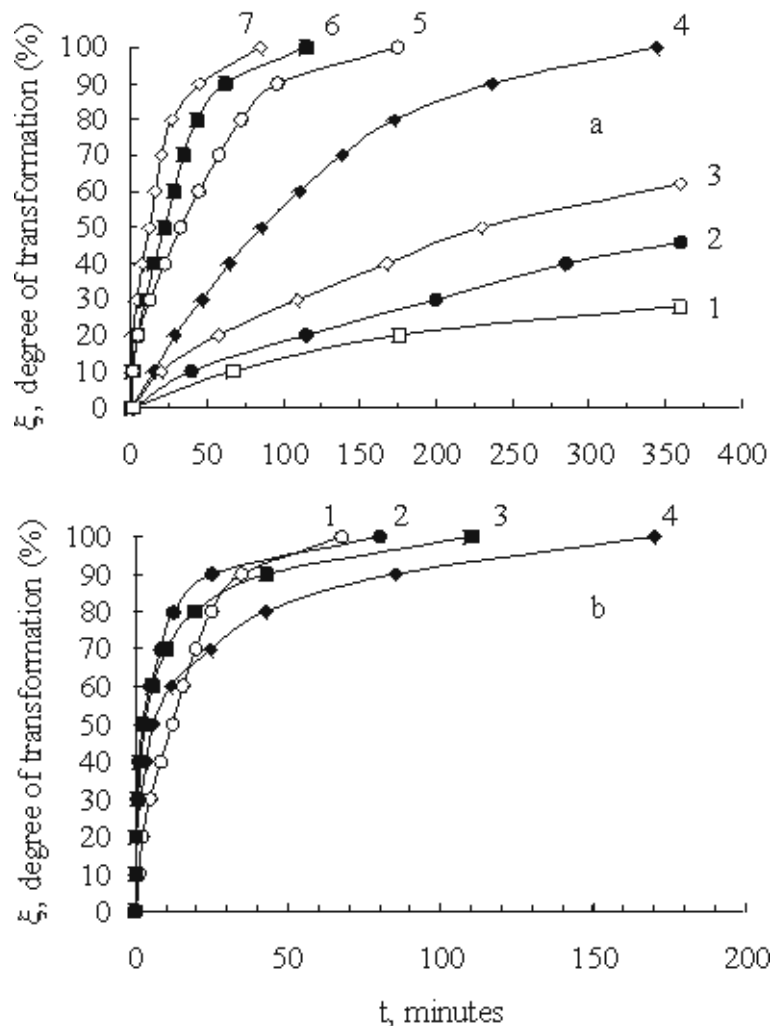


Fig. 2. A direct HIDP transformation in  $Nd_{15}Fe_{77}B_8$  alloy at hydrogen pressure of 0.1 MPa and various isothermal temperatures: (a) 1–610°C; 2–640°C; 3–670°C; 4–690°C; 5–710°C; 6–730°C; 7–750°C; (b) 1–760°C; 2–800°C; 3–830°C; 4–860°C.

Fig. 2b shows the isothermal kinetic curves of direct HIDP-transformations in the  $Nd_{15}Fe_{77}B_8$  (at.%) alloy obtained in the temperature range of 760–860°C and hydrogen pressures of 0.1 MPa. At temperature 760°C (curve 1) a direct phase transition is completed in 67.5 min. A further increasing of temperature results in slowing down the transformation rate. So, this phase transformation at 800°C

(curve 2) is now finished in 80 *min*. At 830°C (curve 3) and 860°C (curve 4) it is completed in 110 and 170 *min*, respectively. These results (Fig. 2b) are in a good agreement with the data in [21] in which the kinetics of a direct phase transformation in the  $\text{Nd}_{12.6}\text{Fe}_{\text{bal}}\text{Co}_{11.0}\text{Zr}_{0.1}\text{B}_{6.0}$  alloy was studied within the temperatures range 740–860°C by measuring electrical resistance. The results of this work are given in Figure 3. It's graphically shown that the transformation develops very quickly at 740°C and in 50 *min* it is over. At temperatures higher than 740°C the transformation rate slows down gradually.

Thus, it is evident from Fig. 1–3, that a maximum rate of direct HIDP-transformations in the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type alloys takes places in the temperature range of 750–800°C and slows down above and below this temperature range.

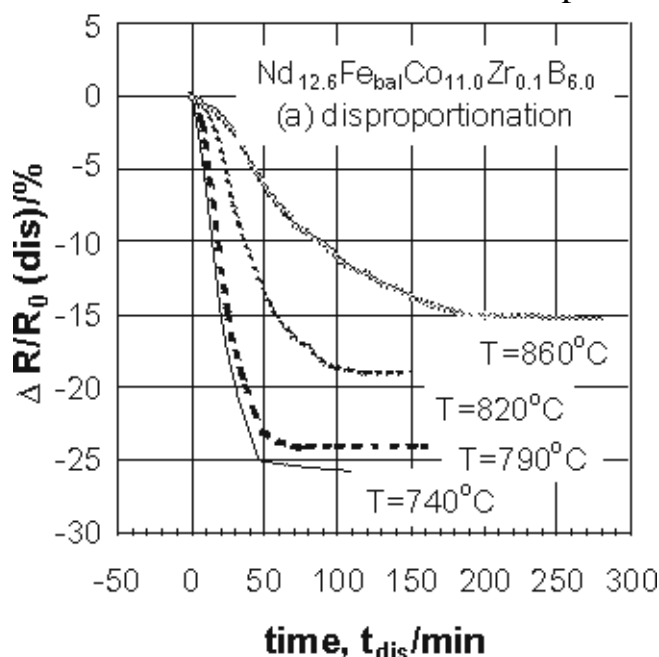


Fig. 3. Relative resistivity changes of  $\text{Nd}_{12.6}\text{Fe}_{\text{bal}}\text{Co}_{11.0}\text{Zr}_{0.1}\text{B}_{6.0}$  alloy during disproportionation in the temperature range of 740–860°C (from [21]).

## 2.2. Influence Of Hydrogen Pressure

An effect of hydrogen pressure on the kinetics of a direct HIDP-transformation in the  $\text{R}_2\text{Fe}_{14}\text{B}$  type commercial alloy was studied in [16] and [17]. These results are generalized in Figure 4.

Fig. 4a describes the kinetics of a direct transformation at the isothermal temperature of 710°C and at different hydrogen pressures. As seen from this figure at hydrogen pressures of 0.1 MPa (curve 1) and 0.15 MPa (curve 2) phase transformations were completed in 265 and 200 *min*, respectively. In case when a direct transformation occurs at hydrogen pressure of 0.2 MPa it is completed in 130 *min* (curve 3).

As can be seen from Fig. 4b at isothermal temperature of 750°C and at pressures of 0.1 MPa (curve 1) and 0.15 MPa (curve 2) a direct phase

transformation is completed in 120 and 85 min, respectively. An increase of hydrogen pressure up to 0.2 MPa (curve 3) results in a great acceleration of a direct transformation and it is completed in 42 min.

