

# Analysis of influence of hydrogen pressure on kinetics of hydrogen-induced direct phase transformation in $\text{Nd}_2\text{Fe}_{14}\text{B}$ type magnetic alloy

*S.B.Rybalka*

Donetsk National Technical University,  
58 Artema St., 83000 Donetsk, Ukraine

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The influence of hydrogen pressure on kinetics of hydrogen induced direct phase transformations in the  $\text{R}_2\text{Fe}_{14}\text{B}$  hard magnetic alloy has been investigated. It has been determined that, as the temperature and the hydrogen pressure increase, a phase transformation significantly accelerates. It has been shown that the kinetics of the phase transformation is controlled by the Fe atoms diffusion and that the rate growth of new  $\alpha$ -Fe phase increase with increase of hydrogen pressure. On the base of Kolmogorov and Lyubov model the kinetic equation describing influence of hydrogen pressure on the isothermal kinetic diagram for this transformation has been obtained.

Исследовано влияние давления водорода на кинетику индуцированного водородом прямого фазового превращения в магнитотвердом сплаве  $\text{R}_2\text{Fe}_{14}\text{B}$ . Установлено, что при повышении температуры и давления водорода фазовое превращение существенно ускоряется. Показано, что кинетика фазового превращения контролируется диффузией атомов Fe и что скорость роста новой фазы  $\alpha$ -Fe увеличивается с увеличением давления водорода. На основе модели Колмогорова и Любова получено кинетическое уравнение, описывающее влияние давления водорода на изотермическую кинетическую диаграмму для данного превращения.

## 1. Introduction

Presently, permanent magnet materials are among key components of numerous electronic, data processing, and medical equipment, as well as other important modern devices. Nowadays permanent magnets with the best magnetic properties are produced from  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type alloys [1]. One of the promising technologies for improvement of magnetic properties of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type alloys is the HDDR-process (Hydrogenation-Disproportionation-Desorption-Recombination). This process is based on direct and reverse hydrogen-induced diffusive phase transformations in the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type hard magnetic alloys [2].

As a rule, interaction of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy with hydrogen leads to the direct transforma-

tion, when the initial alloy decomposes into  $\alpha$ -Fe,  $\text{Fe}_2\text{B}$  and  $\text{NdH}_2$ . Then, removal of hydrogen leads to evolution of a reverse transformation with recombination of the initial  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy, but with a significantly modified structure. As a result, realization of direct and reverse transformations is the base for improvement of magnetic characteristics of permanent magnets produced from this type of alloys [3].

The effect of the hydrogen pressure on the kinetics of hydrogen-induced direct phase transformations in  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type alloys has been studied systematically in [4, 5]. Thus, the main goal is to describe the influence of hydrogen pressure on kinetics of hydrogen-induced direct diffusive phase transformations

