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KINETIC EQUATION FOR HYDROGEN INDUCED DIRECT PHASE TRANSFORMATION IN Nd₂Fe₁₄B HARD MAGNETIC ALLOY

S. B. Rybalka
Donetsk national technical university, Donetsk

Model for evolution of the hydrogen induced direct phase transformation in $Nd_2Fe_{14}B$ hard magnetic alloy has been proposed. On the base of Kolmogorov and Lyubov kinetic theory of the phase transformations has been obtained kinetic equation that well described the isothermal kinetic diagram for this type transformation.
Keywords: kinetics; phase transformations; hard magnetic alloys.

Introduction. As well known phase transformations studies have always been one of the main standpoint areas of solid state physics, metal science, theoretical and practical materials science [1, 2].

For instance, developed by Takeshita and Nakayama new technology well-known as HDDR-process (Hydrogenation-Decomposition-Desorption-Recombination) provides a new strategy to improve the properties of permanent magnets via hydrogen-induced phase transformations in Rare-Earth-Metal type alloys [3]. This HDDR-process allows to obtain nanocrystalline powders from $Nd_2Fe_{14}B$ hard magnetic alloys with fine grain size ~ 0.1-0.3 μm. As result, the practical application of direct and reverse hydrogen-induced phase transformations in hard magnetic alloys of rare-earth and transition metals such as $Nd_2Fe_{14}B$ and Sm_2Fe_{17} allows to improve their structure and magnetic properties and also leads to miniaturization of new technical devices based on $Nd_2Fe_{14}B$ and Sm_2Fe_{17} permanent magnets which used in DVD-ROM, acoustic systems and others devices.

It is obvious that a clear understanding of the kinetic peculiarities of hydrogen-induced phase transformations will allow control of the microstructure and magnetic properties of these materials too.

The isothermal kinetic diagram of the hydrogen induced direct phase transformation in $Nd_2Fe_{14}B$ alloy was obtained experimentally earlier in paper [4]. However, to the present moment some kinetic equation describing isothermal kinetic diagram above-mentioned phase transformations doesn't exist. Thus, the main goal of the present paper is to describe above mentioned isothermal kinetic diagram theoretically within the framework of classical kinetic theory of phase transformation in condensed state.

Results and discussion. At first stage, interaction of $Nd_2Fe_{14}B$ alloy with hydrogen (at hydrogen pressure of ~0.1 MPa) at temperatures ~600-$900^{\circ}C$ leads to hydrogen induced direct phase transformation (decomposition) occurs by the following scheme [3]

$$Nd_2Fe_{14}B \rightarrow NdH_2 + \alpha\text{-}Fe + Fe_2B \tag{1}$$

At second stage, at hydrogen evacuation (in vacuum $\sim10^{-2}$ Torr) from decomposed alloy occurs hydrogen induced reverse phase transformation, i.e. recombination in initial phase of $Nd_2Fe_{14}B$ by the following scheme [3]

$$NdH_2 + \alpha\text{-}Fe + Fe_2B \rightarrow Nd_2Fe_{14}B \tag{2}$$

With direct and reverse transformation completed, the $Nd_2Fe_{14}B$ alloy mainly consists of a fine-grained ferromagnetic phase $Nd_2Fe_{14}B$ that allows to obtain permanent magnets with a high coercive [3,5].

For hydrogen induced direct phase transformation in $Nd_2Fe_{14}B$ ($Nd_{15}Fe_{77}B_8$ at. %) alloy isothermal kinetic diagram was obtained earlier in paper [4]. This diagram is shown in fig. 1.

Earlier on a base of kinetic investigations, SEM and X-ray diffraction studies during direct phase transformation in $Nd_2Fe_{14}B$ type alloys it was showed that transformations of this type maybe classified as diffusive phase transformation in solid state and that the direct transformation process proceeds by the nucleation and growth mechanism [5-11].

In accordance with Becker-Döering model of nucleation kinetics [12-14] if plots dependence $\ln t_{\xi}$ on $1/T$, where t_{ξ} is the time, which is needed for reaching of some degree of transformation ξ and T is the temperature, we can determine an effective energy of phase transformation process. For this goal experimental data from fig. 1 were re-plotted in co-ordinates $\ln t_{\xi}$ versus $1/T$ which are shown in fig. 2.

