Effect of hydrogen pressure on growth kinetics of Nd$_2$Fe$_{14}$B phase during hydrogen-induced reverse phase transformation in Nd$_2$Fe$_{14}$B type hard magnetic alloy

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The effect of initial hydrogen pressure on the growth kinetics of Nd$_2$Fe$_{14}$B phase during hydrogen-induced reverse phase transformation in the industrial Nd$_2$Fe$_{14}$B hard magnetic alloy has been studied. It has been determined that, as the temperature and initial hydrogen pressure increase, the reverse phase transformation is significantly accelerated. It has been shown that the kinetics of growth of Nd$_2$Fe$_{14}$B phase is controlled by the diffusion of Fe atoms and that the growth rate of new Nd$_2$Fe$_{14}$B phase increases with an increase of the initial hydrogen pressure. On the base of the Kolmogorov-Hillert-Smirnov kinetic models the kinetic equation for describing the influence of initial hydrogen pressure on the isothermal kinetic diagram for this transformation has been proposed.

Keywords: intermetallics; permanent magnets; gas–solid reactions

1. Introduction

As well known, permanent magnet materials of a RE-TM (rare-earth–transition-metal) type are key components of numerous modern devices [1]. There are many processing routes for improving of their magnetic properties [2]. In particular, one of the promising technologies for improvement of magnetic properties of RE-TM type alloys is HDDR-process (Hydrogenation–Decomposition–Desorption–Recombination) [3]. The most significant aspect of the HDDR process is that there is a dramatic change in the microstructure from an initial grain size of typically ~150µm to a very fine, uniform grain size of about 0.1–0.3µm [3-6]. 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 [3-5].

The above-mentioned HDDR-process is based on hydrogen-induced reversible phase transformations in the RE-TM type hard magnetic alloys [6]. The transformation process is based on the formation of a RE-TM hydride, which at higher temperatures has a tendency to disproportionate into a mixture of RE-hydride and iron; this is a direct hydrogen induced phase transformation that occurs in the case of NdFeB-based alloys by the following scheme [6]:

\[
\text{Nd}_2\text{Fe}_{14}\text{B} \rightarrow \text{Nd}_2\text{Fe}_{14}\text{BH}_x \rightarrow \text{NdH}_2 + \alpha-\text{Fe} + \text{Fe}_2\text{B}
\] (1)
Further, at the second stage, the subsequent desorption of hydrogen in vacuum (~10^{-2} Torr) at high temperatures from decomposed alloy leads to a recombination into the initial phase of Nd$_2$Fe$_{14}$B; this is a reverse hydrogen induced phase transformation by the following scheme in NdFe$_{B}$-based alloys [6]:

$$\text{NdH}_2 + \alpha\text{-Fe} + \text{Fe}_2\text{B} \rightarrow \text{Nd}_2\text{Fe}_{14}\text{B}$$ (2)

The phase transformation of this type leads to a formation of a fine-grained ferromagnetic phase Nd$_2$Fe$_{14}$B that allows one to obtain permanent magnets with a high coercitivity [4, 5].

Earlier the effect of the hydrogen pressure on the kinetics of hydrogen-induced direct phase transformations in RE-TM type alloys has been studied systematically in [7-10] and it was established that phase transformation process accelerates as hydrogen pressure increases.

Thus, the main aim of this paper is to establish the influence of hydrogen pressure on the kinetics of subsequent hydrogen-induced reverse phase transformations proceeding according to Eq. (2) in the Nd$_2$Fe$_{14}$B type alloys and to describe the kinetic features within a framework of classical kinetic theory of phase transformations in condensed state.

2. Materials and methods

Studies of the reverse phase transformations have been carried out on special hydrogen-vacuum equipment using a Sadikov's type magnetometer [9, 10]. The samples of the industrial $R_2$Fe$_{14}$B type alloy ($R_{36.4}Fe_{62.45}B_{1.15}$, where $R$ is a mixture of rare-earth metals – 33% Nd, 2% Pr, 0.9% Ce and 0.5% Dy, weight %) in the form of a powder with average grain size ~100 μm (~1.25 g) were placed into the reaction chamber, which was evacuated to a pressure of ~1 Pa. Then the samples were heated under vacuum to the desired temperature. After establishing isothermal conditions, the reaction chamber was filled with hydrogen under selected pressures ranging from 0.1 to 0.2 MPa. The direct transformation was continuously monitored under isothermal conditions by measuring the amount of newly formed ferromagnetic phases ($\alpha$-Fe and Fe$_2$B) according to scheme (1). After a completion of the direct transformation, hydrogen was evacuated from the reaction chamber (at following continuous vacuumization down to 10^{-2} Torr) that gave rise to a development of the reverse phase transformation, i.e. the recombination of decomposed phases into the Nd$_2$Fe$_{14}$B phase according to scheme (2).