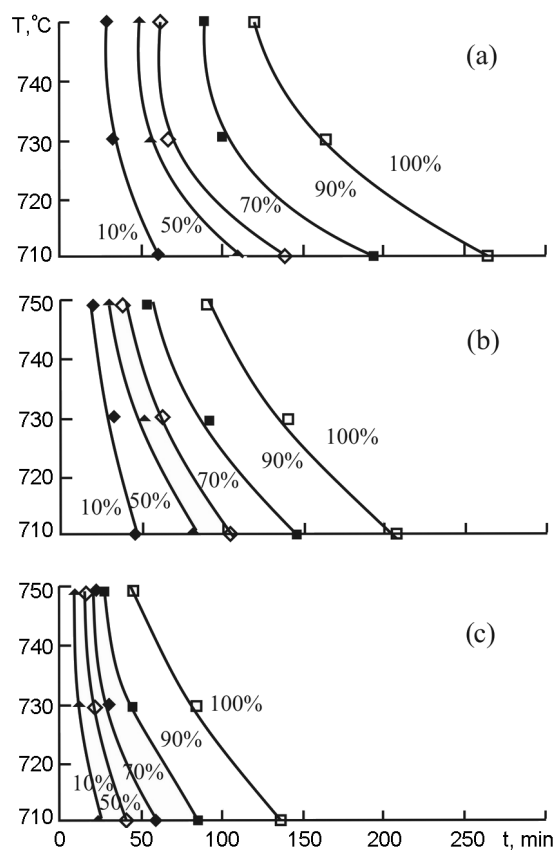


Fig. 1. The isothermal kinetic diagrams for hydrogen induced direct phase transformation in  $R_2Fe_{14}B$  alloy, where  $T$  is the isothermal exposure temperature,  $t$  is the transformation time and 10, 30, 50, 70, 90, 100 % is the degree of the direct transformation at different hydrogen pressure: (a) — 0.1 MPa; (b) — 0.15 MPa; (c) — 0.2 MPa (from [5]).

investigated in the  $Nd_2Fe_{14}B$  type alloys within a framework of kinetic theory of phase transformations in solid state.

## 2. Results and discussion

In Fig. 1, the isothermal kinetic diagrams of the direct phase transformation in the industrial  $R_2Fe_{14}B$  alloy ( $R_{36.4}Fe_{62.45}B_{1.15}$ , where R is mixture of rare-earth metals — 33 % Nd, 2 % Pr, 0.9 % Ce and 0.5 % Dy, weight %) are shown at various temperatures and hydrogen pressures, as earlier obtained in [5]. As follows from Fig. 1, if the temperature and hydrogen pressure increase, the phase transformation evolution accelerates too.

In  $Nd_2Fe_{14}B$  type alloys the hydrogen induced direct phase transformation proceeds by the following scheme: at the first stage, interaction of  $Nd_2Fe_{14}B$  alloy with gaseous hydrogen (as a rule, at hydrogen pressure

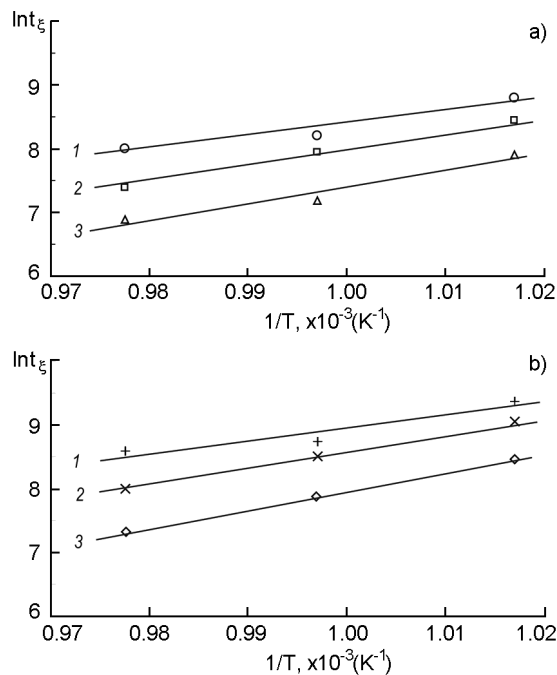
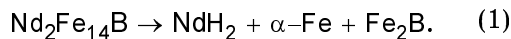


Fig. 2. Dependences  $\ln t_\xi$  vs  $1/T$  for hydrogen induced direct phase transformation in  $R_2Fe_{14}B$  alloy for degrees of transformation 50 % (a) and 90 % (b) and different hydrogen pressures: 1 — 0.10 MPa; 2 — 0.15 MPa; 3 — 0.20 MPa.

of  $\sim 0.1$  MPa) at temperatures  $\sim 600$ – $900^\circ C$  leads to decomposition of the initial  $Nd_2Fe_{14}B$  alloy into three stable phases, i.e.  $\alpha$ -phase of Fe,  $Fe_2B$  and  $NdH_2$  phases [2]:



It is obvious that, from viewpoint of classical kinetic theory of phase transformations in condensed state, the above direct phase transformation in  $Nd_2Fe_{14}B$  type proceeds by the nucleation and growth mechanism [4, 5].