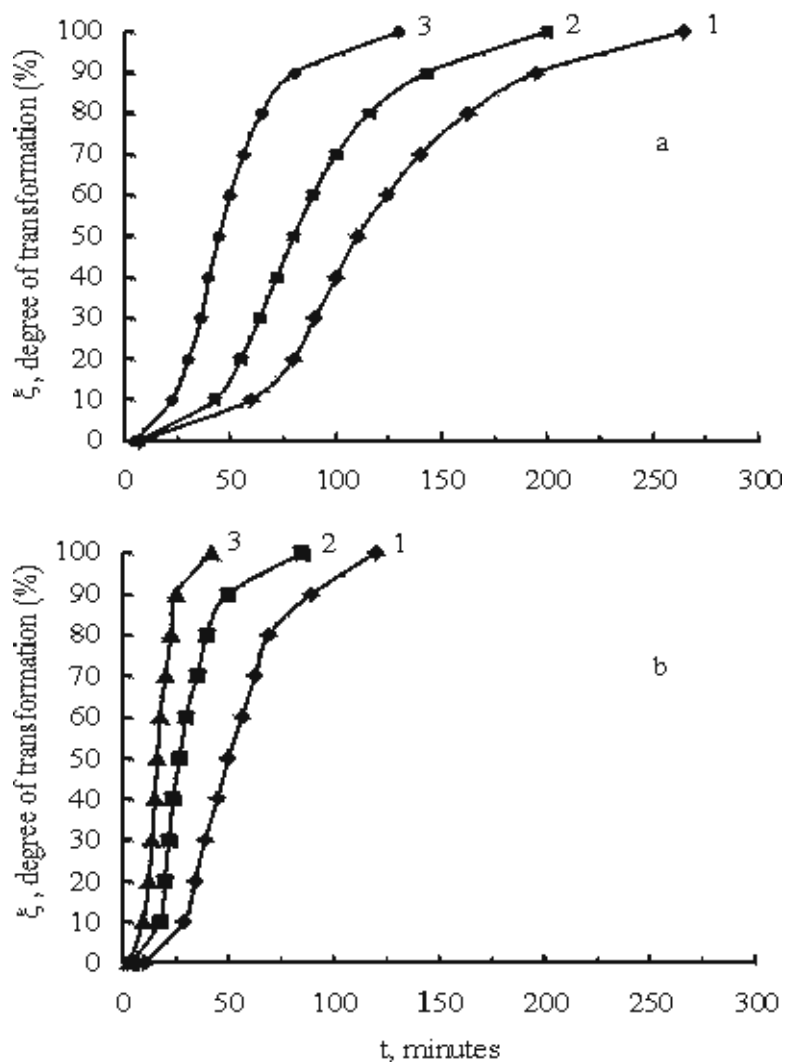


Fig. 4. Kinetic curves of a direct HIDP transformation in a commercial  $R_2Fe_{14}B$  alloy at different isothermal temperatures  $T=710^\circ C$  (a) and  $750^\circ C$  (b) at hydrogen pressures: 1 – 0.1 MPa; 2 – 0.15 MPa; 3 – 0.2 MPa.

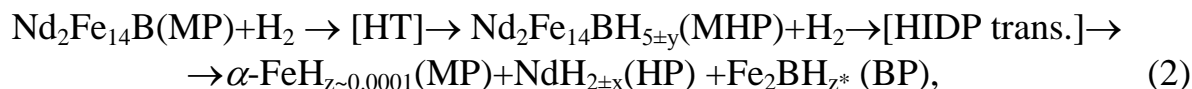
So, as can be seen from Fig. 4, a twofold increase of hydrogen pressure gives an increase of the isothermal direct HIDP-transformation rate of about 2–3 times as big for all temperatures and pressures.

In principle, analogous data were obtained when studying HIDP-transformations in the  $Nd_{15}Fe_{77}B_8$  alloy by the DTA method [22]. It turned out that (See Figure 5) as hydrogen grows from 0.4 up to 11.2 bar a phase transformation rate accelerates greatly and the temperature range of its fastest development shifts to the range of more lower temperatures ( $715 \rightarrow 665^\circ C$ ). Analogous data have been obtained when studying direct HIDP-transformations in  $Sm_2Fe_{16}Ga$  [23].



### 2.3. Discussion

Hydrogen induced hydrogenolysis (disproportionation) of an intermetallic of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type from the viewpoint of physics and metal science is nothing more but a phase transformation in a solid which results in changes of the alloy structure and phase composition [3]. Such a phase transformation can be given in the following *structural* scheme:



where MP is a matrix phase, MHP is a matrix hydride phase, HP is a hydride phase, BP is a boride phase, HT is a hydride (diffusive-cooperative) transformation.

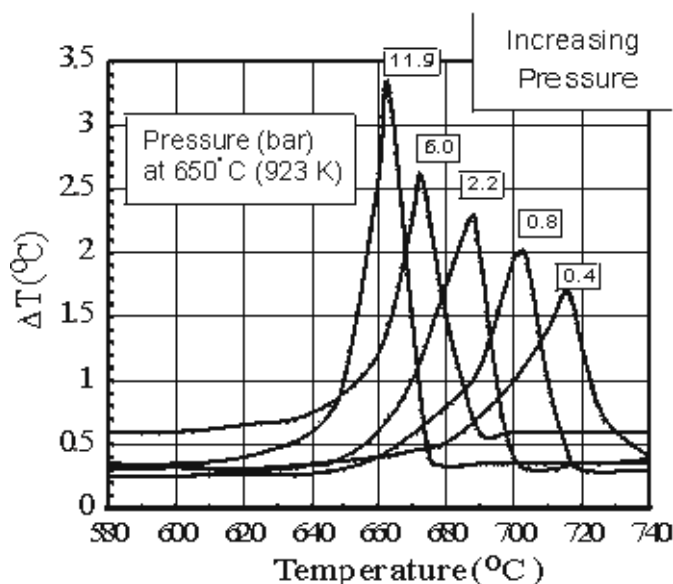


Fig. 5. DTA curves of  $\text{Nd}_{16}\text{Fe}_{76}\text{B}_8$  heated under increasing pressures of  $\text{H}_2$  at  $5^\circ\text{C min}^{-1}$  (from [22]).

HIDP transformation is a hydrogen-induced phase transformation. So, an initial  $\text{Nd}_2\text{Fe}_{14}\text{B}$ -matrix phase being introduced into hydrogen is a thermodynamically unstable phase exchanging energy and a substance (hydrogen) with the outer medium. In its motion towards a thermodynamic equilibrium an initial solid undergoes a series of internal phase transformations which according to scheme (2) are divided into two large stages. The first stage is a hydride transformation with the formation of a hydride of the initial matrix phase. The second one is according to [3] a hydrogen-induced *diffusive* phase transformation with the formation of finite phases separated by the interphase boundaries. These alloy phases are in a thermodynamic equilibrium both with each other and the outer medium. Just because of a necessity of a general and local (by hydrogen) thermodynamic equilibrium all finite phases being constituents of a single solid contain equilibrium quantities of a dissolved hydrogen in their interstitial

subsystems in such a way that hydrogen thermodynamic potentials in all finite phases were equal:

$$\mu_{\text{H}}(\alpha\text{-FeH}_z) = \mu_{\text{H}}(\text{NdH}_{2\pm x}) = \mu_{\text{H}}(\text{Fe}_2\text{BH}_{z^*}) = \mu_{\text{H}}(\text{H}_2\text{-gas}). \quad (3)$$

Hence, a very important consequence follows. As known iron is a hydrogen endothermal occluder. So, hydrogen content in the  $\alpha$ -Fe–matrix is little guaranteed ( $z = 0.01\text{--}0.1$  at.%), for a  $\text{Fe}_2\text{BH}_{z^*}$  phase  $z^*$  is unknown but one can assume that it is a small value too. *Nevertheless, when considering thermodynamic, kinetic, structural and other important aspects of the phase transformations under studying one should not neglect the presence of hydrogen dissolved in  $\alpha$ -Fe and  $\text{Fe}_2\text{B}$ , as well as these phases ( $\alpha$ -Fe and  $\text{Fe}_2\text{B}$ ) participation in hydrogen sorption and hydrogen interphase exchange.*

A detailed thermodynamic analysis of the phase transformations under studying in accordance with equations (2) and (3) requires a consideration of fine structural changes taking place in a solid under the phase transformation development: an occurrence and relaxation of hydrogen concentration stresses and stresses caused by the difference of the specific volumes of transforming phases; formation of coherent, semicoherent and noncoherent interphase boundaries; production of defects of the crystal structure (dislocations, vacancies, *etc.*) and their trapping of hydrogen, of other structural changes well studied in metal science and in solid state physics [3,13]. This is one of the most important problems of future studies.

