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ANALYSIS OF KINETICS OF THE HYDROGEN INDUCED REVERSE PHASE TRANSFORMATION IN $Nd_2Fe_{14}B$ HARD MAGNETIC ALLOY

Sergey B. Rybalka
Donetsk National Technical University

1. Introduction

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].

Recently developed HDDR-process (Hydrogenation-Decomposition-Desorption-Recombination) 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 after HDDR-treatment.

In paper [4] the isothermal kinetic diagram of the hydrogen induced reverse phase transformation in $Nd_2Fe_{14}B$ alloy was obtained experimentally. However, to the present moment the theory describing such phase transformation doesn't exist. The aim of the present paper is to describe above mentioned isothermal kinetic diagram theoretically using the Kolmogorov-Lyubov-Aleksandrov kinetic theory of phase transformations.

2. Results and discussion

In hydrogen atmosphere (~0.1 MPa) and at temperatures of 600-900^{o}C in $Nd_2Fe_{14}B$ alloy hydrogen induced direct phase transformation (decomposition) occurs by the following structural scheme [3]

$$Nd_2Fe_{14}B \rightarrow NdH_2 + 12\alpha\text{-}Fe + Fe_2B \qquad (1)$$

Hydrogen induced reverse phase transformation (recombination) in $Nd_2Fe_{14}B$ alloy occurs at hydrogen evacuation in vacuum (~10^{-2} Torr) by the following structural scheme [3]

$$NdH_2 + 12\alpha\text{-}Fe + Fe_2B \rightarrow Nd_2Fe_{14}B \qquad (2)$$

In paper [4] the isothermal kinetic diagram for hydrogen induced reverse phase transformation in $Nd_2Fe_{14}B$ alloy was obtained by magnetometer measurements. This diagram is shown in Figure 1.

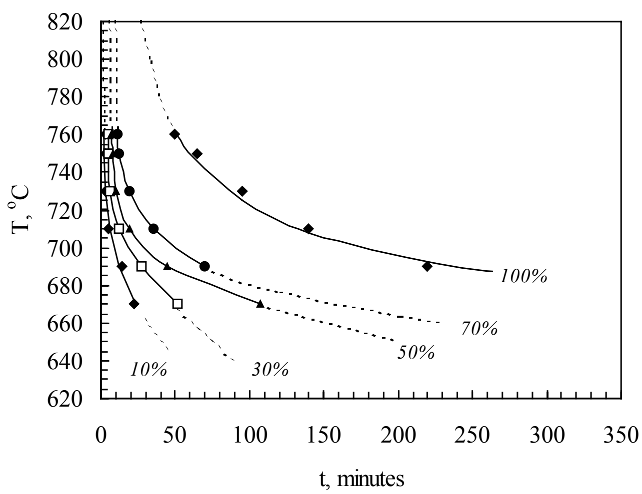

Figure 1. Isothermal kinetic diagram for hydrogen induced reverse phase transformation in $Nd_2Fe_{14}B$ (after Ref. [4]).

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 to *Nd* atoms results in nucleation and growth of $Nd_2Fe_{14}B$ phase.

Earlier on a base of kinetic investigations [4,5] and electron microscopy and X-ray diffraction studies [6] during reverse phase transformation in $Nd_2Fe_{14}B$ type alloys it was showed that transformations of this type is a diffusive phase transformation in solid state and that the reverse transformation process proceeds by the nucleation and growth mechanism. In works [4-6] it was showed that the reverse phase transformation is controlled by diffusion of *Fe* atoms.

As well known from the Kolmogorov's kinetic theory of phase transformation in solid state [7-9], the volume of the transformed area ξ in dependence on transformation time *t* and temperature *T* can be written 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 centres of new phases at time *t*, $\varphi(t)$ is the volume of this centre at time *t*, τ is the nucleation moment of centre of a new phase. For the isothermal conditions it is believed that *I(t)=I=const.*

Further, volume $\varphi(t)$ of a spherical centre of $Nd_2Fe_{14}B$ phase at time *t* may be written as

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

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

The radius $\rho(t)$ of $Nd_2Fe_{14}B$ phase at time *t* according to Lyubov-Aleksandrov theory [8-10] may be written as

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

where $D = D_o e^{-\frac{Q}{RT}}$ is the diffusion coefficient of *Fe* atoms in α-*Fe* matrix in our case, $\beta(\xi)$ is the parameter depending on concentration and degree of transformation ξ, D_o=14 sm^2/s is the diffusion constant, *Q* is the activation energy of diffusion, *T* is the temperature, *R*=8.31 J $(mol\ K)^{-1}$ is gas constant.

The nucleation rate of a new phase in solids according to the Turnbull-Fisher theory [8-11] may 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* is the activation energy, *h* is the Planck's constant, $\gamma=10^6$ mol/m^3.

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

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

From (7) for dependence of transformation time t_ξ, which is necessary for the achievement of some degree of transformation ξ from temperature *T*, it is possible to obtain

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

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

For the further analysis it is necessary to determine all unknown parameters in equation (8). With this aim experimental data from Fig. 1 were replotted in co-ordinates $\ln t_{\xi}$ versus 1/T (Figure 2).