Further, it is possible to find an effective activation energy of phase transformation in accordance with Becker-Doering model of nucleation kinetics [6–8] if the dependence of  $\ln t_\xi$  on  $1/T$  is known, where  $t_\xi$  is the time required for reaching a certain degree of transformation  $\xi$ , and  $T$  is the transformation temperature. For this purpose, the experimental data from Fig. 1 were re-plotted in co-ordinates  $\ln t_\xi$  versus  $1/T$  (Fig. 2).

The determined values of effective energy of phase transformation for various hydrogen pressures and degrees of transformation are given in Table 1.

As can be seen the obtained values of effective activation energy have good agree-

Table 1. The effective activation energy of direct hydrogen induced phase transformation in  $R_2Fe_{14}B$  alloy for various hydrogen pressures  $P$  and degrees of transformation  $\xi$ 

$\xi$ , Degree of transformation	$P = 0.1$ MPa, hydrogen pressure	$P = 0.15$ MPa, hydrogen pressure	$P = 0.2$ MPa, hydrogen pressure
0.5	166.29±7.69 kJ/mol	228.44±8.29 kJ/mol	214.73±7.91 kJ/mol
0.9	164.305±7.42 kJ/mol	220.946±8.23 kJ/mol	242.477±8.27 kJ/mol

ment by order of magnitude with activation energy for iron atoms diffusion in  $R-T$  alloys (where  $R$  is a rare-earth metal,  $T$  — a transition metal) —  $Q = 250$  kJ/mol [9]. Therefore, it is really possible to consider that evolution process of direct phase transformation is controlled by nucleation and growth of the main  $\alpha$ -Fe matrix phase. Thus, in accordance with above described model transformation, we can obtain kinetic equation for direct hydrogen induced phase transformation in  $Nd_2Fe_{14}B$  type alloy taking into account the influence of hydrogen pressure on transformation kinetics.

As well known from Kolmogorov kinetic theory of phase transformation in condensed state [10], the volume of transformed area  $\xi$  can be written as

$$\xi = \frac{V(t)}{V_0} = 1 - \exp\left(-\frac{\pi}{3}I\omega^3t^4\right), \quad (2)$$

where  $V(t)$  is the transformed area volume at time moment  $t$ ,  $V_0$  is the initial untransformed volume,  $I$  is the nucleation rate of centres of new  $\alpha$ -Fe phases,  $\omega$  is the rate of growth of a new  $\alpha$ -Fe phase.

On the other hand, the rate of nucleation  $I$  of new  $\alpha$ -Fe phase centers in condensed systems in accordance with Turnbull-Fisher model [11, 12] in the case of diffusion-controlled growth is

$$I = \gamma \frac{RT}{h} e^{-\frac{W+Q}{RT}}, \quad (3)$$

where  $W$  is the energy necessary for formation of  $\alpha$ -Fe critical nucleus,  $Q$  is the activation energy diffusion of Fe atoms at transition through interface of  $\alpha$ -Fe phases,  $\gamma = 10^{-4}$  mol/m<sup>3</sup> [13],  $R$  is the gas constant,  $h$  is the Planck constant,  $T$  is transformation temperature.

Then, substituting equation (3) into (2) we can obtain kinetic equation for volume of the transformed area  $\xi$  as function of dependence on transformation time  $t$  and transformation temperature  $T$ :

$$\xi(t) = 1 - \exp\left(-\frac{\pi}{3}\gamma \frac{RT}{h} e^{-\frac{W+Q}{RT}} \omega^3 t^4\right). \quad (4)$$

As a rule, phase transformation kinetics for practical application is described by curves showing time transformation  $t$  needed for reaching degree of transformation  $\xi$  depending on transformation temperature  $T$  [2]. Thus, in this case Eq.(4) can be written in the following form:

$$t(\xi, T) = \left(\frac{3h}{\pi\gamma RT}\right)^{1/4} \frac{-\ln(1-\xi)^{1/4}}{\omega^{3/4}} e^{U_i/RT}, \quad (5)$$

where  $U_i = (W + Q)/4$  is the energy of phase transformation process.