From the viewpoint of kinetics and mechanism of a solid state transformations hydrogen induced phase transformations under discussing need a diffusion transport of hydrogen from the outer medium, a diffusion rearrangement of hydrogen among new forming phases, an obligatory condition of this type of transformation is the presence of a long-range diffusion of Fe, Nd, B atoms. The latter is the most important factor.

Just because of such a diffusive specific character these transformations were classified in [3] among the classic phase transformations as ‘hydrogen-induced *diffusive* phase transformations’. According to [3] these transformations are kinetically possible at  $T \geq 0.45T_m$ .  $T_m$  is a melting point of an initial intermetallic alloy. For the alloys  $\text{Nd}_2\text{Fe}_{14}\text{B}$   $T_m \approx 1180^\circ\text{C}$  [9]. In reality a HIDP transformation in the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy is fully braked because of kinetic reasons at  $T \sim 0.5T_m$ .

So, kinetics and mechanism of HIDP transformations are determined by a necessity of hydrogen, boron, iron and neodium diffusion. Hydrogen diffusion coefficients are larger than those of other interstitial atoms (C, B, N and others) by  $10^{12}$  times, and are larger than the coefficients of selfdiffusion and diffusion of substitutional atoms (Fe, Nd and other substitutional atoms) by  $10^{20}\text{--}10^{30}$  times. So, there is no doubt about that the rate of development of HIDP transformations is fully controlled by a long-range diffusion transport of substitutional atoms (Fe, Sm, Nd and others). Speaking figuratively diffusion of intermetallic component

atoms fully and simply defines a kinetic ‘face’ of HIDP transformations. A ‘slow’ hydrogen sorption upon HIDP transformation developing which is correspondingly fixed by experiment [22] *is not connected with the hydrogen diffusion rate (it’s large!)* but only indicates a limiting ‘slow’ rate of a diffusive development of forming new phases ( $\alpha$ -FeH<sub>z</sub>, NdH<sub>2±x</sub> and Fe<sub>2</sub>BH<sub>z\*</sub>).

We would remind that there are known diffusion phase transformations of two types: a spinodal decay and transformations by the mechanism of nucleation and growth. Transformations by the mechanism of a spinodal decay proceed by diffusion of an alloy components at very small distances and therefore they can proceed at rather low temperatures when an alloy is within an *absolute* thermodynamic instability. A spinodal decay progresses at relatively large rates. Phase transformations by the mechanism of nucleation and growth require diffusion of the component atoms at large distances (in comparison with the atomic ones), they proceed at relatively high temperatures and their completion needs a longer period of time. As can be seen in Figs. 1, 2 the shape of kinetic curves at a gradual slowing-down of the transformation rate in the course of time as well as the availability of an incubation period and its dependence on temperature let us suggest [14–18] that phase transformations under investigation progress by the mechanism of nucleation and growth.

For a further analysis in [14–18] there was used the Mehl–Johnson–Avrami phenomenological theory of phase transformations [12]. According to this theory a degree of transformation  $\xi$  can be described by the following expression:

$$\xi = 1 - \exp(-kt^n), \quad (4)$$

where  $t$  is time,  $k$  and  $n$  are constants.

It turned out [14–18] that in all cases experimental kinetic curves on the coordinates ‘ $\ln \ln[1/(1-\xi)] - \ln t$ ’ are well described by straight lines. As an example in Figure 6 there are given data (up to 90% of transformation and temperatures range of 610–760°C) of direct transformations for the alloy Nd<sub>15</sub>Fe<sub>77</sub>B<sub>8</sub> where  $n = 0.8–1.0$  [18]. For the alloy Nd–Fe–B  $n = 0.7–1.02$  [14] and for the alloy R<sub>2</sub>Fe<sub>14</sub>B  $n = 3–3.9$  [15]. According to the Mehl–Johnson–Avrami theory [12] these values of  $n$  correspond to the diffusive-controlled transformations proceeding by the mechanism of nucleation and growth.

Transformations by the mechanism of nucleation and growth more fully studied in steels [24] can have two types of kinetic diagrams. The C-like diagrams take place when, as temperature falls and overcooling from the critical point of a phase transformation grows, there first dominates an increase of the rate of generating a new phase centers, and then a diffusion braking of a transformation development begins dominating.

Other transformations (for example, transformations upon steel heating) have kinetic diagrams of another type. Here as temperature grows, both factors act in the same direction, and at a further temperature growth a transformation just accelerates.

It's of interest to analyse what type of the isothermal diagram is typical for hydrogen-induced direct phase transformations for alloys of the  $Nd_2Fe_{14}B$  type. Such a diagram for the alloy  $Nd_{15}Fe_{77}B_8$  plotted by the experimental data of Fig. 2 is given in Figure 7.

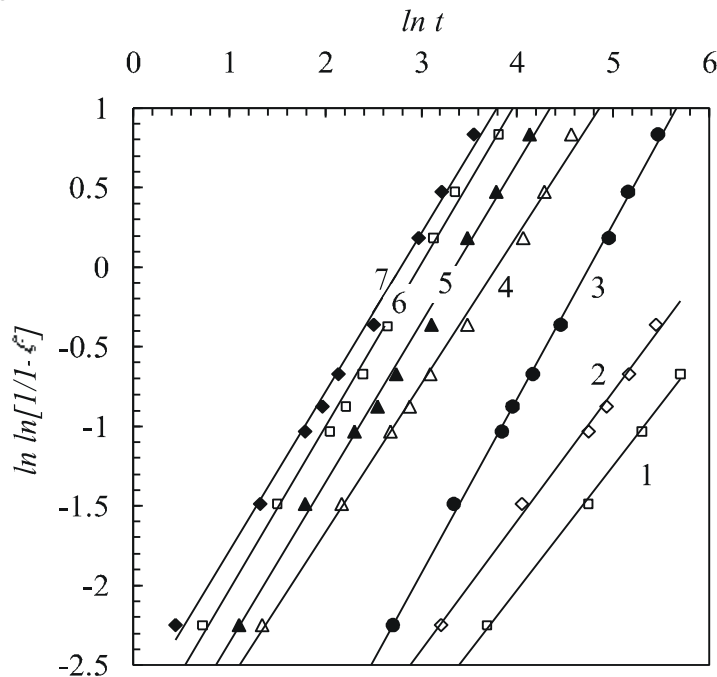


Fig. 6. Plots of  $\ln \ln[1/(1-\xi)]$  versus  $\ln t$  for a direct HIDP transformation in  $Nd_{15}Fe_{77}B_8$  alloy at various isothermal temperatures: 1–640°C; 2–670°C; 3–690°C; 4–710°C; 5–730°C; 6–750°C; 7–760°C.