The development of the reverse transformations was then followed by continuously monitoring the decrease of the amount of ferromagnetic phases in the sample. The resulting data were plotted as isothermal kinetic diagrams of the reverse transformations occurring in the $R_2$Fe$_{14}$B compound.

3. Results and discussion

Shown in Fig. 1 are the isothermal kinetic diagrams of the reverse phase transformation in the industrial $R_2$Fe$_{14}$B alloy at various temperatures and initial hydrogen pressures. As follows from Fig. 1, if the reverse phase transformation starts at a higher initial hydrogen pressure, it leads to an increase of phase transformation rate for all transformation temperatures. In general, a twofold increase of the initial hydrogen pressure (from 0.1 MPa up to 0.2 MPa) results in an approximately 1.5 to 2 times acceleration of the reverse phase transformation evolution in the $R_2$Fe$_{14}$B alloy.

As can be seen from Eq. (2), for a transformation of this type diffusion of alloy's components is needed and in fact earlier on a base of kinetic, TEM and X-ray diffraction studies during reverse phase transformation in Nd$_2$Fe$_{14}$B type alloys it has been shown that transformations of this type can be classified as a diffusion phase transformation in the solid state and that the reverse transformation process proceeds by the nucleation and growth mechanism [11,12].

![Fig. 1. The isothermal kinetic diagrams for hydrogen induced reverse phase transformation in $R_2$Fe$_{14}$B alloy. $T$ is the isothermal exposure temperature, $t$ is the transformation time and 10, 30, 50, 70, 90, 100% are the degrees of the reverse transformation at different initial hydrogen pressures: (a) – 0.10 MPa; (b) – 0.15 MPa; (c) – 0.20 MPa.](image-url)
by the nucleation and growth mechanism. Further, one can determine the effective activation energy of phase transformation process in accordance with Becker-Döering model of nucleation kinetics [13,14] plotting the dependence $\ln t_\xi$ vs $1/T$, where $t_\xi$ is the time needed for reaching the degree of transformation $\xi$ and $T$ is the transformation temperature. This dependence plotted on the basis of experimental data from Fig. 1 is presented in Fig. 2.

The values of effective activation energy of phase transformation for various hydrogen pressures and degrees of transformation thus obtained are given in Table 1.

As can be seen from Table 1, all the values of effective activation energy obtained are in a good order-of-magnitude agreement with the activation energy for iron atoms diffusion in $\alpha$-phase of Fe ($Q_{Fe}=259.54, 284.2$ kJ/mol [15, 16]). This confirms that the process of reverse phase transformation is indeed controlled by a diffusion of iron atoms to the new centres of Nd$_2$Fe$_{14}$B phase. On the other hand, it is evident that the driving force of this transformation is a dissociation of NdH$_2$ phase due to the desorption of H$_2$. Thus, basing on the above-described transformation model, let’s obtain the kinetic equation for a hydrogen induced reverse phase transformation in Nd$_2$Fe$_{14}$B type alloy taking into account the influence of the hydrogen pressure during direct phase transformation stage on the reverse transformation kinetics.

