Kinetic model for hydrogen-induced direct phase transformations in R_2Fe_{17} (R - Sm, Y) type alloys

S.B. Rybalka

sbrybalka@yandex.ru

Bryansk State Technical University, 50-letiya Oktyabrya boulevard 7, 241035 Bryansk, Russia

Model for evolution of the hydrogen induced direct phase transformation in R_2Fe_{17} (R – Sm, Y) type hard magnetic alloys has been proposed. It is shown that evolution process of hydrogen-induced direct phase transformation in R_2Fe_{17} type hard magnetic alloys is controlled by diffusion process of Fe atoms in low temperatures interval of 330-750°C and in high temperatures interval of 780-860°C phase transformation process is controlled by growth kinetics of rare-earth RH_2 hydride phase. It have been determined the values of an effective activation energy for hydrogen induced direct phase transformation in Sm_2Fe_{17} alloy that varying from 109 up to 230 kJ/mol for and from 162 up to 242 kJ/mol for Y_2Fe_{17} alloy, consequently. It has been established that the above values of effective activation energy in low temperature region (330-750°C) have good agreement with an activation energy of data for diffusion of Fe atoms in Rare-Earth metals - Q=250 kJ/mol and also self-diffusion of Fe atoms in α-Fe phase of iron ~250.6 kJ/mol. Because of this were calculated the value of free energy of critical nucleus of α-Fe phase formation for Sm_2Fe_{17} and Y_2Fe_{17} alloy that equals 239.9×10^3 J/mol and 353.4×10^3 J/mol, consequently. On the base of above-mentioned data has been proposed model for evolution of the hydrogen induced direct phase transformation in R2Fe17 (R – Sm, Y) type hard magnetic alloys, in particulary, 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 two main phases: RH_2 hydride phase and α-Fe phase. In accordance with above described model 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 in R_2Fe_{17} (R – Sm, Y) type hard magnetic alloys.

Keywords: kinetics, phase transitions, magnetic alloys; intermetallics; gas–solid reactions.

1. Introduction

As well known phase transformations studies have always been one of the main standpoint areas of condensed matter physics, metal science, theoretical and practical materials science [1,2]. At present the intermetallic compounds of R_2M_{17} (R=Sm, Y, Dy, Ho, Gd) type have attracted much attention because of their interesting magnetic properties [3,4]. In particularly, R_2M_{17} compounds demonstrate very interesting magnetic phenomenon during their interaction with interstitial atoms (H, N, C, B) [5-7].

In particular, the new perspective technology well known as a HDDR-process (Hydrogenation-Decomposition-Desorption-Recombination) in R_2M_{17} type alloys (Sm_2Fe_{17}, Sm_2Co_{17} etc.) alloys for permanent magnets allows improve their structure and magnetic properties by hydrogen-induced reversible phase transformations [8].

The most significant aspect of the HDDR process is that there is a dramatic change in the microstructure alloy from an initial grain size of typically ~150μm to a very fine, uniform grain size of about 0.1-0.3μm [8]. On magnetisation, the HDDR nanocrystalline powder exhibits an appreciable coercivity and this means that, in its simplest net shape form, the powder can be mixed with a thermosetting resin to produce an isotropic and anisotropic permanent magnet by compression moulding. As result, the practical application of hydrogen-induced reversible phase transformations in hard magnetic alloys of rare-earth and transition metals such as $Nd_2Fe_{14}B$, Sm_2Fe_{17} and Y_2Fe_{17} allows to improve their structure and magnetic properties and also leads to miniaturization of new technical devices based on $Nd_2Fe_{14}B$, Sm_2Fe_{17} and Y_2Fe_{17} permanent magnets which used in electric motors, 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 diagrams of the hydrogen induced direct phase transformations in Sm_2Fe_{17} and Y_2Fe_{17} alloys were obtained experimentally earlier [9-11]. 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.

2. Results and discussion

At first stage, at HDDR-treatment the R_2Fe_{17} alloy undergoes the direct hydrogen-induced phase transformation at

temperatures above 500°C in hydrogen atmosphere about 0.1 MPa with decomposition of initial alloy on hydride YH_2 phase and α-phase of Fe that can be described by the following phase scheme:

$$R_2Fe_{17} + H_2 \rightarrow RH_2 + \alpha - Fe. \qquad (1)$$
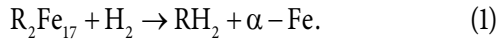
Then, the reverse phase transformation takes place during hydrogen evacuation at higher temperatures with recombination decomposed phases into initial Y_2Fe_{17} matrix phase and can be described by the following phase reaction:

$$RH_2 + \alpha - Fe \rightarrow R_2Fe_{17} + 2H_2 \uparrow \rightarrow R_2Fe_{17}. \qquad (2)$$
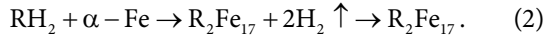
Earlier on a base of detailed kinetic investigations, SEM and X-ray diffraction studies during direct phase transformation (see Eq. (1)) in $Nd_2Fe_{14}B$, Sm_2Fe_{17} and Y_2Fe_{17} type alloys it was established that transformations of this type maybe classified as diffusive phase transformation in solid state and that the direct transformation process proceeds by the nucleation and growth mechanism [9-14].