As follows from [25] the alloy  $Nd_2Fe_{14}B$  when being in the atmosphere of hydrogen at  $P_{H_2} = 0.1$  MPa and  $T > 1000^\circ C$  is thermodynamically stable. In this connection in Fig. 7 there is marked a critical point for a direct HIDP-transformation, *vis.*  $T_c \approx 1000^\circ C$  ( $P_{H_2} = 0.1$  MPa).

So, comparing [14,15,18] and [20, 21, 25] one comes to a following conclusion. Close to the critical point ( $T < T_c$ ) a direct transformation progresses slowly and gradually accelerates as temperature falls down (Fig. 7, field *a*). At 750–800°C (Fig. 7, field *b*) it has maximum rates, and then as temperature falls down it slows down quickly. At  $T < 600^\circ C$  a transformation does not progress because of a full kinetic braking. So, it's quite evident that direct transformations in alloys of the  $Nd_2Fe_{14}B$  type are characterized by the isothermal kinetic diagrams of the C-type. In the field *a* the development of transformations is controlled by the rate of a new phase nucleation. As temperature falls down the rate of a new phase nucleation increases quickly and dominates over a decrease of the diffusion rate. That's why as temperature falls down, the transformation rate increases (the field

a). In the field *c* a transformation is controlled by the atom diffusion of an alloy components, and that's why as temperature falls, a transformation rate decreases quickly and below 600°C a transformation doesn't practically progress. In the field *b* there is an optimum combination of the rate of a new phase nucleation and the diffusion rate, and therefore a transformation rate is maximum.

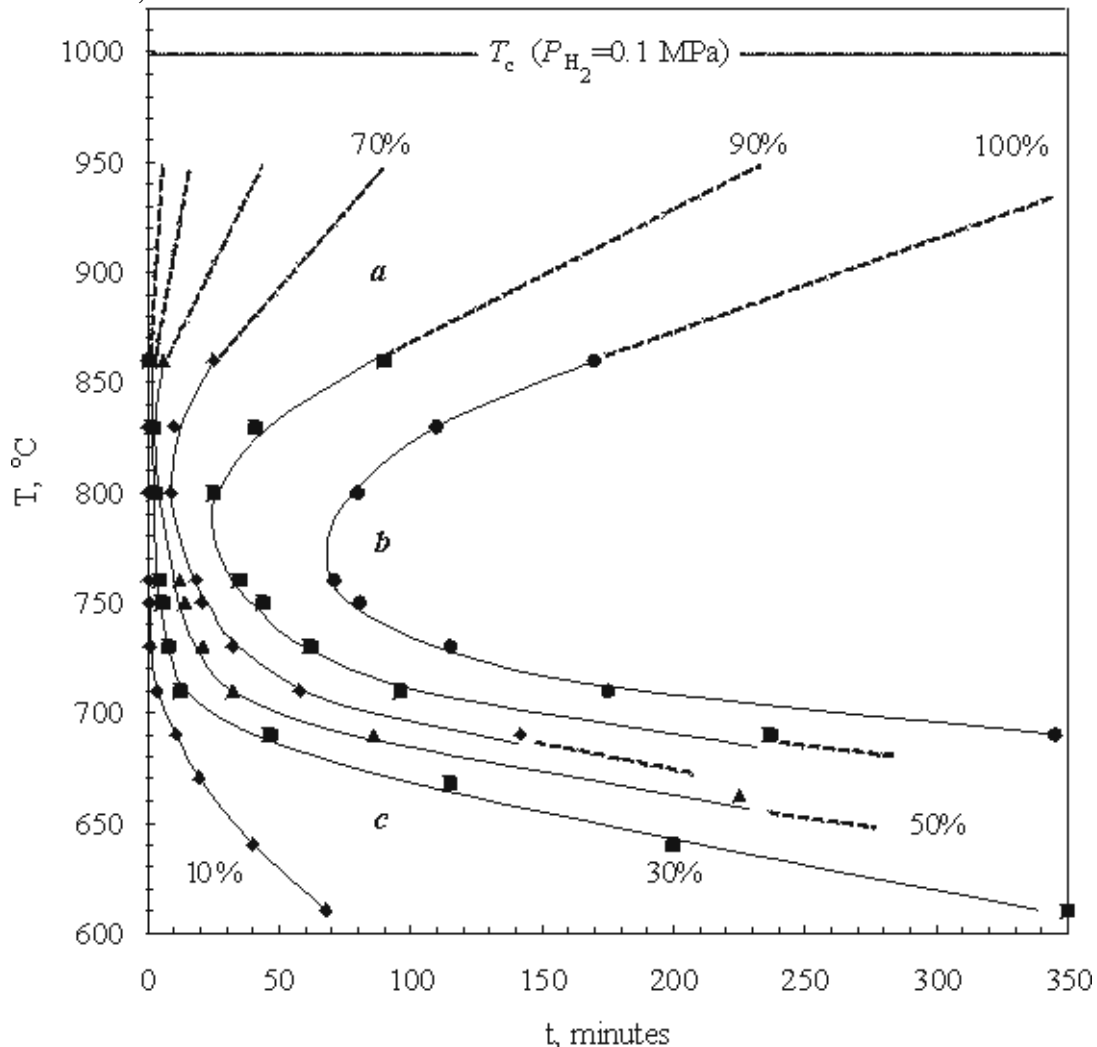


Fig. 7. Isothermal kinetics diagram of a direct HIDP transformation in  $Nd_{15}Fe_{77}B_8$  alloy at hydrogen pressure of 0.1 MPa.

From the viewpoint of solid-state physics and materials science it's of a great importance that unknown before phase transformations caused in quite an unusual way, that is by introducing one more chemical element (hydrogen) into an alloy, obey the same general regularities which were fixed for transformations in polymorphous materials.

Let's now discuss hydrogen pressure influence on the kinetics of direct hydrogen-induced phase transformations. As mentioned above it was found out that a hydrogen pressure increase makes a hydrogen-induced direct phase transformation proceed faster [16, 17].

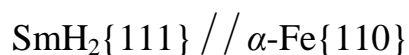
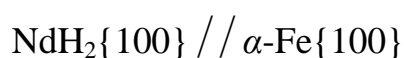
There are some possible factors which promote such a strong hydrogen pressure influence on the rate of progressing a transformation under investigation. A thermodynamic factor is important here. Really as hydrogen pressure grows, hydrogen content in a hydride phase of neodymium ( $\text{Nd}_2\text{H}_{2\pm x}$ ) increases and the heat of a neodymium hydride forming increases too (that is a neodymium hydride free energy becomes more negative). It's clear that by this reason a transformation thermodynamic motive force increases and the transformation has to speed up.

Another factor is merely kinetic. As a transformation is controlled by diffusion of the components atoms, then any acceleration of a mutual diffusion has correspondingly to speed up a phase transformation progressing. As long ago as 50 years academician Kurdyumov and his collaborators experimentally showed [26] that a few interstitial atoms (carbon) dissolved in  $\gamma$ -iron result in a very large increase of iron self-diffusion coefficients. Then Krivoglaz and Smirnov [27] theoretically revealed the mechanism of this phenomenon. It means that as the concentration of interstitial atoms increases, an equilibrium concentration of vacancies in an alloy grows [28,29]. Diffusion of substitutional atoms accelerates correspondingly as it proceed by the vacancy mechanism. In the 1980s an acceleration of diffusion phenomena in steels and alloys under the influence of hydrogen as an interstitial element was repeatedly fixed by experiment and used in corresponding technologies [30]. Then an extrastrong increase of the concentration of vacancies in metals under hydrogen influence was determined by experiment [31] and comprehended theoretically [32,33].

