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# The effect of hydrogen pressure and temperature on kinetics of hydrogen-induced direct phase transformation in hard magnetic alloy

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## Abstract

The kinetics of hydrogen-induced direct phase transformations in the  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  hard magnetic alloy has been investigated. It has been determined that, as the temperature and the hydrogen pressure increase, a phase transformation significantly accelerates. According to the Johnson–Mehl–Avrami model the equations describing the isothermal kinetic diagrams for these transformations have been deduced. It has been shown that the kinetics of the phase transformation is controlled by the Fe-atoms diffusion. An increase of hydrogen pressure results in an increase in the free energy of the  $\text{NdH}_2$  hydride formation and this is the main factor in accelerating a hydrogen-induced direct phase transformation evolution in the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type alloys.

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## 1. Introduction

It is well known, that at the present moment, permanent magnets with the best magnetic properties are made from  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type alloys. The hydrogenation–disproportionation–desorption–recombination-process (HDDR)—can result in a considerable improvement in their magnetic properties. The hydrogen-induced direct and reverse diffusive phase transformations in the hard magnetic alloys are the basis for this process [1].

A hydrogen influence leads to the fact that at higher temperatures (600–900 °C) the  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  alloy becomes thermodynamically unstable and undergoes a direct transformation, i.e. decomposes into  $\alpha\text{-Fe}$ ,  $\text{Fe}_2\text{B}$  and  $\text{NdH}_2$ . On hydrogen removal, a reverse transformation develops causing a recombination of an initial  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  alloy but with a significantly modified structure. A realization of direct and reverse transformations favours an improvement of magnetic characteristics of permanent magnets produced from this type of alloys [2].

The influence of the hydrogen pressure on the kinetics of hydrogen-induced diffusive phase transformations in  $\text{Nd}_2\text{Fe}_{14}\text{B}$  type alloys has been studied systematically in [3,4] at hydrogen pressures of 0.1–0.7 MPa and temperatures of 670–750 °C.

Thus, the aim of this paper is to describe the kinetics of hydrogen-induced direct diffusive phase transformations investigated in the  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  alloy within a wider temperature range 630–750 °C and at higher hydrogen pressures, and to give a theoretical description of these transformations.

## 2. Experimental

The investigations of the kinetics of the direct phase transformations have been carried out by a magnetometrical method, as specified in [5].  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  powders were placed in a chamber which was evacuated up to  $\sim 1$  Pa. The alloy was then heated in vacuum to temperatures within 630–750 °C with continuous evacuation. After establishing isothermal conditions, the chamber was filled with hydrogen up to a stipulated pressure (either 0.3, 0.5 or 0.7 MPa). The phase transformation was monitored continuously by meaning the

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increase of the amount of ferromagnetic phases in the sample. According to there findings, the isothermal diagrams have been plotted.

### 3. Results and discussion

Fig. 1 shows the isothermal diagrams of the direct phase transformations in the  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  alloy at various temperatures and hydrogen pressures. Analyzing Fig. 1 it should be noted at first that, as temperature increases, the phase transformation accelerates. It is evident because as the temperature increases, a new phases nucleation rate and the diffusive coefficient increase, respectively [5]. Secondly, an increase of gaseous hydrogen pressure also leads to an increase in the rate of phase transformation. Let's consider in detail the influence of the hydrogen pressure on the kinetics.

As shown in [5], these transformations may be classified as diffusion-controlled phase transformations controlled by a nucleation and growth mechanism. It can be seen that evolution of the phase transformation process is determined

by two phases ( $\text{NdH}_2$  and  $\alpha\text{-Fe}$ ) nucleation and growth. Thus, the driving force of the phase transformation is the formation of  $\text{NdH}_2$  hydride. Thus, as the hydrogen pressure increases the hydrogen atom concentration increases, too. It causes the free energy of a rare-earth hydride  $\text{NdH}_2$  formation to decrease, as the authors [6] believed with respect to the phase decomposition in the  $\text{Nd}_{15}\text{Fe}_{76}\text{B}_8$  type alloy.

