Theoretical analysis of reverse hydrogen-induced diffusive phase transformation kinetics in $Nd_{15}Fe_{77}B_8$ alloy

S.B.Rybalka

Donetsk State Technical University, 58 Artem St., 283000 Donetsk

Received July 7, 2001

Kinetics of the hydrogen induced reverse phase transformation in $Nd_{15}Fe_{77}B_8$ alloy at isothermal conditions was described. In terms of the Kolmogrov-Lyubov theory the kinetic diagram of this transformation was calculated. It is shown that kinetics of a reverse phase transformation is controlled by diffusion of Fe atoms in α-Fe matrix.

Описана кинетика индуцированного водородом обратного фазового превращения в сплаве $Nd_{15}Fe_{77}B_8$ в изотермических условиях. На основе теории Колмогорова-Любова рассчитана кинетическая диаграмма этого превращения. Показано, что кинетика обратного фазового превращения контролируется диффузией атомов Fe в матрице α-Fe.

Studies of phase transformation have always been one of the main standpoint areas of solid state physics, metal science, theoretical and practical materials science [1, 2]. The HDDR-process (hydrogenation-decomposition-desorption-recombination) developed recently is based on direct and reverse hydrogen-induced phase transformation in hard magnetic alloy of $Nd_2Fe_{14}B$ type [3]. This process allows to produce permanent magnets from these alloys with improved magnetic characteristics. In [4], the isothermal kinetic diagram of the hydrogen-induced reverse phase transformation in $Nd_{15}Fe_{77}B_8$ alloy was obtained experimentally. Today, however, there is no theory describing such phase transformation. The aim of this work is to describe the above-mentioned isothermal kinetic diagram theoretically using the Kolmogorov-Lyubov kinetic theory of phase transformation.

In hydrogen atmosphere, the hydrogen-induced direct phase transformation (decomposition) in $Nd_2Fe_{14}B$ alloy occurs according to the following scheme [3]:

$$Nd_2Fe_{14}B \to NdH_2 + 12\alpha\text{–}Fe + Fe_2B. \quad (1)$$

The reverse phase transformation (recombination) in $Nd_2Fe_{14}B$ alloy occurs in vacuum according to the following scheme [3]:

$$NdH_2 + 12\alpha\text{–}Fe + Fe_2B \to Nd_2Fe_{14}B. \quad (2)$$

Isothermal kinetic diagram for hydrogen-induced reverse phase transformation in $Nd_{15}Fe_{77}B_8$ (at. %) alloy was obtained in [4] by magnetometric measurements. This diagram is shown in Fig. 1. Basing on kinetic investigations [4, 5] and electron microscopy and X-ray diffraction studies [6] of the reverse phase transformation in $Nd_2Fe_{14}B$ type alloys, it was shown before that transformations of this type is a diffusive phase one in solid state and that the reverse transformation proceeds be the nucleation and growth mechanism.

As follows from Becker-Doering theory [7], plotting the dependence $\ln t_\xi$ on $1/T$, where t_ξ is the time required to attain a certain transformation degree ξ and T is the temperature, we can determine the effective energy of phase transformation process. To that end, the experimental data from Fig. 1 were re-plotted in $\ln t_\xi$ vs. $1/T$ co-ordinates (Fig. 2). Thus, the slopes of the straight

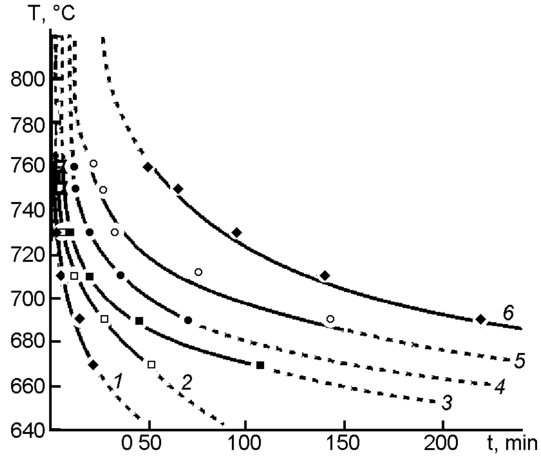

Fig. 1. Isothermal kinetic diagrams for hydrogen-induced reverse phase transformation in $Nd_{15}Fe_{77}B_8$. T is the isothermal exposure temperature; t, the transformation time; 10 (*1*), 30 (*2*), 50 (*3*), 70 (*4*), 90 (*5*), 100% (*6*), the reverse transformation degrees (from [4]).

lines give us the effective activation energy values for hydrogen-induced reverse phase transformation. The activation energy $Q_{eff.}$ amounts 216 to 248 kJ/mol being in a good agreement with the activation energy of Fe atoms diffusion in α-Fe matrix ($Q_{\alpha\text{-}Fe}$ = 259.54 кJ/mol [8]). Therefore, in fact, the evolution process of reverse phase transformation can be considered to be controlled by diffusion of Fe atoms. In [4–6], it was also shown that the reverse phase transformation is controlled by diffusion of Fe atoms.