### Table 1.

<table>
<thead>
<tr>
<th>$\xi$, degree of transformation</th>
<th>$P=0.1$ MPa, initial hydrogen pressure</th>
<th>$P=0.15$ MPa, initial hydrogen pressure</th>
<th>$P=0.2$ MPa, initial hydrogen pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>$198.31 \pm 7.51$ kJ/mol</td>
<td>$181.24 \pm 6.78$ kJ/mol</td>
<td>$214.23 \pm 8.05$ kJ/mol</td>
</tr>
<tr>
<td>0.7</td>
<td>$225.29 \pm 7.95$ kJ/mol</td>
<td>$177.83 \pm 7.96$ kJ/mol</td>
<td>$216.62 \pm 8.23$ kJ/mol</td>
</tr>
<tr>
<td>0.9</td>
<td>$224.46 \pm 8.14$ kJ/mol</td>
<td>$224.99 \pm 7.96$ kJ/mol</td>
<td>$198.96 \pm 8.21$ kJ/mol</td>
</tr>
</tbody>
</table>

In accordance with the well known Kolmogorov kinetic theory of phase transformations in condensed matter [17], the relative volume of transformed area $\xi$ during the reverse phase transformation can be written as follows:

$$\xi = \frac{V(t)}{V_0} = 1 - \exp \left(-\frac{\pi}{3} I \omega^3 t^4 \right),$$

(3)

where $V(t)$ is the transformed area volume at time moment $t$, $V_0$ is the initial untransformed volume, $I$ is the nucleation rate of centres of new Nd$_2$Fe$_{14}$B phases, $\omega$ is the rate of growth of a new Nd$_2$Fe$_{14}$B phase.

On the other hand, according to Turnbull-Fisher model [18, 19], the nucleation rate $I$ of new Nd$_2$Fe$_{14}$B phases centers in the case of diffusion-controlled growth is

$$I = \gamma \frac{R T}{h} e^{-\frac{AG+Q}{RT}},$$

(4)

where $AG$ is the energy necessary for the formation of Nd$_2$Fe$_{14}$B critical nucleus, $Q$ is the activation energy for the diffusion of Fe atoms to centres of new Nd$_2$Fe$_{14}$B phase, $\gamma=10^{-4}$ mol/m$^3$ [20], $R$ is the gas constant, $h$ is the Planck constant, $T$ is transformation temperature.

Then, substitute equation (4) into (3) we can obtain kinetic equation for volume of the transformed area $\xi$ in dependence on $t$ transformation time and transformation temperature $T$:

$$\xi(t) = 1 - \exp \left(-\frac{\pi}{3} \gamma \frac{R T}{h} e^{-\frac{AG+Q}{RT \omega^3}} t^4 \right),$$

(5)

As a rule, for practical applications the phase transformation kinetics are described by curves showing the transformation time $t$ needed for reaching the degree of transformation $\xi$ as a function of the transformation temperature $T$ [22]. For this purpose, Eq. (5) can be rewritten in the following form:
Following the classical theory of nucleation rate in condensed systems, in isothermal conditions the rate of nucleation \( I \) described by Eq. (4) is constant, because \( W \) and \( Q \) as a rule are constant for a given alloy [20, 22]. Therefore, one can assume that the nucleation rate of \( \text{Nd}_2\text{Fe}_{14}\text{B} \) phase is independent of the initial hydrogen pressure. Now, assuming that the activation energy for the transition of atoms through the interphase boundaries, \( Q \), in our case is equal to the activation energy for the diffusion of Fe atoms in the \( \alpha \)-Fe phase, \( Q=259.54 \) kJ/mol [16], and the energy necessary for the formation of \( \text{Nd}_2\text{Fe}_4\text{B} \) critical nucleus, \( \Delta G =314.1 \) kJ/mol [23], determine the nucleation rate \( I \) and growth rate, \( \omega \), of the new \( \text{Nd}_2\text{Fe}_4\text{B} \) phase during the phase transformation. Basing on Eq. (4) and the kinetic data from Fig. 1, values of \( I \) and \( \omega \) for various hydrogen pressures and temperatures for the transformation degree \( \xi=0.9 \) were calculated and the results are presented in Table 2.

Nucleation rate, \( I \) and growth rate, \( \omega \), of a new \( \text{Nd}_2\text{Fe}_4\text{B} \) phase during phase transformation determined for various hydrogen pressures \( P \) and transformation temperatures \( T \) for the transformation degree \( \xi=0.9 \) in \( \text{R}_2\text{Fe}_{14}\text{B} \) alloy.