Further, in isothermal conditions the rate of nucleation is constant, and, in accordance to classical theory of nucleation, the rate of nucleation  $I$  of new phase centers in condensed systems is described by Eq.(3), where  $W$  and  $Q$  as a rule are constants for the same alloy. Therefore, we can assume that the rate of nucleation of  $\alpha$ -Fe phase is not dependent on hydrogen pressure. Let us now determine the rate of nucleation  $I$  and rate of growth of a new  $\alpha$ -Fe phase  $\omega$  assuming that the activation energy at transition of atoms through interface of phases  $Q$  is equal in our case to the activation energy of diffusion of Fe atoms in  $R-T$  type alloys  $Q = 250$  kJ/mol, and the energy necessary for formation of  $\alpha$ -Fe critical nucleus is  $W \approx 495.8$  kJ/mol in accordance to data from [9]. Thus, using Eq.(3) and kinetic data from Fig. 1, the values of rate of nucleation  $I$  and rate of growth of  $\alpha$ -Fe phase  $\omega$  during phase transformation were determined for various hydrogen pressures and temperatures for degree of transformation  $\xi = 0.9$  (Table 2).

Figure 3 shows the growth rate of  $\alpha$ -Fe phase  $\omega$  versus hydrogen pressure  $P$  plotted on the basis of data from Table 2. As follows from Fig. 3, the rate of growth  $\omega$  increases with increase in hydrogen pressure at all temperatures. Further, according to Lyubov kinetic approach [13] we assume that the dependence of the rate of growth  $\omega$  on hydrogen pressure  $P$  can be approximated by a function of the following type:

Table 2. The rate of nucleation  $I$  and rate of growth of a new  $\alpha$ -Fe phase  $\omega$  of phase transformation determined for various hydrogen pressures  $P$  and transformation temperatures  $T$  for degree of transformation  $\xi = 0.9$  in  $R_2Fe_{14}B$  alloy

$T$ , temperature (K)	$I$ , rate of nucleation ( $m^{-3}\cdot s^{-1}$ )	$\omega$ , rate of growth at $P = 0.1$ MPa ( $m\cdot s^{-1}$ )	$\omega$ , rate of growth at $P = 0.15$ MPa ( $m\cdot s^{-1}$ )	$\omega$ , rate of growth at $P = 0.2$ MPa ( $m\cdot s^{-1}$ )
983	$2.757\cdot 10^{-7}$	$7.522\cdot 10^{-4}$	$1.137\cdot 10^{-3}$	$2.437\cdot 10^{-3}$
1003	$1.737\cdot 10^{-6}$	$9.416\cdot 10^{-4}$	$1.203\cdot 10^{-3}$	$3.154\cdot 10^{-3}$
1023	$1.019\cdot 10^{-5}$	$9.978\cdot 10^{-4}$	$1.386\cdot 10^{-3}$	$3.402\cdot 10^{-3}$

$$\omega = B \frac{\Delta F - \Delta F_s}{RT} e^{-\frac{U(P)}{RT}}, \text{ where } B \text{ is constant,}$$

$\Delta F$  is the molar difference of the free energies of initial and final phases,  $\Delta F_s$  is the driving force of phase transformation which in our case is proportional to the free energy required for the  $NdH_2$  phase formation,  $U(P)$  is the activation energy of transition of Fe atoms through interface of  $\alpha$ -Fe phases depending on hydrogen pressure.

The activation energy of transition of atoms through interface of  $\alpha$ -Fe phases  $U(P)$  in accordance with Smirnov theory [14] depends on concentration of interstitial atoms (atoms hydrogen in our case) as follows:  $U(P) = Q_{m.p.} - Q_i \cdot c$ , where  $Q_{m.p.}$  is the activation energy of matrix phase atoms diffusion in the absence of an interstitial atoms,  $Q_i$  is the energy interaction between matrix phase atoms and interstitial atoms,  $c$  is the concentration of an interstitial atoms that in our case is proportional to hydrogen pressure  $P$ . Thus, equation for activation energy transition of Fe atoms through interface of  $\alpha$ -Fe phases can be written in the following form:  $U(P) = Q_{m.p.} - Q_i \cdot P$ , where  $P$  is the hydrogen pressure in MPa in our case.