Thus, that is a hydrogen caused acceleration of the diffusion of atoms of the components (Nd, Fe), which is to all appearance the most important factor responsible for a direct transformation acceleration depending on a hydrogen pressure growth.

A very important scientific general principle emerges hence: hydrogen is not only a necessary thermodynamic factor which makes for a possibility of solid-state phase transformations in alloys of the  $\text{R}_x\text{M}_y$  type (where R and M are rare-earth and 3d-transition metals), but *the most important kinetic factor which determines the rate of these transformations progress and the low-temperature (kinetic) limit of their possible practical realization.*

Let's now touch upon structural aspects of direct HIDP transformations. In this sphere experimental data are still being stored. There are some of them. According to [21,34] the crystal orientation relationship between an  $\alpha$ -Fe matrix phase and a hydride phase for the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  and  $\text{Sm}_2\text{Fe}_{17}$ -type alloys are as follows:





In the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type alloys a hydrogen phase precipitates in the form of rods, and  $\text{Fe}_2\text{B}$  grains with an average size of  $\sim 100 \text{ nm}$  are randomly distributed in an  $\alpha\text{-Fe}$  matrix phase. On alloys  $\text{Sm}_2\text{Fe}_{17}$  [23,34] it was shown that the finite sizes of a hydride rod- or spherical-like  $\text{Sm}_2\text{H}_2$  phases depend on the transformation temperature. At  $T = 600^\circ\text{C}$  they are some nanometers, at  $T = 775^\circ\text{C}$  their sizes are  $20\text{--}100 \text{ nm}$ , and at  $T = 850^\circ\text{C}$  they are  $50\text{--}100 \text{ nm}$ .

Thus, there takes place a general regularity of the ‘nucleation and growth’ transformations which is that, as temperature falls down, a number of centers of a new phase nucleation grows and the finite structure is more fine-dispersive.

### 3. Reverse HIDP-Transformations

An experimental investigation of a reverse HIDP-transformation is given in [18,35,36]. At first, each sample underwent a direct HIDP-transformation in hydrogen atmosphere up to the full decomposition. Then hydrogen was evacuated from the reaction chamber. From this moment on, a decrease of the quantity of ferromagnetic phases in a sample was continuously determined at different isothermal temperatures by the method described in section 2 of this paper.

#### 3.1. Effect Of Temperature

Figure 8 shows isothermal kinetic curves of a reverse HIDP-transformation in the  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  alloy [18].

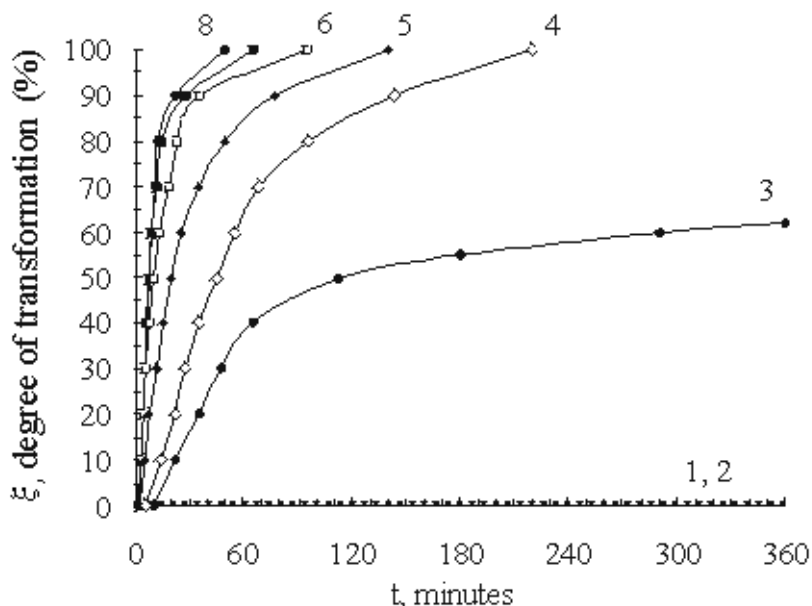


Fig. 8. A reverse HIDP transformation in  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  alloy at vacuum up to  $10^{-2}$  Torr and various isothermal temperatures: 1– $610^\circ\text{C}$ ; 2– $640^\circ\text{C}$ ; 3– $670^\circ\text{C}$ ; 4– $690^\circ\text{C}$ ; 5– $710^\circ\text{C}$ ; 6– $730^\circ\text{C}$ ; 7– $750^\circ\text{C}$ ; 8– $760^\circ\text{C}$ .

As can be seen from this figure, at isothermal temperatures 610°C (curve 1) and 640°C (curve 2) the reverse transformation within an experimental time does not develop. The increase of temperature up to 670°C (curve 3) results in some developing of a transformation, which reached 62%. At isothermal temperature 690°C (curve 4) this phase transformation has a more high rate, and is finished in

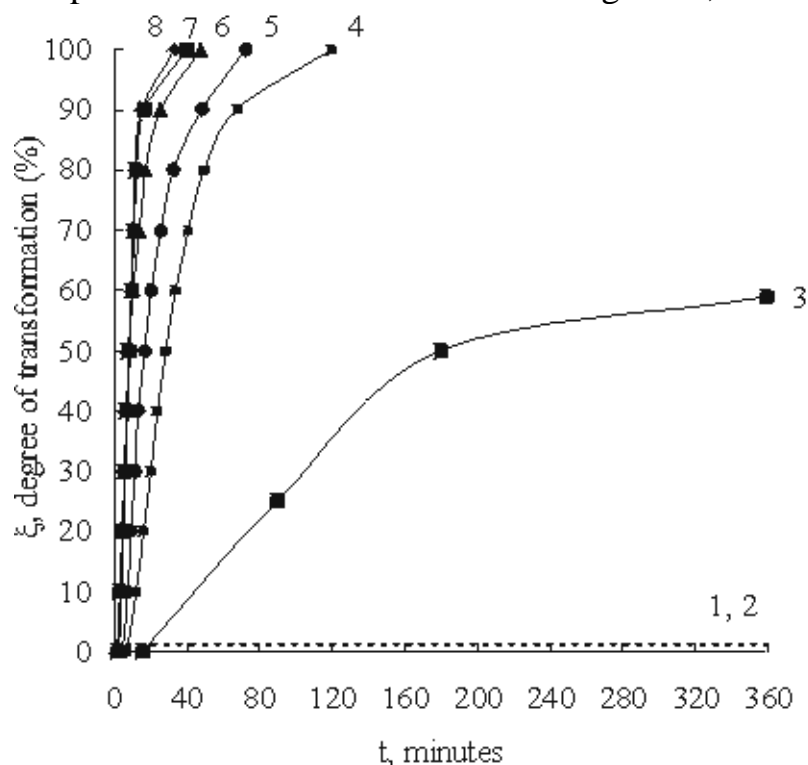


Fig. 9. A reverse HIDP transformation in a commercial  $R_2Fe_{14}B$  alloy at vacuum up to  $10^{-2}$  Torr and various isothermal temperatures: 1–610°C; 2–640°C; 3–670°C; 4–690°C; 5–710°C; 6–730°C; 7–750°C; 8–760.

220 min. A further increasing of isothermal temperature up to 710°C (curve 5) and 730°C (curve 6) induces an acceleration of the phase transformation, which is completed in 140 and 95 min, respectively. And finally, at 750°C (curve 7) and 760°C (curve 8) the reverse transformation is completed in 65 and 50 min, respectively.