The slopes of the straight lines give us the values of the effective activation energies for hydrogen induced direct phase transformation. Obtained values of effective activation energy equal to $Q_1 = 213 \div 265$ kJ/mol in low temperature region (670-760°C) and $Q_2 = -(146 \div 214)$ kJ/mol in high temperature region (800-860°C). In our case obtained values Q_1 for low temperature region (670-760°C) transformation have good agreement with an activation energy of data for diffusion of Fe atoms in Rare-Earth metals
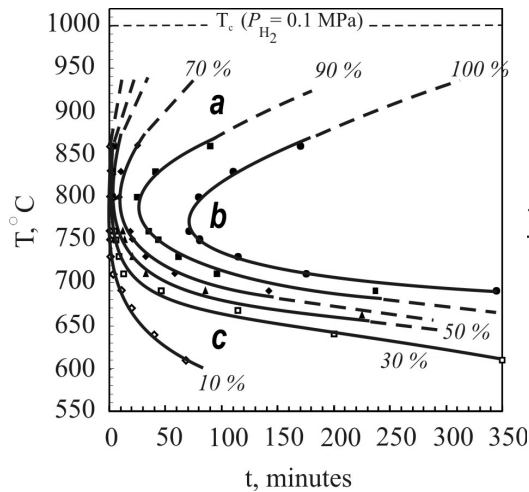
Fig. 1. The isothermal kinetic diagram for hydrogen induced direct phase transformation in $Nd_2Fe_{14}B$, where T is the temperature, t is the transformation time and 10, 30, 50, 70, 90 100% is the degrees of the direct transformation (from [4]).
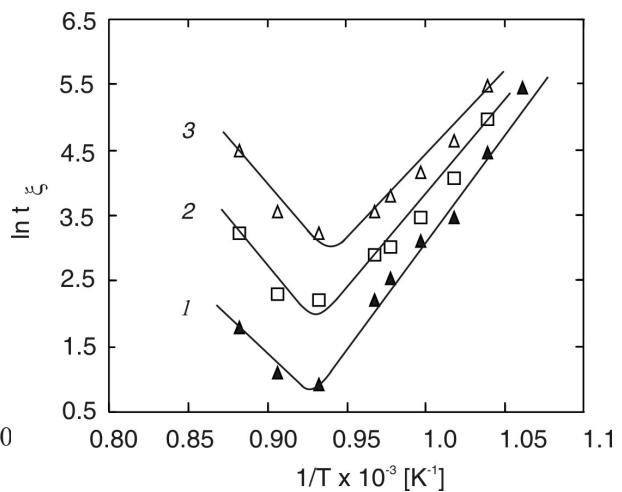
Fig. 2. Dependence $\ln t_\xi$ vs $1/T$ for hydrogen induced direct phase transformation in $Nd_2Fe_{14}B$ alloy for degrees of transformation: $1 - 0.5$, $2 - 0.7$, $3 - 0.9$.

– Q=250 kJ/mol [15] and for high temperature region (800-860°C) effective energy activation Q_2 is equal to enthalpy of NdH_2 phase formation ($\Delta H_{NdH_2} = -(187.7 \pm 3.3)$ kJ/mol [16]).

Therefore, it is really possible to consider that evolution process of direct phase transformation is controlled by diffusion process of Fe atoms in temperatures interval of 670-760°C and in temperatures interval of 800-860°C phase transformation process controlled by growth kinetics of NdH_2 hydride phase. On the other hand, as can be seen from scheme (1) there is a reason to believe that diffusion of hydrogen into $Nd_2Fe_{14}B$ alloy leads to nucleation and growth process of NdH_2 hydride phase and then diffusion of Fe atoms leads to formation of α-Fe phase and Fe_2B phase. Thus, in our case we can believe that evolution process of transformation is controlled by two main process, i.e. nucleation and growth process of the main phases: NdH_2 hydride phase and α-Fe phase.

In accordance with above described model let's obtain kinetic equations for direct hydrogen induced phase transformation in $Nd_2Fe_{14}B$ alloy. As well known from the Kolmogorov kinetic theory of phase transformation in solid state [17], the volume of the transformed area ξ in dependence on t transformation time can be written as

$$\xi(t) = \frac{V(t)}{V_o} = 1 - \exp\left[-\int_0^t I(t)\varphi(t-\tau)dt \right], \qquad (3)$$

where $V(t)$ is the transformed area volume at time t, V_o is the initial volume, $I(t)$ is the nucleation rate of centres of new phases at time t, $\varphi(t)$ is the volume of this nucleation centre at time t, τ is the nucleation moment of centre of a new phase. For the isothermal conditions as in our case it is believed that $I(t) = I = const$.