Further, let us denote  $B \frac{\Delta F - \Delta F_s}{RT} = A(P)$ . Finally, equation for the rate of growth of new  $\alpha$ -Fe phase  $\omega$  as function of hydrogen pressure  $P$  in  $R_2Fe_{14}B$  alloy can be written as  $\omega = A(P) e^{-\frac{Q_{m.p.} - Q_i \cdot P}{RT}}$ .

Then, all coefficients in above-mentioned equation have been calculated in Statistica 6.0 program by using data for rate of growth  $\omega$  vs. hydrogen pressure  $P$  and transformation temperature  $T$  from Table 2. Finally, the rate of growth of  $\alpha$ -Fe phase  $\omega$  as function of hydrogen pressure  $P$  in  $R_2Fe_{14}B$  alloy can be represented by the following equation:

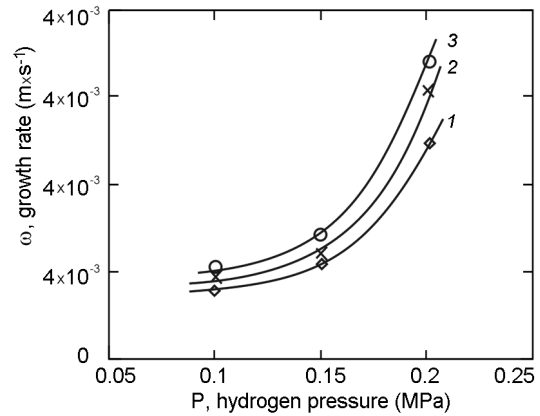


Fig. 3. The growth rate of  $\alpha$ -Fe phase  $\omega$  vs hydrogen pressure  $P$  for various transformation temperatures: 1 — 710°C; 2 — 730°C; 3 — 750°C for degree of transformation  $\xi = 0.9$  in  $R_2Fe_{14}B$  alloy.

Table 3. The preexponential function  $A(P)$  at different hydrogen pressures determined for the degree of direct hydrogen induced transformation  $\xi = 0.9$  in  $R_2Fe_{14}B$  alloy

$P$ , hydrogen pressure (MPa)	$A(P)$ , the preexponential function in Eq.(5) for $R_2Fe_{14}B$ alloy
0.1	$12.1\cdot 10^{-1}$
0.15	$12.4\cdot 10^{-1}$
0.2	$12.7\cdot 10^{-1}$

$$\omega = A(P) e^{-\frac{70.03 \cdot 10^3 - 97.72 \cdot 10^3 \cdot P}{RT}}, \quad (6)$$

where  $A(P)$  is the preexponential function depending on hydrogen pressure  $P$  (MPa), presented in Table 3 for various hydrogen pressures.

As can be seen from Table 3,  $A(P)$  function increase with increase of hydrogen pressure that is possible if  $\Delta F_s$  (that is proportional to the formation energy of a  $NdH_2$

phase) will decrease that has been obtained experimentally [15–18]. On the other hand,  $U(P)$  decrease with hydrogen pressure increase. In our case hydrogen atoms can be considered too as interstitial atoms and its influence lead to increase of diffusion of matrix atoms (Fe atoms in our case) as was shown earlier in works [19–21]. Hence, the rate growth of new phase  $\omega$  depends on two main factors: decreasing of formation energy of a  $\text{NdH}_2$  phase  $\Delta F_S$  with hydrogen pressure increase and decreasing of activation energy transition of Fe atoms through interface of  $\alpha$ -Fe phase  $U(P)$  with hydrogen pressure increase.