The results of the kinetic study [36] of a reverse phase transformation in a commercial  $R_2Fe_{14}B$  type alloy ( $R$  is Nd, Pr and other rare-earth elements) are generalized in Figure 9. As can be seen from Fig. 9, at isothermal temperatures of 610°C (curve 1) and 640°C (curve 2), the reverse phase transformation doesn't develop in 6 hrs. An increase of temperature up to 670°C (curve 3) results in some developing of a transformation by 59%, only. At 690°C (curve 4), it requires 120 min to complete the reverse phase transformation. At 710°C (curve 5) and 730°C (curve 6), the transformation is completed in 72.5 and 45 min, respectively. A further increase in temperature of the isothermal exposure causes a greater acceleration of the reverse phase transformation. So, at 750°C (curve 7) and 760°C



(curve 8) reverse phase transformations occur with the maximum rate and are completed in 40 and 33 min, respectively.

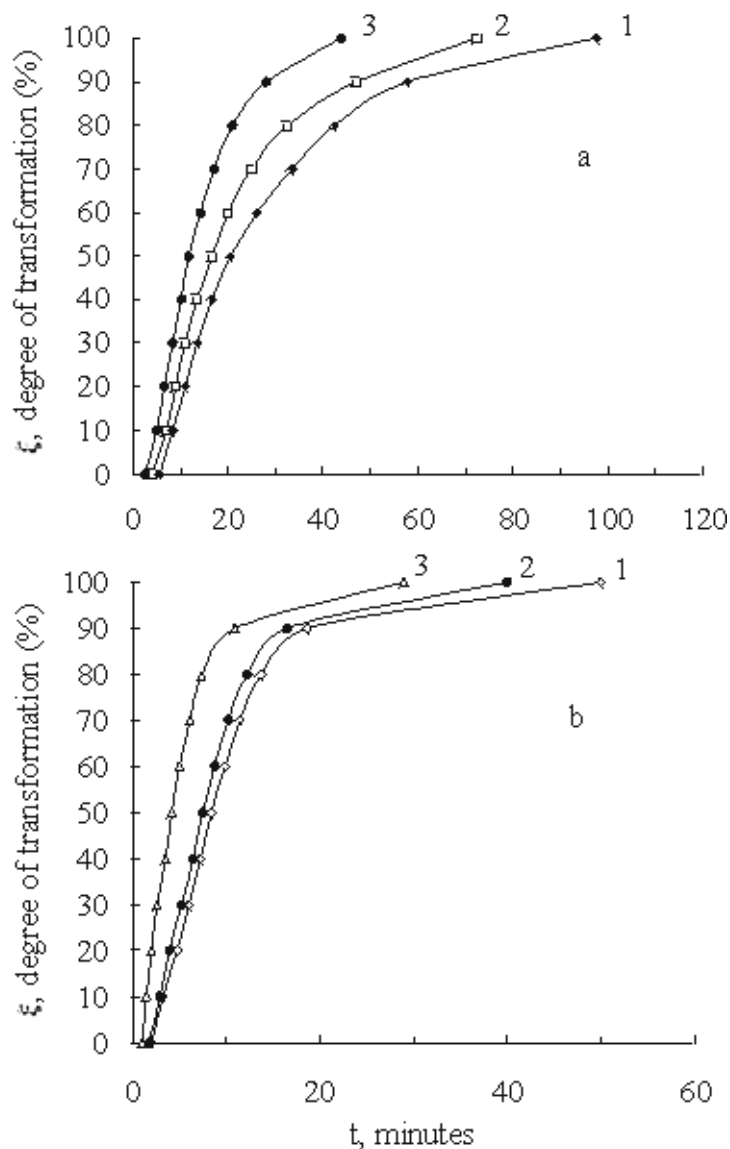


Fig. 10. Kinetic curves of a reverse HIDP transformation in a commercial  $R_2Fe_{14}B$  alloy at different isothermal temperatures  $T = 710^\circ\text{C}$  (a) and  $750^\circ\text{C}$  (b) at initial hydrogen pressures: 1–0.1 MPa; 2–0.15 MPa; 3–0.2 MPa.

So, as shown in Figs. 8, 9, in the temperature range of  $700\text{--}750^\circ\text{C}$  the reverse HIDP-transformation occurs with large rates, and then gradually slows down to full stop at temperatures near to  $600^\circ\text{C}$ .

Further, if to compare the kinetics of reverse and direct HIDP-transformations [Figs. 1–2a] it can be seen that reverse transformations proceed with large rates by 1.1–1.4 times.

### 3.2. An Initial Hydrogen Pressure Effect

The effect of an initial hydrogen pressure (i.e., hydrogen pressure during a direct HIDP-transformation) on the kinetics of a reverse transformation in a commercial  $R_2Fe_{14}B$  type alloy was studied by Rybalka. These results are shown in Figure 10 (a, b).

Fig. 10a describes the kinetics of a reverse transformation at isothermal temperature of  $710^\circ\text{C}$ . As seen in this figure, at initial hydrogen pressures of 0.1 MPa (curve 1) and 0.15 MPa (curve 2) phase transformations were finished in 97.5 and 72.5 min, respectively. In case when a reverse transformation starts at hydrogen pressure of 0.2 MPa it is completed in 43.5 min (curve 3).

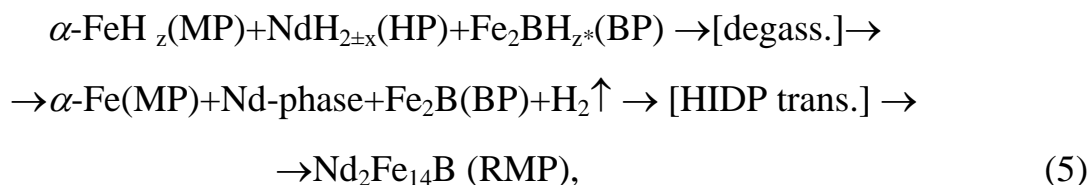
As can be seen in Fig. 10b, at isothermal temperature of  $750^\circ\text{C}$  and initial pressures of 0.1 MPa (curve 1) and 0.15 MPa (curve 2) a reverse phase transformation is completed in 50 and 40 min, respectively. An increase of the initial pressure up to 0.2 MPa (curve 3) results in accelerating a reverse transformation and it is finished in 29 min.

So, a twofold increase of the initial hydrogen pressure (from 0.1 MPa up to 0.2 MPa) results in an acceleration of the reverse phase transformation in the  $R_2Fe_{14}B$  alloy in 1.5–2 times.

### 3.3. Discussion

If an alloy of the  $Nd_2Fe_{14}B$  type which underwent a direct HIDP transformation is subjected to degassing by a special vacuum treatment at temperatures above  $600^\circ\text{C}$ , a reverse HIDP transformation will develop in the alloy and it will lead to the recovery of an initial phase composition of the alloy, the latter having an improved, more ground structure.

Phase transformations in this case can be presented by the following structural scheme:



where MP, HP, BP have the same meaning as in scheme (2), RMP is a refined matrix phase.

So, in its moving to a thermodynamic equilibrium an initial polyphase alloy undergoes a series of phase and structural transformations which according to (5) can be conventionally divided into two large stages. The first stage is an alloy degassing and hydrogen evacuation into a gaseous phase. The second stage is a proper reverse HIDP-transformation with the formation of a structurally refined matrix phase  $Nd_2Fe_{14}B$ . In principle the 1st and 2nd stages can be fully separated in time and by temperature under certain conditions. Under usual conditions the 2<sup>nd</sup>

stage as a rule is put over the 1<sup>st</sup> one, and a reverse HIDP transformation starts to progress before hydrogen is fully evacuated from the alloy.