On the other hand, as can be seen from scheme (2), there is a reason to believe that diffusion of hydrogen from NdH_2 hydride and then diffusion of Fe and B atoms towards Nd ones result in nucleation and growth of $Nd_2Fe_{14}B$ phase.

It is well known from the Kolmogorov-Lyubov kinetic theory of phase transformation in solid state [9–11] that the volume of transformed area ξ can be written as a function of t (transformation time) and temperature T as

$$\xi = 1 - \exp\left[-\int_0^t I(t)\varphi(t-\tau)dt\right], \quad (3)$$

where $I(t)$ is the nucleation rate of new phase centers at time point t; $\varphi(t)$, the volume of this center at time point t; τ, the nucleation moment of a new phase center. For isothermal conditions, it is believed that $I(t) = I$ = const.

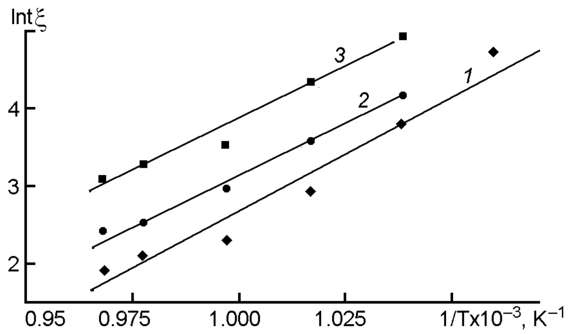

Fig. 2. $\ln t_\xi$ vs $1/T$ dependences for hydrogen-induced reverse phase transformation in $Nd_{15}Fe_{77}B_8$ for transformation degree: 0.5 (*1*); 0.7 (*2*); 0.9 (*3*).

Further, the volume growth of a spherical $Nd_2Fe_{14}B$ phase center $\varphi(t)$ can be written as

$$\varphi(t) = \frac{4}{3}\pi\rho^3(t), \quad (4)$$

where $\rho(t)$ is the center radius at time point t.

For diffusion-controlled growth of $Nd_2Fe_{14}B$ phase, the radius $\rho(t)$ can be written as [8, 10, 11]

$$\rho(t) = 2\beta(\xi)\sqrt{Dt}. \quad (5)$$

where $D = D_0\exp(-Q/RT)$ is the diffusion coefficient of Fe atoms in α-Fe matrix; $\beta(\xi)$, the parameter depending on concentration and degree of transformation ξ; D_0 = 14 cm^2/s, the diffusion constant; Q = 259.54 kJ/mol, the diffusion activation energy of Fe atoms in α-Fe matrix [8]; T, temperature; R = 8.31 J·(mol·K)$^{-1}$, the gas constant.

The new phase nucleation rate in solids, according to the Turnbull-Fisher theory [10–12], can be written as

$$I = \gamma\frac{RT}{h}e^{-\frac{W+U}{RT}}, \quad (6)$$

where W is the free energy of critical nucleus of $Nd_2Fe_{14}B$ formation; U, the activation energy; h, the Planck constant; $\gamma = 10^6$ mol/m^3.

Substitution of equations (4), (5) and (6) into (3) for $t \geq \tau$ results in the equation

$$\xi = 1 - \exp\left[-\frac{8\pi\gamma RT}{15h}\beta^3(\xi)D_0^{3/2}e^{-\frac{W+U+\frac{3}{2}Q}{RT}}t^{\frac{5}{2}}\right]. \quad (7)$$

For temperature dependence of transformation time t_ξ reqiured to attain a certain degree of transformation ξ, it is possible to obtain from (7):

$$t_\xi = a \cdot [-\ln(1-\xi)]^{\frac{2}{5}} \left[\frac{1}{T}\right]^{\frac{2}{5}} \cdot e^{\frac{\frac{2}{5}(W+U)+\frac{3}{5}Q}{RT}}, \quad (8)$$

where $a = \left(\frac{15h}{8\pi\gamma R\beta^3(\xi)D_0^{3/2}}\right)^{\frac{2}{5}}$.

For the further analysis, all unknown parameters in equation (8) are to be determined. In our case, we can believe that $(W + U) + Q = Q_{eff.}$, where W is the free energy of critical nucleus for $Nd_2Fe_{14}B$ phase formation; Q, the diffusion activation energy of Fe atoms in α-Fe matrix; $Q_{eff.}$, the effective energy of reverse phase transformation. Values of activation energy U are unknown, but we can believed these values to be approximately equal to dissociation energy of NdH_2 hydride $E_{dis.} = -81.4$ kJ/mol [13]. Further, using activation energy values obtained before for reverse phase transformation, the parameters in the equation (8) were determined and shown in the Table.