Presented in Figure 3 is the dependence the growth rate of \( \text{Nd}_2\text{Fe}_4\text{B} \) phase versus the hydrogen pressure \( P \) plotted on the basis of data from Table 2. As follows from Fig. 3, the of growth rate \( \omega \) increases with an increase of the hydrogen pressure at all temperatures. Futhermore, basing on Lyubov’s and Hillert’s kinetic approach [20, 21] for the diffusion-controlled growth, we assume that the dependence of \( \omega \) on \( P \) and \( T \) can be approximated by following function:

\[
\omega = M \frac{\Delta F - \Delta F_0}{RT} e^{-\frac{U(P)}{RT}},
\]

where \( M \) is proportional to the mobility the interface of growing \( \text{Nd}_2\text{Fe}_{14}\text{B} \) phase, \( \Delta F \) is the difference of molar free energies of the initial and final phases, \( \Delta F_0 \) is the driving force of phase transformation, which in our case is proportional to the dissociation energy of \( \text{NdH}_2 \) phase, \( U(P) \) is the activation energy for the transition of Fe atoms across the interface of \( \text{Nd}_2\text{Fe}_{14}\text{B} \) phase that in turn depends on the hydrogen pressure.

On the other hand, following Smirnov’s theory [24], the activation energy for the transition of atoms through an interface of \( \text{Nd}_2\text{Fe}_{14}\text{B} \) phases \( U(P) \) can depend on the concentration of interstitial atoms (hydrogen atoms in our case) as follows: \( U(P) = \Delta E_{m-p} Q \times c \), where \( \Delta E_{m-p} \) is the activation energy for the diffusion of matrix phase atoms in the absence of interstitial atoms, \( Q \) is the interaction energy between matrix phase atoms and interstitial atoms, \( c \) is the concentration of interstitial atoms that in our case is proportional to the initial hydrogen pressure \( P \).

<table>
<thead>
<tr>
<th>( T ), temperature (K)</th>
<th>( I ), nucleation rate (m(^{-2} )s(^{-1} ))</th>
<th>( \omega ), rate of growth at ( P=0.1 ) MPa (m(^{-2} )s(^{-1} ))</th>
<th>( \omega ), rate of growth at ( P=0.15 ) MPa (m(^{-2} )s(^{-1} ))</th>
<th>( \omega ), rate of growth at ( P=0.2 ) MPa (m(^{-2} )s(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>983</td>
<td>0.392×10(^9)</td>
<td>3.448×10(^{10})</td>
<td>5.125×10(^{10})</td>
<td>6.064×10(^{10})</td>
</tr>
<tr>
<td>1003</td>
<td>1.623×10(^9)</td>
<td>4.336×10(^{10})</td>
<td>5.939×10(^{10})</td>
<td>7.114×10(^{10})</td>
</tr>
<tr>
<td>1023</td>
<td>6.357×10(^9)</td>
<td>8.895×10(^{10})</td>
<td>10.291×10(^{10})</td>
<td>12.42×10(^{10})</td>
</tr>
</tbody>
</table>

Therefore, the equation for the activation energy for the transition of Fe atoms through a \( \text{Nd}_2\text{Fe}_4\text{B} \) interface can be written in the following form: \( U(P)=Q_{m-p} Q \times P \), where \( P \) is the initial hydrogên pressure in MPa. Denoting \( M \frac{\Delta F - \Delta F_0}{RT} = A(P) \), the equation for the dependence of growth rate \( \omega \) on the initial hydrogen pressure \( P \) can be written in the following form:

\[
\omega = A(P)e^{-\frac{113.08+1078.77\times P}{RT}},
\]

where \( A(P) \) is the preexponential function depending on the hydrogen pressure \( P \), the values of which are presented in Table 3 for various hydrogen pressures.

The preexponential function \( A(P) \) at different initial hydrogen pressures \( P \) determined for degree of reverse hydrogen induced transformation \( \xi=0.9 \) in \( \text{R}_2\text{Fe}_{14}\text{B} \) alloy.