As follows from Becker-Döering model of nucleation kinetics [2,15-16] 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 were re-plotted in co-ordinates $\ln t_\xi$ versus $1/T$ which are shown in Fig. 1 and Fig. 2. The slopes of the straight lines give us the values of the effective activation energies for hydrogen induced direct phase transformations. The obtained values of an activation energy determined for
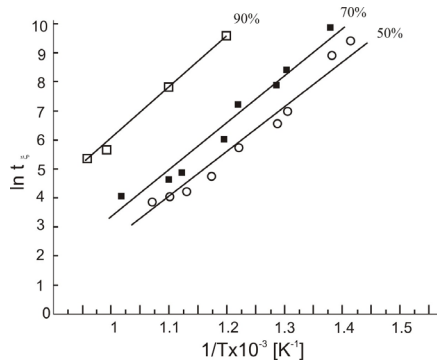
Fig. 1. Dependence $\ln t_\xi$ on $1/T$ for direct phase transformations in Sm_2Fe_{17} alloy for 30, 50 and 70 % of degrees of phase transformation [9].
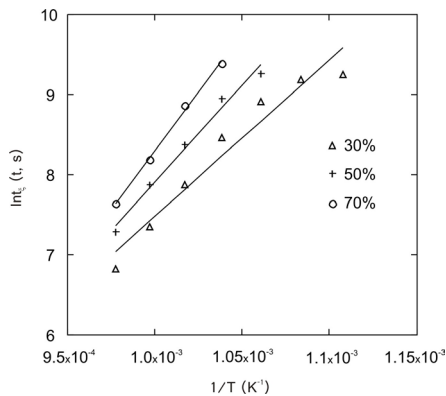
Fig. 2. Dependence $\ln t_\xi$ on $1/T$ for direct phase transformations in Y_2Fe_{17} alloy for 30, 50 and 70 % of degrees of phase transformation [11].

some degrees of transformation varying from 109 up to 230 kJ/mol for Sm_2Fe_{17} alloy [9] and from 162 up to 242 kJ/mol for Y_2Fe_{17} alloy [11]. Obtained above values of effective activation energy in low temperature region (330-750°C) have good agreement with an activation energy of data for diffusion of Fe atoms in Rare-Earth metals - Q=250 kJ/mol [17] and self-diffusion of Fe atoms in α-Fe phase of iron ~250.6 kJ/mol [18]. For comparison activation energy for hydrogen atoms diffusion in R_2Fe_{17} type alloys equals ~(31±10) kJ/mol [19] that less by one order of values. Earlier it was established that for $Nd_2Fe_{14}B$ alloy in high temperature region (780-860°C) effective energy activation is equal to the energy of NdH_2 hydride phase formation (ΔG_{NdH_2}= - (187.7±3.3) kJ/mol [20]).

Therefore, it is really possible to consider that evolution process of direct phase transformation is controlled by diffusion process of Fe atoms in low temperatures interval of 330-750°C and in high temperatures interval of 780-860°C phase transformation process controlled by growth kinetics of rare-earth RH_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 R_2Fe_{17} alloy leads to nucleation and growth process of RH_2 hydride phase and then diffusion of Fe atoms leads to formation of α-Fe 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 two main phases: RH_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 R_2Fe_{17} type alloys. As well known from the Kolmogorov kinetic theory of phase transformation in solid state [21], the volume of the transformed area ξ in dependence on t transformation time can be written as

$$\xi(t) = \frac{V(t)}{V_0} = 1 - \exp\left[-\int_0^t I(t)\varphi(t-\tau)dt\right], \qquad (3)$$

where $V(t)$ is the transformed area volume at time t, V_0 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 [22] 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 RH_2 and α-Fe nucleation centres at time moment t, correspondingly.

Further, growth of volume of a spherical centre of RH_2 phase $\varphi_1(t)$ may be written as:

$$\varphi_1(t) = \frac{4}{3}\pi r_1^3(t), \qquad (5)$$

where $r_1(t)$ is the radius of this centre at time t.

Nucleation process of RH_2 phase we can be considered as in single-component system taking into account of high diffusive mobility of hydrogen atoms to rare-earth atoms in R_2Fe_{17} alloy and in this case according to theory of absolute reaction rates [23] radius $r_1(t)$ of RH_2 centre at time t:

$$r_1(t) = \frac{\pi d^4 \Delta g}{9h} e^{-\frac{U}{RT}} t, \qquad (6)$$

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:

$$\varphi_2(t) = \frac{4}{3} \pi r_2^3(t), \qquad (7)$$

where $r_2(t)$ is the radius of α-Fe centre at time t.