In general case, according to the Lyubov kinetic theory approach [18] integral in Eq. (3) we can divide in two integrals: from 0 to τ and from τ to t, where τ is time which is necessary for growth of nucleus of new phase up to critical size. Thus, equation (3) maybe written in following form:

$$\xi(t) = 1 - \exp\left[-\left(\int_0^\tau I\varphi_1(t-\tau)dt + \int_\tau^t I\varphi_2(t-\tau)dt \right) \right], \qquad (4)$$

where τ is time which is necessary for growth of nucleus of new phase up to critical size, $\varphi_1(t)$ and $\varphi_2(t)$ is the volume of new phases of NdH_2 and α-Fe nucleation centres at time moment t, correspondingly.

Further, growth of volume of a spherical centre of NdH_2 phase $\varphi_1(t)$ may be written as:

$$\varphi_1(t) = \frac{4}{3}\pi\rho_1^3(t), \qquad (5)$$

where $\rho_1(t)$ is the radius of this centre at time t.

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Nucleation process of NdH_2 phase we can be considered as in single-component system taking into account of high diffusive mobility of hydrogen atoms to neodymium atoms in $Nd_2Fe_{14}B$ alloy and in this case according to theory of absolute reaction rates [19] radius $\rho_1(t)$ of NdH_2 centre at time t :

$$\rho_1(t) = \frac{\pi d^4 \Delta g}{9h} \exp\left(-\frac{U}{RT}\right)t, \qquad (6)$$

where Δg is change of free energy at formation of volume unit of new phase, U is activation energy of atoms at transition through interface of phases, d is diameter of diffusing atom (hydrogen atoms in our case), h is the Planck constant, R is the gas constant, T is transformation temperature, t is some time moment.

Analogously, growth of volume of a spherical centre of α-Fe phase $\varphi_2(t)$ may be written as:

$$\varphi_2(t) = \frac{4}{3}\pi\rho_2^{\ 3}(t), \qquad (7)$$

where $\rho_2(t)$ is the radius of α-Fe centre at time t.

On the other hand, it's known [6-7] that at diffusive-controlled transformations boundary of new phase moves by parabolic low and $\rho_2(t)$ may be written in following form:

$$\rho_2(t) = 2\beta(\xi)\sqrt{Dt}, \qquad (8)$$

where $D = D_o e^{-\frac{Q}{RT}}$ is the diffusion coefficient of Fe atoms, Q is the activation energy of Fe atoms diffusion, R is the gas constant, $\beta(\xi)$ is kinetic parameter, T is the transformation temperature, t is some time moment.

Further, rate of nucleation I of new phase's centers in condensed systems in accordance with Turnbull-Fisher model [20] is

$$I = \gamma\frac{RT}{h}\exp\left(-\frac{W+U}{RT}\right), \qquad (9)$$

where W is the energy necessary for formation of critical nucleus, U is the activation energy at transition of atoms through interface of phases, $\gamma = 10^{-4}$ mol/m³ [18], R is the gas constant.

Then, substitute equations (4)-(9) in (3) we can obtain kinetic equation for volume of the transformed area ξ in dependence on t transformation time and temperature T:

$$\xi(t) = 1 - \exp\left[-\frac{\pi^4 d^{12}\Delta g RT\gamma}{3^7 h^4} e^{-\frac{W+4U}{RT}} t^4_{cr.} - \frac{64\pi RT\gamma}{15h}\beta(\xi)^3 D_o \frac{3}{2} e^{-\frac{W+U+\frac{3}{2}Q}{RT}} \left(t^{5/2}-\tau^{5/2}\right)\right] \qquad (10)$$

As a rule, phase transformation kinetics for practical application describes by curves showing time transformation t needs for reaching some degree of transformation ξ dependence on transformation temperature T [2]. Thus, Eq. (10) has been written in following form:

$$t(\xi,T) = \left[\frac{15h\ln\left(\frac{1}{1-\xi}\right)e^{\frac{W+U+\frac{3}{2}Q}{RT}}}{64\pi RT\gamma\beta(\xi)^3 D_o^{3/2}} + \frac{5\pi^3 d^{12}\Delta g^3}{3^6 64 h^3 \gamma\beta(\xi)^3 D_o^{3/2} h^3} e^{\frac{\frac{3}{2}Q-3U}{RT}}\tau^4 + \tau^{5/2}\right]^{\frac{2}{5}} \qquad (11)$$

Let's consider further two main possible extreme cases, i.e. $t \geq \tau$ and $t \leq \tau$. In the case when transformation time $t \geq \tau$ we can obtain equation:

$$t(\xi,T) = \left[\frac{15h\ln\left(\frac{1}{1-\xi}\right)}{64\pi RT\gamma\beta^3(\xi)D_o^{3/2}}\right]^{\frac{2}{5}} e^{\frac{\frac{2}{5}(W+U)+\frac{3}{5}Q}{RT}}. \qquad (12)$$