Besides the above-mentioned thermodynamic factor, it is necessary to note a possibility of a kinetic factor influence controlled by diffusion. As shown in [7], in such temperature range the process of a phase transformation is controlled by the Fe-atoms diffusion. As shown *experimentally* in [8], an increase of an interstitial atoms concentration leads to an increase of a metal self-diffusion coefficient. Then in [9], it was shown *theoretically* that an increase of the interstitial atoms concentration (hydrogen atoms in our case) leads to an increase of a metal self-diffusion coefficient. An increase of the interstitial atoms concentration causes an increase of equilibrium vacancies in a metal, according to [10]. In [11] a significant growth of equilibrium vacancies in a metal was experimentally registered at high temperatures and hydrogen pressures, and their growth contributes to the increase of a diffusive decomposition rate of alloys by several orders of magnitude. Besides these factors, the phase transformation process is accompanied by significant concentration stresses emerging due to a difference in the specific volumes of the resultant phases. As noted in [12], an influence of concentration stresses can lead to a significant increase of the diffusion coefficient.

In summary, it is possible to conclude that two main factors, that is thermodynamic (conditioned by a decrease of a free energy of a rare-earth hydride  $\text{NdH}_2$  formation) and kinetic (conditioned by an acceleration of diffusion of metal atoms with an increase of hydrogen pressure), interacting can lead to an acceleration of the phase transformation.

Let's approximate the experimental results using the Johnson–Mehl–Avrami kinetic theory of phase transformations. Kinetics of the phase transformation under isothermal conditions may be described as follows:

$$\xi = 1 - e^{-kt^n}, \quad (1)$$

where  $\xi$  is the degree of transformation,  $t$  is the transformation time,  $k$  and  $n$  are constants.

Values of the  $n$  constant can be found from  $\ln \ln[1/(1 - \xi)]$  versus  $\ln t$  dependence (Fig. 2). It has been shown that at all temperatures and hydrogen pressures there are two linear parts,  $n$  values varying from 0.73 up to 1.09.

According to Kahn theory [13], this is provoked by the exhaustion of nucleation sites. Before exhaustion the  $k$  coefficient is proportional to the nucleation rate  $I$  and growth  $\omega$  ( $k \sim I\omega^3$ ), and after—it is proportional to the growth rate only ( $k \sim \omega^n$ ).

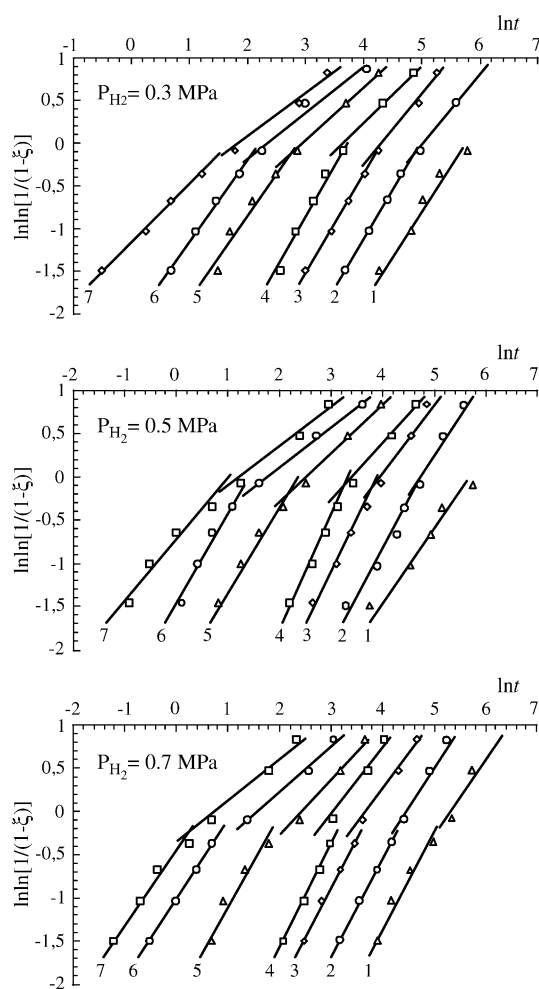


Fig. 1. Isothermal diagrams of hydrogen-induced direct phase transformations in the  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  alloy at various hydrogen pressures.