Let the interfacial energy σ be estimated. In the classical theory, the free energy of nucleus formation may be written as

$$W = \frac{16}{3}\pi\frac{\sigma^3}{\Delta G V}, \quad (9)$$

where σ is the interfacial energy per unit area; ΔG, free energy between the old and new phases per unit molar volume; V, the molar volume. Value of ΔG is unknown, but according to [7], for many metals $\Delta G \approx 3.612 \cdot 10^3$ J/mol. Then, σ estimation using Eq.(9) and data from the Table give us the value $\sigma \approx 0.59$ J/m^2. This value agrees well with interfacial energy for pure Nd, where σ is 0.68 J/m^2 [14].

Basing on Eq.(8) and data from the Table, equations describing the kinetics of reverse hydrogen-induced phase transformation in $Nd_{15}Fe_{77}B_8$ alloy for degrees of transformation ξ equal to 0.5, 0.7 and 0.9 were calculated to be as follows:

$$t_{\xi=0.5} = 2.93 \cdot 10^{-11} \cdot [-\ln(1-\xi)]^{2/5} \times \left(\frac{1}{T}\right)^{0.4} \cdot e^{\frac{248.8}{RT}}, \quad (10)$$

$$t_{\xi=0.7} = 1.90 \cdot 10^{-9} \cdot [-\ln(1-\xi)]^{2/5} \times \left(\frac{1}{T}\right)^{0.4} \cdot e^{\frac{216.6}{RT}}, \quad (11)$$

$$t_{\xi=0.9} = 1.46 \cdot 10^{-9} \cdot [-\ln(1-\xi)]^{2/5} \times \left(\frac{1}{T}\right)^{0.4} \cdot e^{\frac{221.6}{RT}}. \quad (12)$$

Table. Estimated values of parametres in Eq.(8) for reverse hydrogen-induced phase transformation in $Nd_{15}Fe_{77}B_8$ alloy for transformation degree of 0.5, 0.7 and 0.9

	$Q_{eff.}$, kJ/mol	U, kJ/mol	W, kJ/mol	β(ξ)
0.5	248.8	−81.4	314.1	0.02274
0.7	216.6	−81.4	233.6	$3.263 \cdot 10^{-3}$
0.9	221.6	−81.4	246.1	$4.064 \cdot 10^{-3}$

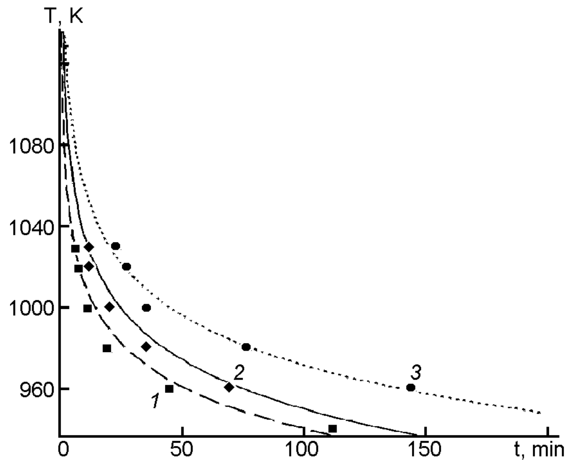

Fig. 3. Calculated isothermal kinetic diagrams for hydrogen-induced reverse phase transformation in $Nd_{15}Fe_{77}B_8$ alloy for transformation degree; 0.5(1); 0.7 (2); 0.9 (3). Points are experimental data from [4] for the reverse phase transformation degrees 0.5 (□), 0.7 (♦), 0.9 (•).

Further, the isothermal kinetic diagram of reverse hydrogen-induced phase transformation in $Nd_{15}Fe_{77}B_8$ alloy was plotted using the equations (10)–(12). This diagram is shown in Fig. 3. It is seen from this Figure that the calculated curves approximate well the experimental data from [4].

As is seen from Fig. 3, the proposed model also predicts an acceleration of reverse phase transformation at temperature elevation. In fact, as follows from [15], where isothermal recombination process in $Nd_{32}Dy_{1.5}Fe_{65}Nb_{0.5}B_{1.0}$ was studied at temperatures ranging from 765 to 860°C by in-situ powder neutron diffraction, increase of the isothermal temperature results in acceleration of the reverse transformation process.

Thus, the proposed model describing well the kinetics of hydrogen-induced diffusive reverse phase transformations in $Nd_{15}Fe_{77}B_8$ alloy basing on Eq.(8) can be considered as a first step for the further development of this model for description of such transformations in $Nd_2Fe_{14}B$ type alloys.

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