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Further, for case when transformation time $t \leq \tau$ we can obtain following equation:

$$t(\xi, T) = \frac{3h}{\pi d^2 \Delta g^{3/4}} \left[\frac{27 \ln\left(\frac{1}{1-\xi}\right)}{RT\gamma} \right]^{\frac{1}{4}} e^{\frac{\frac{W}{4}+U}{RT}}. \tag{13}$$

Finally combines equation (12) and (13) it is possible to obtain kinetic equation for dependence of transformation time $t(\xi, T)$ from degree of transformation ξ and transformation temperature T :

$$t(\xi, T) = \left[\frac{15h \ln\left(\frac{1}{1-\xi}\right)}{64\pi RT\gamma\beta^3(\xi)D_o^{3/2}} \right]^{\frac{2}{5}} e^{\frac{\frac{2}{5}(W+U)+\frac{3}{5}Q}{RT}} + \frac{3h}{\pi d^2 \Delta g^{3/4}} \left[\frac{27 \ln\left(\frac{1}{1-\xi}\right)}{RT\gamma} \right]^{\frac{1}{4}} e^{\frac{\frac{W}{4}+U}{RT}}. \tag{14}$$

Thus, rewrite Eq. (14) in following simple form:

$$t(\xi, T) = a_1 \cdot [-\ln(1-\xi)]^{\frac{2}{5}} \left[\frac{1}{T}\right]^{\frac{2}{5}} \cdot e^{\frac{\frac{2}{5}(W+U)+\frac{3}{5}Q}{RT}} + a_2 \cdot [-\ln(1-\xi)]^{\frac{1}{4}} \left[\frac{1}{T}\right]^{\frac{1}{4}} \cdot e^{\frac{\frac{W}{4}+U}{RT}}, \tag{15}$$

where

$$a_1 = \left(\frac{15h}{64\pi\gamma R\beta^3(\xi)D_o^{\frac{3}{2}}} \right)^{\frac{2}{5}}, \quad a_2 = \frac{3h}{\pi d^3 \Delta g^{3/4}} \left[\frac{27}{R\gamma}\right]^{\frac{1}{4}}.$$

Thus, for the further analysis it is necessary to determine all unknown parameters in equation (15). In our case we can believed that above determined effective activation energies (fig. 2) Q_1 and Q_2 equal correspondently $Q_1 \cong \frac{2}{5}(W+U)+\frac{3}{5}Q$ and $Q_2 \cong \frac{W}{4}+U$, where W is the free energy of critical nucleus of α-Fe phase formation, Q is the activation energy of Fe atoms diffusion (in our case we can take on following data for diffusion of Fe atoms in Rare-Earth metals – Q =250 kJ/mol, D_o =1 mm²/s [15]). Then, using obtained earlier activation energies Q_1 and Q_2 from fig. 2 has been determined energy formation of critical nucleus of α-Fe phase W , activation energy of hydrogen atoms at transition through interface of NdH$_2$ phases U and others parameters in Eq. (15) which are shown in table.

Table

Values of the parameters in Eq. (15) for direct hydrogen induced phase transformation in Nd$_2$Fe$_{14}$B alloy
for degrees of transformation: 0.5, 0.7 and 0.9, respectively

ξ , degree of transformation	Q_1, kJ/mol	Q_2, kJ/mol	U, kJ/mol	W, kJ/mol	$\beta(\xi)$	a_1	a_2
0.5	265.5	-146.55	-290.2	574.65	100.8×10^{-1}	6.0×10^{-12}	2.58×10^7
0.7	233.18	-170.71	-296.33	502.48	58.0×10^{-5}	6.36×10^{-10}	7.25×10^9
0.9	213.06	-214.65	-338.6	495.8	27.0×10^{-12}	7.42×10^{-9}	2.0×10^{12}