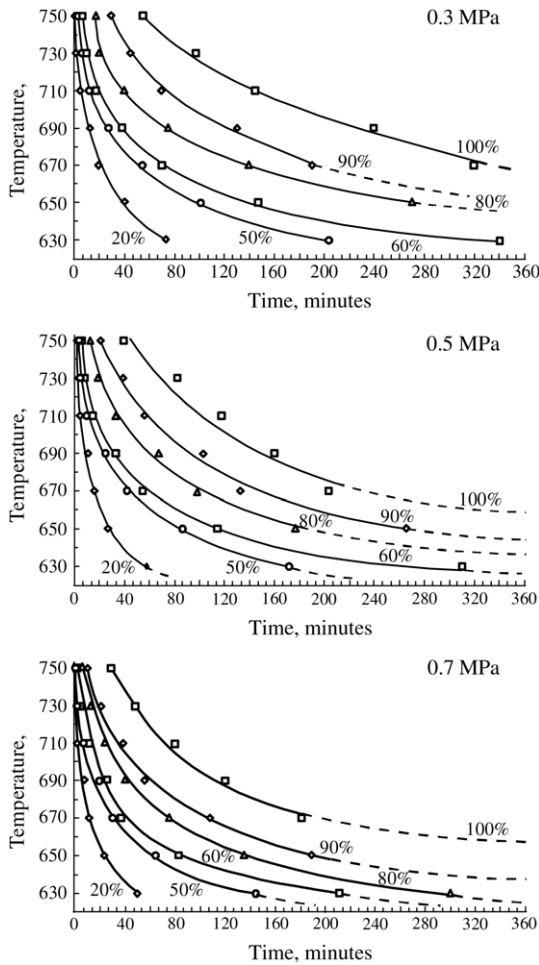


Fig. 2. Avrami curves of the hydrogen-induced direct phase transformations in the  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  alloy at various temperatures: (1) 630 °C; (2) 650 °C; (3) 670 °C; (4) 690 °C; (5) 710 °C; (6) 730 °C; (7) 750 °C.

From (1), the time for obtaining a particular degree of transformation  $\xi$  can be written as:

$$t_{\xi} = \frac{[-\ln(1 - \xi)]^{1/n}}{k^{1/n}}. \quad (2)$$

As shown in [13,14], the growth rate, controlled by diffusion, according to Zener–Hillert theory, is described as follows:

$$k^{1/n} \sim \frac{\Delta F - \Delta F_S}{RT} \exp\left(-\frac{U}{RT}\right), \quad (3)$$

where  $\Delta F$  is the molar difference of the free energies of initial and final phases,  $\Delta F_S$  is the thermodynamic stimulus for the transformation to begin, and this stimulus is proportional to the free energy required for the  $\text{NdH}_2$  formation,  $U$  is an activation energy,  $T$  is temperature,  $R$  is a gas constant.