Finally, substitute Eq.(6) into Eq.(5) we can written the final equation describing dependence transformation time  $t$  needs for reaching some degree of transformation  $\xi$  on hydrogen pressures  $P$  and transformation temperature  $T$ :

$$t(\xi, T, P) = \left( \frac{3h}{\pi\gamma RT} \right)^{1/4} \frac{(-\ln(1 - \xi))^{1/4}}{\left( A(P) e^{\frac{70.03 \cdot 10^3 - 97.72 \cdot 10^3 \cdot P}{RT}} \right)^{3/4}} e^{\frac{W+Q}{4RT}} \quad (7)$$

In Fig. 4 the isothermal kinetic diagram is shown for hydrogen induced direct phase transformation in  $\text{R}_2\text{Fe}_{14}\text{B}$  alloy calculated on the basis of Eq.(7) and data from Table 3.

Thus, it is possible to conclude that the obtained Eq.(7) adequately describes the effect of hydrogen pressure on kinetics of induced direct phase transformation in  $\text{R}_2\text{Fe}_{14}\text{B}$  alloy in terms of two main factors, i.e. decreasing of formation energy of a  $\text{NdH}_2$  phase  $\Delta F_S$  with hydrogen pressure increase and decreasing of activation energy transition of Fe atoms through interface of growing  $\alpha$ -Fe phase  $U(P)$  with hydrogen pressure increase.

#### 4. Conclusions

The influence of hydrogen pressure on the kinetics of hydrogen induced direct phase transformations in the  $\text{R}_2\text{Fe}_{14}\text{B}$  alloy has been considered. It has been established that the kinetics of phase transformation is controlled by diffusion of Fe atoms and the rate growth of  $\alpha$ -Fe phase  $\omega$  increase with increase of hydrogen pressure.

On the base of Kolmogorov and Lyubov kinetic models of evolution of phase transformation in condensed state, the equations describing the isothermal kinetic diagrams of such type of transformations have been obtained. It has been found that the effect

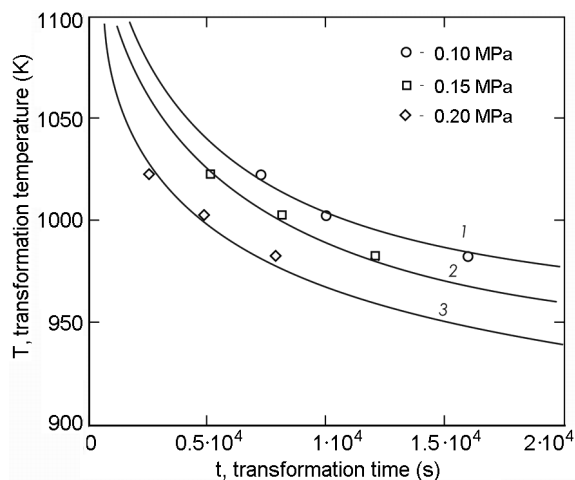


Fig. 4. The isothermal kinetic diagrams for hydrogen induced direct phase transformation in  $\text{R}_2\text{Fe}_{14}\text{B}$  alloy calculated by Eq.(7) for degree of transformation  $\xi = 0.9999$  for various hydrogen pressures: 1 — 0.10 MPa; 2 — 0.15 MPa; 3 — 0.20 MPa. The points are experimental data for these hydrogen pressures (Ref. [5]).

of hydrogen pressure on kinetics of hydrogen induced direct transformations in  $\text{R}_2\text{Fe}_{14}\text{B}$  alloy can be described by an equation of the above-presented type (7).

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## **Аналіз впливу тиску водню на кінетику ініційованого воднем прямого фазового перетворення у магнітному сплаві типу $\text{Nd}_2\text{Fe}_{14}\text{B}$**

***С.Б.Рибалка***

Досліджено вплив тиску водню на кінетику ініційованого воднем прямого фазового перетворення у магнітотвердому сплаві  $\text{R}_2\text{Fe}_{14}\text{B}$ . Встановлено, що при підвищенні температури і тиску водню фазове перетворення істотно прискорюється. Показано, що кінетика фазового перетворення контролюється дифузією атомів Fe і що швидкість росту нової фази  $\alpha\text{-Fe}$  збільшується зі збільшенням тиску водню. На підставі моделі Колмогорова і Любова отримано кінетичне рівняння, що описує вплив тиску водню на ізотермічну кінетичну діаграму для даного перетворення.