By its nature a reverse HIDP transformation is also *diffusive* one and its rate is limited by the diffusion of atoms of the alloy components (Nd, Fe, B).

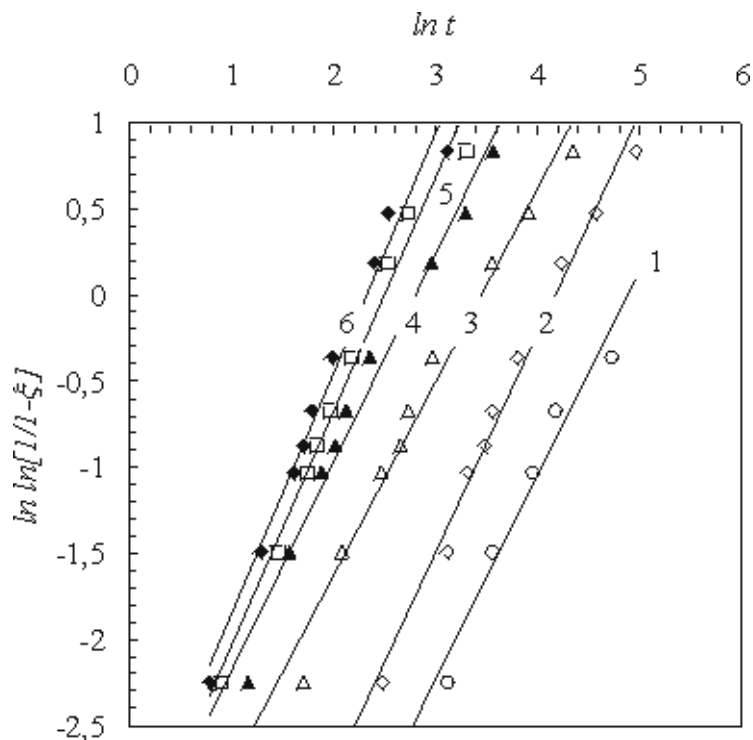


Fig. 11. Plots of  $\ln \ln[1/(1-\xi)]$  versus  $\ln t$  for a reverse HIDP transformation in  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  alloy at various isothermal temperatures: 1–670°C; 2–690°C; 3–710°C; 4–730°C; 5–750°C; 6–760°C.

But there is a principal difference in structural mechanisms and kinetics of direct and reverse transformations. Really, as discussed above a direct transformation proceeds by the *mechanism of nucleation and growth*. Within the modern knowledge in the field of solid-state physics and materials science this transformation mechanism is characterized by an obligatory nucleation of new phases ( $\alpha\text{-FeH}_z$ ,  $\text{NdH}_{2\pm x}$ ,  $\text{Fe}_2\text{BH}_z$ ) in the form of separate nuclei larger than a critical size. Another picture is observed for a reverse HIDP transformation. Two structural mechanisms are possible here.

The first mechanism is a classical mechanism of nucleation and growth. It has been discussed above. Now we can only add that it means a fluctuational, *activated* new phase nucleation. For example, one can imagine that near a phase boundary ( $\text{NdH}_{2\pm x}$  и  $\alpha\text{-FeH}_z$ ) or at the joint of three phases ( $\text{NdH}_{2\pm x}$ ,  $\alpha\text{-FeH}_z$  and  $\text{Fe}_2\text{BH}_{z^*}$ ) nuclei of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type occur under the alloy degassing. They are separated by an interphase boundary from initial phases and are larger than a critical size. Then these nuclei grow due to a long-range diffusion of Nd, Fe and B atoms and, hence, there is observed their boundary ‘motion’. The fact that kinetics of reverse HIDP-

transformations is well described by the Mehl–Avrami–Johnson phenomenological theory (see Figure 11) favours this mechanism. For the alloy  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$   $n = 1.18\text{--}1.4$ , which corresponds to a diffusion-controlled transformation proceeding by the mechanism of nucleation and growth. Let's tentatively call this mechanism 'activationless'.

The 2<sup>nd</sup> possible mechanism is activationless as there is no activated nucleation of new phases centers, but under a polyphase alloy ( $\alpha\text{-FeH}_z$ ,  $\text{NdH}_{2\pm x}$ ,  $\text{Fe}_2\text{BH}_{z*}$ ) degassing a motion towards a thermodynamical equilibrium is done *by a mere interdiffusion* of atoms of the alloy components (Nd, Fe, B) till a complete homogenization is reached and the matrix phase  $\text{Nd}_2\text{Fe}_{14}\text{B}$  is formed. This mechanism was first suggested in [34] to realize the 'recombination' of the HDDR process in the alloy  $\text{Sm}_2\text{Fe}_{17}$ . This mechanism of a reverse transformation can be tentatively called 'activationless' or 'homogenizational'.

As shown in subsection 3.1 a reverse HIDP transformation proceeds faster than a direct one (compare Figs. 1–2 and Figs. 8–9). As the 2<sup>nd</sup> mechanism is not necessarily connected with an activationless nucleation, its rate is limited only by the rate of the interdiffusion of atoms (Fe, Nd, B). So, the homogenizational mechanism makes it possible to understand an experimentally fixed fact that a reverse transformation in most cases proceeds faster than a direct one.

As to the influence of an initial hydrogen pressure on kinetics of a reverse phase transformation the following can be said. As known [37] a growing hydrogen pressure results in an increase of its solubility in metals. As shown in [38], a diffusion flow of atoms leads to the formation of an excess concentration of vacancies. In a case of a reverse transformation when hydrogen is evacuated, a diffusion flow of atoms occurs, and this might lead to an increase of the concentration of vacancies. Then, the larger an initial hydrogen pressure, the larger the diffusion flow of hydrogen atoms and, correspondingly, the larger the excess concentration of vacancies. To all appearances this is the reason of an acceleration of both the diffusion of substitutional atoms and reverse transformations. It might also be that at a larger hydrogen pressure at the stage of a direct transformation a number of nucleation centers of new phases ( $\text{NdH}_2$ ,  $\alpha\text{-Fe}$ ,  $\text{Fe}_2\text{B}$ ) increases, and that can lead to a decrease of atoms diffusion distances at a reverse transformation. A confirmation of these suggestions needs further more detailed studies.

A reverse transformation kinetically differs from a direct one by the character of an isothermal kinetic diagram. As shown in [18,35,36] within the temperature range from 600°C up to 760°C a reverse transformation accelerates. Nowadays we don't know any experimental data how a further increase of temperature effects the rate of a reverse transformation.

As mentioned above a reverse transformation can in principle proceed by two mechanisms, namely, an activationless and homogenizational ones. At present the latter is more preferable [34]. So, as temperature raises, kinetics of reverse

transformations proceeding by this mechanism has only to increase. This opinion is shared by the authors of [21,22] as well as the authors of this paper.