Substituting (3) into (2) we can obtain:

$$t_{\xi} = \frac{[-\ln(1 - \xi)]^{1/n} RT}{\Delta F - \Delta F_S} e^{U/RT}. \quad (4)$$

Table 1

Values of an activation energy  $U$  (kJ/mol) for hydrogen-induced direct phase transformations in the  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  alloy for various hydrogen pressures  $P_{\text{H}_2}$  and degrees of transformation  $\xi$

$\xi$ (%)	$P_{\text{H}_2}$		
	0.3 MPa	0.5 MPa	0.7 MPa
50	291.855	292.620	300.689
70	237.034	256.006	255.682
90	194.030	195.542	226.580

Table 2

Values of  $\lambda$  in Eq. (5) for various hydrogen pressures  $P_{\text{H}_2}$  and degrees of transformation  $\xi$

$\xi$ (%)	$P_{\text{H}_2}$		
	0.3 MPa	0.5 MPa	0.7 MPa
50	$5.367 \times 10^{-15}$	$1.093 \times 10^{-15}$	$0.348 \times 10^{-15}$
70	$5.269 \times 10^{-12}$	$0.379 \times 10^{-12}$	$0.254 \times 10^{-12}$
90	$1.123 \times 10^{-9}$	$0.709 \times 10^{-9}$	$0.011 \times 10^{-9}$

Let's denote  $\lambda$  as  $\lambda = \frac{RT}{\Delta F - \Delta F_S}$ . Thus,

$$t_{\xi} = \lambda [-\ln(1 - \xi)]^{1/n} e^{U/RT}. \quad (5)$$

It is possible to find an activation energy  $U$  and  $\lambda$  coefficient by plotting the dependence  $\ln t_{\xi}$  versus  $1/T$  [13]. Values of an activation energy and  $\lambda$  determined for various hydrogen pressures and degrees of transformation are given in Tables 1 and 2.

As can be seen from Table 1, all values of an activation energy correspond to the values of an activation energy of the iron atoms diffusion in R–T alloys (where R is a rare-earth metal, T – a transition metal) and amounts to 250 kJ/mol [15]. Thus, the assumption as to a controlling role of the iron atom diffusion can be considered as well-grounded.

Then, we may suppose that at a constant temperature, the  $\lambda$  coefficient is proportional to the driving force of the transformation, i.e.  $\lambda \sim 1/(\Delta F - \Delta F_S)$ . As can be seen from Table 2 for all hydrogen pressures and degrees of transformation the regularity is as follows: as hydrogen pressure increases, the  $\lambda$  coefficient decreases.

Thus, as the hydrogen pressure increases, the energy difference  $\Delta F - \Delta F_S$  increases, too. It can be possible if  $\Delta F_S$  (that is proportional to the formation energy of a  $\text{NdH}_2$  phase) will decrease. Hence, the above-mentioned assumptions about the  $\text{NdH}_2$  phase free energy of formation decrease as the hydrogen pressure increases in the process of realizing the hydrogen-induced phase transformations in the  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  alloy have appeared to be true.

#### 4. Conclusions

An influence of temperature and hydrogen pressure on the kinetics of hydrogen-induced phase transformations in the  $\text{Nd}_{15}\text{Fe}_{77}\text{B}_8$  alloy has been investigated.

It has been established that with an increase of hydrogen pressure and temperature, the lines of beginning and completion of transformations in isothermal diagrams shift in the directions of shorter time periods, i.e. the transformations accelerate.

Kinetics of phase transformation in the temperature range of 630–750 °C and hydrogen pressures of 0.3–0.7 MPa has been proved to be controlled by the iron atoms diffusion.

Using the models of Johnson–Mehl–Avrami and Zener–Hillert the equations describing the isothermal kinetic diagrams of such type of transformations have been derived. It has been found that to describe kinetics of hydrogen-induced transformations the following equation can be used:

$$t_{\xi} = \frac{[-\ln(1 - \xi)]^{1/n} RT}{\Delta F - \Delta F_S} e^{U/RT}$$

There has been established that an acceleration of hydrogen-induced direct phase transformations in the Nd<sub>15</sub>Fe<sub>77</sub>B<sub>8</sub> alloy at a hydrogen pressure increase is mainly conditioned by a free energy of the NdH<sub>2</sub> formation.

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