As follows from table values of activation energy of hydrogen atoms at transition through interface of NdH$_2$ phases $U = - (290 \div 340)$ kJ/mol have good agreement with enthalpy of formation of NdH$_2$ phase $\Delta H_{NdH_2} = -(187.7 \pm 3.3)$ kJ/mol [16]. Moreover, estimated values of energy of critical nucleus of α-Fe phase formation $W = 495 \div 575$ kJ/mol have reasonable order of magnitude for energy of critical nucleus phase formation in solid body [14]. On the base of Eq. (15) and data from Table 1 the isothermal kinetic diagram of direct hydrogen-induced phase transformation in Nd$_2$Fe$_{14}$B alloy has been plotted. This diagram is shown in fig. 3. As can be seen from this figure the calculated curves well approximate experimental data from paper [4].
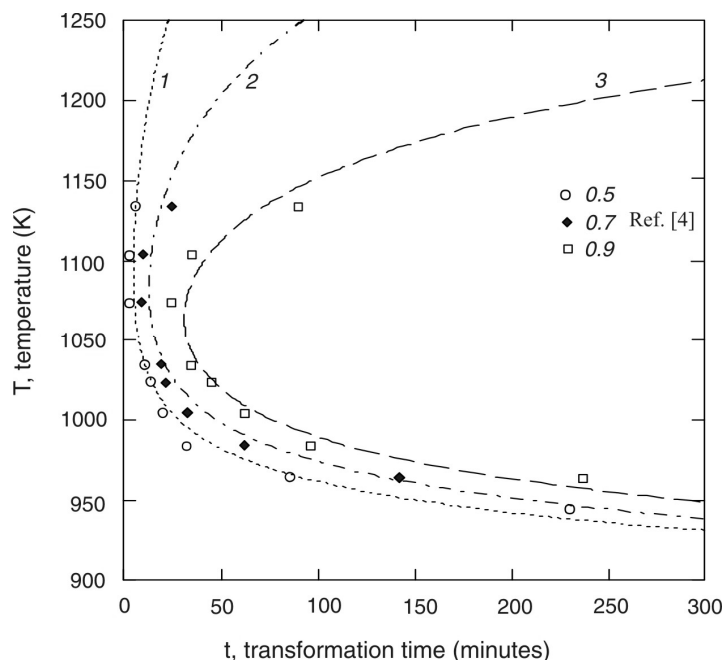
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Fig. 3. The isothermal kinetic diagram of hydrogen induced direct phase transformation in Nd$_2$Fe$_{14}$B
alloy calculated by Eq. (15) for degrees of transformation: *1* − 0.5; *2* − 0.7; *3* − 0.9.
Points are experimental data for same degrees of transformation [Ref. 4]

As seen from Fig. 3 the proposed model also describes subsequent slowing down of direct phase transformation evolution at temperatures above ~ 1200-1300 K (curve *3* in fig. 3) that has been determined experimentally in Nd-Fe-B type alloys [21-22].

Thus, kinetic equation of form Eq. (14) obtained on the base of Kolmogorov and Lyubov kinetic theory of the phase transformations well describes the kinetics of hydrogen induced direct phase transformations in Nd$_2$Fe$_{14}$B alloy. Above-mentioned kinetic approach in future can be applied not only for Nd$_2$Fe$_{14}$B type alloys but and others RE-type hard magnetic alloys for permanent magnets (Sm-Fe, Pr-Fe-B, Sm-Co, Er-Fe-B, Y-Fe etc.).

Conclusions. It is proposed model for evolution of hydrogen-induced direct phase transformation in hard magnetic Nd$_2$Fe$_{14}$B alloy. On the base of Kolmogorov and Lyubov kinetic theory of the phase transformations kinetic equation for this transformation has been obtained. It is shown that the experimental isothermal kinetic diagram of hydrogen induced direct phase transformation in Nd$_2$Fe$_{14}$B $_8$ alloy can be well described by the equation of the following form:

$$t(\xi,T) = a_1 \cdot \left[-\ln(1-\xi)\right]^{\frac{2}{5}} \left[\frac{1}{T}\right]^{\frac{2}{5}} \cdot e^{\frac{\frac{2}{5}(W+U)+\frac{3}{5}Q}{RT}} + a_2 \cdot \left[-\ln(1-\xi)\right]^{\frac{1}{4}} \left[\frac{1}{T}\right]^{\frac{1}{4}} \cdot e^{\frac{\frac{W}{4}+U}{RT}},$$

where $t(\xi,T)$ is the time needs for reaching of some degree of transformation ξ at some transformation temperature T, a_1 and a_2 is the kinetic parameters, W is the energy necessary for formation of critical nucleus of α-Fe phases, U is the activation energy of hydrogen atoms at transition of atoms through interface of NdH$_2$ phases, Q is the activation energy of Fe atoms diffusion.

РЕЗЮМЕ

Предложена модель для развития индуцированного водородом прямого фазового превращения в магнитотвердом сплаве Nd$_2$Fe$_{14}$B. На основе кинетической теории фазовых превращений Колмогорова и Любова получено кинетическое уравнение, хорошо описывающее изотермическую кинетическую диаграмму для превращений такого типа.

Ключевые слова: кинетика; фазовые превращения; магнитотвердые сплавы.

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