<table>
<thead>
<tr>
<th>( P ), initial hydrogen pressure (MPa)</th>
<th>( A(P) ), the preexponential function in Eq. (7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>94.73×10(^{-2})</td>
</tr>
<tr>
<td>0.15</td>
<td>97.41×10(^{-2})</td>
</tr>
<tr>
<td>0.20</td>
<td>98.76×10(^{-2})</td>
</tr>
</tbody>
</table>

As can be seen from Table 3, \( A(P) \) increases with an increase of the initial hydrogen pressure that is possible if the mobility of interface \( M \) increases. In our case hydrogen atoms can be considered as interstitial atoms and increase of their concentration leads to an increase of the diffusion rate.
of matrix atoms (Fe, Nd, B atoms in our case) as was shown in [25-26]. Moreover, the concentration of hydrogen atoms was larger in the case when reverse transformation started at higher hydrogen pressure; in this case the diffusion rate of matrix atoms increased that in turn leads to an increase of the interface mobility $M$. On the other hand, $U(P)$ decreases with the hydrogen pressure. Hence, the growth rate of new Nd$_2$Fe$_{14}$B phase depends on two main factors: increase of interface mobility $M$ with hydrogen pressure and decrease of activation energy for the transition of Fe atoms through Nd$_2$Fe$_{14}$B phase interface $U(P)$ with hydrogen pressure.

The influence of initial hydrogen pressure on the kinetics of hydrogen induced reverse phase transformations in the industrial R$_2$Fe$_{14}$B alloy has been studied. It has been established that increase of the temperature and initial hydrogen pressure results in a considerable acceleration of the rate of reverse phase transformation. It has been obtained that the kinetics of reverse phase transformation process is controlled by the diffusion of Fe atoms and the growth rate of Nd$_2$Fe$_{14}$B phase $\phi$ increases with an increase of the initial hydrogen pressure.

On the basis of Kolmogorov-Hillert-Smirnov kinetic models of phase transformation in condensed state the equation for a description of the effect of initial hydrogen pressure on the isothermal kinetic diagrams of such type of transformations has been obtained. It has been shown that effect of initial hydrogen pressure on the kinetics of hydrogen induced reverse transformations in R$_2$Fe$_{14}$B alloy can be described by the following equation:

$$t(\xi, T, P) = \frac{3h}{\pi \gamma R T} \times \frac{(-\ln(1-\xi))^\frac{1}{2}}{A(P)\gamma^4 RT} e^{-\frac{Q + \Delta G}{RT}},$$

(9)

where $t(\xi, T, P)$ is the transformation time for various degrees of transformation $\xi$ at different temperatures $T$ and initial hydrogen pressure $P$, $\Delta G$ is the energy necessary for the formation of a critical nucleus of Nd$_2$Fe$_{14}$B phase, $Q$ is the activation energy for the diffusion of Fe atoms to centers of Nd$_2$Fe$_{14}$B phase, $\gamma = 10^{-4}$ mol/m$^3$, $R$ is the gas constant, $h$ is the Planck constant, $T$ is temperature, $Q_{mp}$ is the activation energy for the diffusion of matrix atoms in the absence of interstitial atoms, $A(P)$ is the preexponential function that depends on the hydrogen pressure, $P$ is the initial hydrogen pressure.

To conclude with, from the practical point of view the increase of hydrogen during the direct transformation results in a decrease of the treatment time during the reverse transformation that is a very promising way to reduce the treatment time and cost for the production of Nd$_2$Fe$_{14}$B powders for permanent magnets of such type.

**4. Conclusions**

Finally, substituting Eq. (7) into Eq. (6), one can write the final equation describing the dependence of transformation time $t$ needed for reaching of a transformation degree $\xi$ on hydrogen pressures $P$ and transformation temperature $T$:

$$t(\xi, T, P) = \frac{3h}{\pi \gamma R T} \times \frac{(-\ln(1-\xi))^\frac{1}{2}}{A(P)\gamma^4 RT} e^{-\frac{Q + \Delta G}{RT}},$$

(8)

Fig. 4 shows the isothermal kinetic diagram for hydrogen induced reverse phase transformation in R$_2$Fe$_{14}$B alloy calculated on the basis of Eq. (8) and data from Table 3.

From this figure one can conclude that Eq. (8) well describes the experimental results on the influence of the initial hydrogen pressure value on the kinetics of reverse phase transformation in R2Fe14B alloy in terms of two main kinetic factors, i.e. increase of mobility of interfaces M with hydrogen pressure and decrease of activation energy for the transition of Fe atoms across Nd2Fe14B phase interface U(P) with the hydrogen pressure.

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