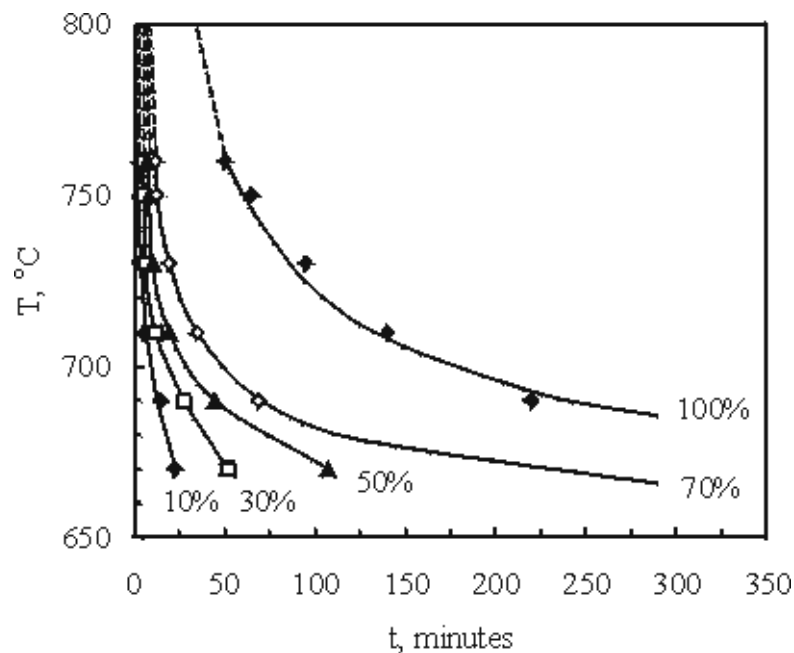


Fig. 12. Isothermal kinetic diagram of a reverse HIDP transformation in  $Nd_{15}Fe_{77}B_8$  alloy at initial hydrogen pressure of 0.1 MPa and vacuum up to  $10^{-2}$  Torr.

So, it can be believed that the isothermal kinetics diagram for reverse HIDP transformations will have the shape graphically shown in Figure 12. One should notice that for a reverse transformation (after heating above  $600^\circ\text{C}$  and removing a kinetic braking) there are no critical temperatures above which the transformation does not proceed. This is a direct consequence that a phase mixture obtained at a direct transformation after hydrogen desorption (see structure scheme (5)) is thermodynamically unstable within the whole interval of the alloy existence up to a melting temperature. Some experimental data on structure forming at a reverse HIDP-transformation in alloys of the  $Nd_2Fe_{14}B$  type are given in [9,11,21,25,39].

#### 4. Conclusions

Intermetallics of the  $R_xM_y$  type (where R and M are rare-earth and 3d-transition metals, respectively) under hydrogen influence become thermodynamically unstable and undergo decomposition into a rare-earth metal hydride and a diluted solid solution of hydrogen in a 3d-transition metal. From the viewpoint of chemistry this reaction is classified as 'hydrogenolysis of a chemical compound'. In many cases this reaction causes an intermetallics degradation or even a full loss of their performance. For example, intermetallics of the  $LaNi_5$  type, used for hydrogen storage, gradually loses their hydrogen capacity as a result of hydrogenolysis during their use.

But in the case of intermetallics of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type there was found a possibility to improve their structure and magnetic properties by using reactions of this type. And there was developed the so-called HDDR process (Hydrogenation–Decomposition–Desorption–Recombination). From the viewpoint of metals physics the HDDR-process is based on hydrogen-induced diffusive phase transformations. Under hydrogen influence at temperatures  $0.45T_m \leq T < T_c$  in an alloy of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type a direct transformation develops. As a result a monophase alloy undergoes a phase transformation going into a polyphase state:  $\alpha\text{-FeH}_z$  (matrix), a hydride  $\text{NdH}_{2\pm x}$  phase and a boride phase  $\text{Fe}_2\text{BH}_{z^*}$ . It is well determined that this phase transformation proceeds by the mechanism of nucleation and growth. Diffusion of substitutional atoms is a necessary condition for the development of phase transformations of this class. That's why they are classified as hydrogen-induced *diffusive* phase transformations.

Kinetics of this transformation is described by the C-shaped kinetic diagram. A little bit below critical temperature ( $T < T_c$ ) this phase transformation is controlled by the rate of nucleation of centers of new phases ( $\alpha\text{-FeH}_z$ ,  $\text{NdH}_{2\pm x}$ ,  $\text{Fe}_2\text{BH}_{z^*}$ ). As overcooling increases the rate of a direct transformation grows first because of a fast growth of the rate of nucleation of centers of new phases. Then at the optimum combination of a phase nucleation and diffusion rates a direct transformation rate reaches its maximum. At a further overcooling a slowing-down of the substitutional atom diffusion starts dominating, the rate of a transformation sharply decreases. Below a definite temperature ( $T \sim 600^\circ\text{C}$ ) a HIDP transformations in alloys of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type are fully braked by kinetic reasons. A hydrogen pressure increase ( $T < T_c$ ) causes an increase of the rate of a transformation. The boundaries and degree of this hydrogen pressure influence have not been studied in detail yet.

A decomposed polyphase alloy ( $\alpha\text{-FeH}_z$ ,  $\text{NdH}_{2\pm x}$ ,  $\text{Fe}_2\text{BH}_{z^*}$ ) being subjected to degassing undergoes at  $T \geq 0.45T_m$  a reverse diffusive phase transformation with the formation of the monophase alloy  $\text{Nd}_2\text{Fe}_{14}\text{B}$  but with an improved structure and magnetic properties. A long-range (in comparison with interatomic) diffusion of atoms (Nd, Fe, B) is a necessary condition for the development of these transformations. That's why these transformations are also classified as *diffusive*. Under degassing there is no critical points and a transformation is thermodynamically possible within the whole range of temperatures up to a melting one. At present it is admissible that a reverse transformation can proceed both by the mechanism of nucleation and growth and by the homogenizational mechanism. As well as direct transformations, at low temperatures ( $T \leq 0.45T_m$ ) these transformations don't proceed by the kinetic reasons (the diffusion of substitutional atoms is fully suppressed). As temperature raises, diffusion accelerates. Other possible factors operate in this direction. Correspondingly kinetic diagrams for reverse transformations differ in principle from the ones for direct transformations. As temperature raises, reverse transformations accelerates

only. Under similar conditions they proceed, as a rule, at larger rates than direct transformation do. It's wonder that the hydrogen pressure growth at which direct transformations proceed effects a reverse transformation making it accelerate.

So, hydrogen, is not only a necessary thermodynamic condition which makes the development of HIDP transformations possible, but hydrogen is also a very strong kinetic factor which (side by side with temperature) determines the rate of the development of these transformations, the type of their kinetic diagrams and other specific features of phase transformations of this type in a solid.

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# Progress In Hydrogen Treatment Of Materials

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For Hydrogen Economy development being in advance in the 21<sup>st</sup> century, the World Hydrogen Movement should steadily pay special attention to all materials–hydrogen problems.

First, there should be created novel more stable to hydrogen degradation structural materials and novel preventive technologies. This problem being one of the fundamentals of safety is of an absolutely great importance. Really, it cannot be allowed that the hydrogen economy entering into the mankind life would be rejected by the public relation because of some unforeseen case, some new ‘Hindenburg syndrom’.

Secondly, hydrogen economy will require advanced functional materials (hydrides, membranes, electrodes, magnets and catalytic materials, *etc.*) and adequate technologies of a new generation. More and more wide use of hydrogen treatment (side by side with other kinds of treatments) will allow to extend possibilities of Hydrogen Materials Science and Engineering, and will greatly promote hydrogen economy development in new directions.

At last, it is necessary to emphasize the importance of systematic intimate communication between two hydrogen world communities: hydrogen energy community, as it is, and materials–hydrogen one. Now additional possibilities in this area appear due to the activities of the Permanent Working International Scientific Committee on Hydrogen Treatment of Materials under the auspices of International Association for Hydrogen Energy.

*Professor Victor A. Goltsov*  
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