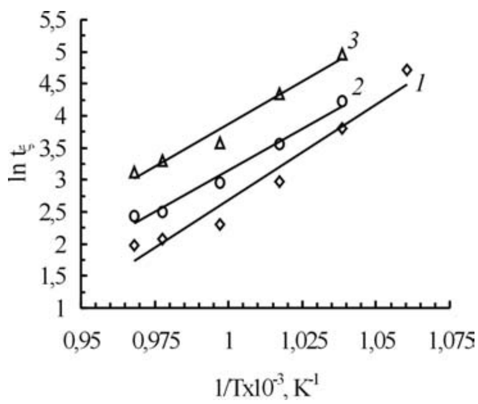

Figure 2. $\ln t_{\xi}$ vs *1/T* dependence for hydrogen induced reverse phase transformation in $Nd_2Fe_{14}B$ for degrees of transformation: *1*-0.5; *2*-0.7; *3*-0.9.

So, the slopes of the straight lines give us the values of the effective activation energies for hydrogen induced reverse phase transformation. In our case the effective activation energy of this process $Q_{eff.} = \frac{2}{5}(W+U) + \frac{3}{5}Q$. Values of activation energy equal to $Q_{eff.} = 216 - 248$ kJ/mol. These values have good agreement with an activation energy of a diffusion of Fe atoms in α-Fe matrix ($Q_{\alpha\text{-Fe}}$=259.54 кJ/mol [12]). Therefore, it is really possible to consider that evolution process of reverse phase transformation is controlled by diffusion of Fe atoms. Then it is believed that activation energy *U* is an approximately equal to dissociation energy of NdH_2 hydride $E_{dis.}$= – 81.4 kJ/mol [13]. Determined by this means parameters in the equation (8) are showed in the Table 1.

On the base of equation (8) and data from Table 1 the equations describing the kinetics of reverse hydrogen induced phase transformation in $Nd_2Fe_{14}B$ alloy for degrees of transformation 0.5, 0.7 and 0.9 were calculated

$$t_{0.5} = 2.93 \cdot 10^{-11} \cdot 0.8636 \cdot \left(\frac{1}{T}\right)^{0.4} \cdot e^{\frac{29939}{T}}, \qquad (9)$$

$$t_{0.7} = 1.90 \cdot 10^{-9} \cdot 1.077 \cdot \left(\frac{1}{T}\right)^{0.4} \cdot e^{\frac{26067}{T}}, \qquad (10)$$

$$t_{0.9} = 1.46 \cdot 10^{-9} \cdot 1.396 \cdot \left(\frac{1}{T}\right)^{0.4} \cdot e^{\frac{26671}{T}}. \qquad (11)$$

Table 1. Estimated values of the parametres in Equation (8) for reverse hydrogen induced phase transformation in $Nd_2Fe_{14}B$ alloy for degrees of transformation 0.5, 0.7 and 0.9, respectively.

	$Q_{eff.}$, кJ/mol	U, кJ/mol	W, кJ/mol	$\beta(\xi)$
0.5	248.8	-81.4	314.1	0.02274
0.7	216.6	-81.4	233.6	3.263×10^{-3}
0.9	221.6	-81.4	246.1	4.064×10^{-3}

Further, the isothermal kinetic diagram of reverse hydrogen induced phase transformation in $Nd_2Fe_{14}B$ alloy was plotted by the equations (9)–(11). This diagram is shown in Figure 3.

As can be seen from this figure the calculated curves have well approximates data from paper [4].

As seen from Fig. 3 proposed model predicts an acceleration of reverse phase transformation evolution at temperature increase. Really, as follows from paper [14], where recombination process was studied in $Nd_{32}Dy_{1.5}Fe_{65}Nb_{0.5}B_{1.0}$ at isothermal temperatures from 765 up to 860^{o}C by in-situ powder neutron diffraction, increase of the isothermal temperature results in acceleration process of reverse phase transformation.

Therefore, proposed model describing the kinetics of hydrogen induced diffusive reverse phase transformations in $Nd_2Fe_{14}B$ alloy 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.

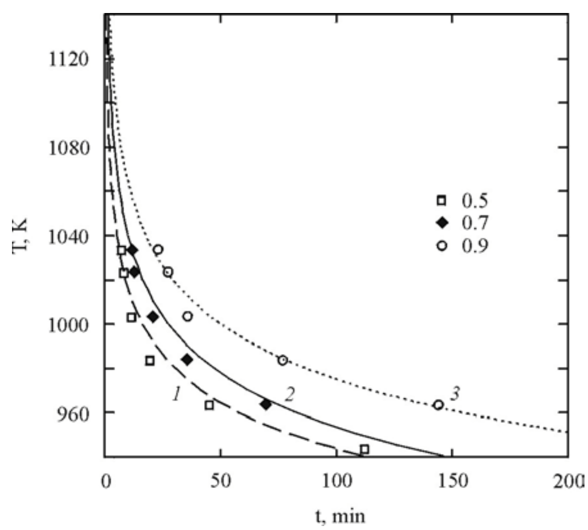

Figure 3. Calculated isothermal kinetic diagram of hydrogen induced reverse phase transformation in $Nd_2Fe_{14}B$ alloy for degrees of transformation: *1*-0.5; *2*-0.7; *3*-0.9. Points are experimental data (from Ref. [4]).

3. Acknoledgements

Thus, the isothermal kinetic diagram of hydrogen induced reverse phase transformation in $Nd_2Fe_{14}B$ type alloy can be well described by the equation of form (8). Also is shown, that the kinetics of reverse phase transformation is controlled by a diffusion of Fe atoms.

SUMMARY

Kinetics of the hydrogen induced reverse phase transformation in $Nd_2Fe_{14}B$ alloy at isothermal conditions was described. The isothermal kinetic diagram of this transformation in $Nd_2Fe_{14}B$ alloy was calculated on base of the Kolmogrov-Lyubov-Aleksandrov theory. It is shown that kinetics of a reverse phase transformation is controlled by diffusion of *Fe* atoms.

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