On the other hand, it's known [2,22] that at diffusive-controlled transformations boundary of new phase moves by parabolic low and $r_2(t)$ may be written in following form:

$$r_2(t) = 2\beta\sqrt{Dt}, \qquad (8)$$

where $D = D_0 e^{-\frac{Q}{RT}}$ is the diffusion coefficient of Fe atoms, Q is the activation energy of Fe atoms diffusion, R is the gas constant, β 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 [24] is

$$I = \gamma \frac{RT}{h} e^{-\frac{W}{RT}} e^{-\frac{U}{RT}}, \qquad (9)$$

where W is the energy necessary for formation of critical nucleus, U is the activation energy at transition of atoms through interface of phases, $\gamma = 10^6$ mol/m³ [22], 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:

$$\xi(t) = 1 - \exp\left[-\frac{\pi^4 d^{12} \Delta g^3 RT\gamma}{3^7 h^4} e^{-\frac{W+4U}{RT}} t^4_{cr.} - \right.$$
$$\left. -\frac{64\pi RT\gamma}{15h} \beta^3 D_0^{\frac{3}{2}} e^{-\frac{W+U+\frac{3}{2}Q}{RT}} \left(t^{5/2} - \tau^{5/2}\right) \right]. \qquad (10)$$

where $t_{cr.}$ is time which is equal to time for nucleus growth of new phase up to critical size.

For practical application phase transformation kinetics as a rule describes by curves showing time transformation t needs for reaching some degree of transformation ξ dependence on transformation temperature T [2,22]. Thus, Eq. (10) has been written in following form:

$$t(\xi,T) = \left(\frac{15h\ln\left(\frac{1}{1-\xi}\right)e^{\frac{W+U+\frac{3}{2}Q}{RT}}}{64\pi RT\gamma\beta^3 D_0^{3/2}} + \frac{15h\ln\left(\frac{1}{1-\xi}\right)e^{\frac{W+U+\frac{3}{2}Q}{RT}}}{64\pi RT\gamma\beta^3 D_0^{3/2}} + \right.$$
$$\left. + \frac{5\pi^3 d^{12}\Delta g^3}{3^6 64 h^3 \gamma\beta^3 D_0^{3/2} h^3} e^{\frac{\frac{3}{2}Q - 3U}{RT}} \tau^4 + \tau^{5/2} \right)^{2/5}. \qquad (11)$$

Afterward let's consider 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:

$$t(\xi,T) = \left(\frac{15h}{64\pi\gamma R\beta^3(\xi)D_0^{\frac{3}{2}}} \right)^{\frac{2}{5}} \left[-\ln(1-\xi) \right]^{\frac{2}{5}} \times$$
$$\times \left[\frac{1}{T} \right]^{\frac{2}{5}} e^{\frac{\frac{2}{5}(W+U)+\frac{3}{5}Q}{RT}}. \qquad (12)$$

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

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

Then 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:

$$t(\xi,T) = \left[\frac{15h\ln\left(\frac{1}{1-\xi}\right)}{64\pi RT\gamma\beta^3 D_0^{3/2}} \right]^{\frac{2}{5}} e^{\frac{\frac{2}{5}(W+U)+\frac{3}{5}Q}{RT}} +$$
$$+ \frac{3h}{\pi d^3 \Delta g^{3/4}} \left[\frac{27\ln\left(\frac{1}{1-\xi}\right)}{RT\gamma} \right]^{\frac{1}{4}} e^{\frac{W+U}{4 RT}}. \qquad (14)$$

Finally, for direct hydrogen-induced phase transformations in R_2Fe_{17} type alloys in low temperature region (330-750°C) we can obtain the following equation:

$$t(\xi,T) = \left[\frac{15h\ln\left(\frac{1}{1-\xi}\right)}{64\pi RT\gamma\beta^3 D_0^{3/2}} \right]^{\frac{2}{5}} e^{\frac{\frac{2}{5}(W+U)+\frac{3}{5}Q}{RT}}. \qquad (15)$$

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 earlier effective activation energies (see Fig. 1 and Fig. 2) $Q_{ef.}$ equal correspondently

$$Q_{ef.} \cong \frac{2}{5}(W+U) + \frac{3}{5}Q,$$

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_0=1 mm²/s [17]), U is the activation energy of hydrogen atoms at transition of atoms through interface of RH_2 phases which is equal to energy of RH_2 hydride phase formation nucleus. Because of this as follows from kinetic data for $Nd_2Fe_{14}B$ alloy [25] the kinetic parameter in Eq. (15) $\beta \approx 10^{-3} \div 10^{-5}$. Then, using obtained effective activation energies and above-mentioned data were obtained all unknown parameters in Eq. (15) which are shown in Table 1.

As follows from Table 1 value of free energy of critical nucleus of α-Fe phase formation for Y_2Fe_{17} alloy is larger than the same for Sm_2Fe_{17} alloy, but less than estimated values of

energy of critical nucleus of α-Fe phase formation in $Nd_2Fe_{14}B$ alloy where W=495÷575 kJ/mol [25]. Above-mentioned values of the energy have reasonable order of magnitude for energy of critical nucleus phase formation in solid body [2,20].

Then on the base of Eq. (15) and data from Table 1 the isothermal kinetic diagrams for direct hydrogen-induced phase transformation in low temperatures interval (330-750°C) in R_2Fe_{17} (R – Sm, Y) type alloys have been plotted. These diagrams are shown in Fig. 3. As can be seen from this figure the calculated curves well approximate experimental kinetic data from papers [9-11].

Thus, kinetic equation of form Eq. (15) 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 R_2Fe_{17} alloys. Above-mentioned kinetic approach in future can be applied for others RE-Fe type hard magnetic alloys for permanent magnets (Pr-Fe, Er-Fe, Ho-Fe etc.).

Table 1. Values of the parameters in Eq. (15) for direct hydrogen induced phase transformation in R_2Fe_{17} (R – Sm, Y) type alloys:

R_2Fe_{17} (R - Sm, Y) type alloy	Q_{ef}, average effective activation energy of direct transformation [9,11], J/mol	W, energy of critical nucleus of α-Fe phase formation, J/mol	U, energy of RH_2 (R - Sm, Y) hydride phase nucleus formation [18], J/mol
Sm_2Fe_{17}	156.76×10^3	239.9×10^3	-223×10^3
Y_2Fe_{17}	202.16×10^3	353.4×10^3	-235×10^3

Fig. 3. The isothermal kinetic diagrams of hydrogen induced direct phase transformation in R_2Fe_{17} (R – Sm, Y) type alloys calculated by Eq. (15) for different degrees of transformation ξ.

3. Conclusions

Model for evolution of hydrogen-induced direct phase transformations in hard magnetic R_2Fe_{17} (R – Sm, Y) type alloys has been proposed. It is shown that evolution process of hydrogen-induced direct phase transformation in R_2Fe_{17} type hard magnetic alloys is controlled by diffusion process of Fe atoms in low temperatures interval of 330-750°C and in high temperatures interval of 780-860°C phase transformation process is controlled by growth kinetics of rare-earth RH_2 hydride phase. On the base of Kolmogorov and Lyubov kinetic theory of the phase transformations kinetic equation for these transformations has been obtained. It is shown that the experimental isothermal kinetic diagram of hydrogen induced direct phase transformation in R_2Fe_{17} alloys in low temperatures interval (330-750°C) can be well described by the equation of the following form:

$$t(\xi,T) = \left(\frac{15h}{64\pi\gamma R\beta^3(\xi)D_0^{\frac{3}{2}}}\right)^{\frac{2}{5}} \cdot \left[-\ln(1-\xi)\right]^{\frac{2}{5}}\left[\frac{1}{T}\right]^{\frac{2}{5}} \cdot e^{\frac{\frac{2}{5}(W+U)+\frac{3}{5}Q}{RT}}$$

where $t(\xi,T)$ is the time needs for reaching of some degree of transformation ξ at some transformation temperature T, β is the kinetic parameter, W is the energy necessary for formation of critical nucleus of α-Fe phases, U is the energy of RH_2 hydride phase formation nucleus, Q is the activation energy of Fe atoms diffusion.

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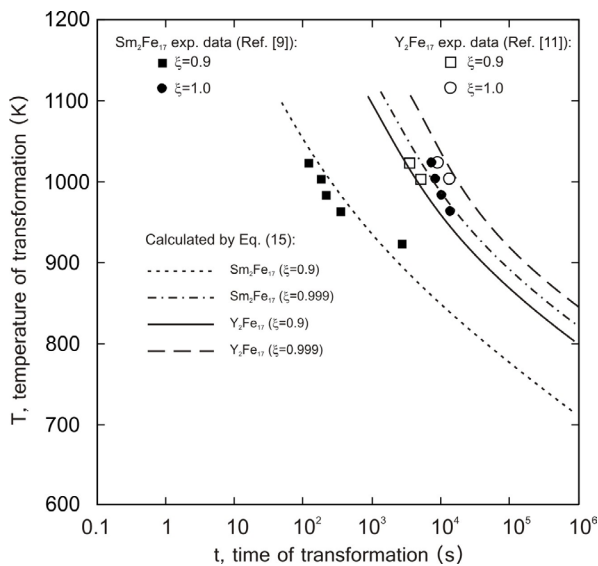
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