The kinetics of hydrogen-induced diffusive phase transformations in Sm$_2$Fe$_{17}$ alloys

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Abstract: The kinetics of hydrogen-induced direct and reverse phase transformations in Sm$_2$Fe$_{17}$ alloys have been investigated. It is shown that a decrease in temperature leads to a significant slowdown of the direct and reverse phase transformations' evolution. It has been specified that these phase transformations proceed by the mechanism of nucleation and growth. Isothermal kinetic diagrams of both direct and reverse phase transformations have been plotted and the activation energy values for these hydrogen-induced phase transformations have been defined. It is shown that phase transformation kinetics in the interval of the temperatures under study is controlled by a mutual diffusion of the alloy's components.

Keywords: kinetics; hydrogen; phase transformations.

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1 Introduction

The hydrogen treatment of materials is a new area of materials science based on specific features of hydrogen and hydrogen-induced phase transformations in materials (Goltsov, 2001).

The practical application of direct and reverse hydrogen-induced phase transformations (the so-called Hydrogenation-Decomposition-Desorption-Recombination (HDDR) process) in hard magnetic alloys of rare earth and transition metals such as Nd$_2$Fe$_{14}$B and Sm$_2$Fe$_{17}$ allows the improvement of their structure and magnetic properties (Ragg *et al.*, 1997; Okada *et al.*, 1995). A positive change of the magnetic properties of the abovementioned alloys leads to the miniaturisation of new technical devices based on Nd$_2$Fe$_{14}$B and Sm$_2$Fe$_{17}$ permanent magnets.

A characteristic feature of these alloys is that upon hydrogenation, they lose their thermodynamical stability and undergo a phase transformation at higher temperatures, namely, decomposition into a rare earth component hydride and an α-phase of Fe (for an Nd$_2$Fe$_{14}$B-type alloy there is an additional Fe$_2$B phase (Ragg *et al.*, 1997)).

Hydrogen evacuation causes a reverse phase transformation with the formation of the initial fine-grained structure.

At temperatures above 500°C, Sm$_2$Fe$_{17}$ alloys undergo a direct hydrogen-induced phase transformation described by the following scheme:

$$\text{Sm}_2\text{Fe}_{17} + \text{H}_2 \rightarrow \text{SmH}_2 + \alpha\text{-Fe}. \tag{1}$$

This transformation results in the formation of SmH_2 particles up to 50 nm in diameter distributed in the α-Fe matrix (Okada *et al.*, 1995).

A reverse phase transformation takes place in the course of hydrogen evacuation at higher temperatures and can be described by the following reaction:

$$SmH_2 + \alpha\text{-Fe} \rightarrow Sm_2Fe_{17} + 2H_2\uparrow \rightarrow Sm_2Fe_{17}. \tag{2}$$
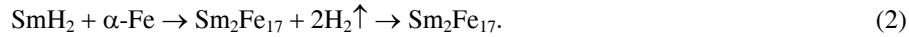
With recombination stage completed, the alloy mainly consists of a fine-grained ferromagnetic phase Sm_2Fe_{17} in a high coercive state.

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 this material.

For instance, the investigation of the kinetics of such a type of direct and reverse hydrogen-induced transformations previously carried out in $Nd_2Fe_{14}B$-type alloys (Goltsov, 2001; Goltsov *et al.*, 2000; Rybalka *et al.*, 2003; 2005) gives us a possibility to establish the basic features of these transformations: temperature intervals of the development of transformations in $Nd_2Fe_{14}B$-type alloys, to establish a diffusive-controlled character of the transformations, to plot for the first time the Temperature-Time-Transformation diagrams (T-T-T or isothermal kinetics diagrams) for the transformations and establish an influence of kinetics on the microstructure of the alloys (Rybalka *et al.*, 2005).

The purpose of this work is to investigate the kinetics of hydrogen-induced direct and reverse transformations in Sm_2Fe_{17} alloys within 550°C–750°C at a hydrogen pressure of 0.1 MPa and in vacuum (about ~1 Pa).

2   Materials and methods

The investigation of the kinetics of direct and reverse hydrogen-induced phase transformations has been carried out on special hydrogen-vacuum equipment using a specialised version of Sadikov's magnetometric method (Rybalka *et al.*, 2003; 2005; Goltsov *et al.*, 2000).

The basis of the method of registration of the evolution of phase transformations is the fact that in the experimental temperature interval (320°C–750°C), the initial Sm_2Fe_{17} alloy is paramagnetic ($T_c = 254$ °C), but the one phase of transformation products (α-phase of Fe) is ferromagnetic (see Equations 1 and 2). This fact gives us a possibility to register a phase transformation evolution by increasing or decreasing the quantity of the α-Fe ferromagnetic phase during a phase transformation.

The Sm_2Fe_{17} alloy was made in the laboratory of Tver State University and was then crushed into powder, the particles being 50–600 μm in diameter.

The Sm_2Fe_{17} powders (~1.25 g) were placed into the chamber that was evacuated up to 0.1 Pa. The alloy was then heated in a vacuum to temperatures within 320°C–750°C with a continuous evacuation. After establishing isothermal conditions, the chamber was filled with hydrogen up to 0.1 MPa. A phase transformation was continuously monitored by increasing or decreasing a ferromagnetic phase amount in the sample. According to these findings, isothermal diagrams have been plotted.

X-ray analysis was done in Fe-Kα radiation with the use of a DRON-3 diffractometer.

3 Results and discussions

3.1 Direct hydrogen-induced phase transformations in the Sm$_2$Fe$_{17}$ alloy

Thus, we will emphasise that heating the Sm$_2$Fe$_{17}$ alloy in hydrogen-filled atmosphere results in the development of direct phase transformations leading to the alloy's decomposition with a hydride SmH$_{2+x}$ phase and α-Fe phase being formed (see Equation 1).

The results of the research on the kinetics of hydrogen-induced direct phase transformations in the Sm$_2$Fe$_{17}$ alloy are generalised in Figure 1 in the form of kinetic curves. As seen from Figure 1, at 750°C, 690°C and 650°C, a hydrogen-induced direct phase transformation is completed in 120, 230 and 300 min, respectively. At lower temperatures, a direct phase transformation is not fully completed during the experimental time and only 87% of completeness is reached at 610°C and is gradually slowed down to 10% of completeness at 330°C. Thus, as temperature decreases from 750°C to 330°C, the direct phase transformation under study is greatly slowed down and at 320°C, a transformation does not develop during the experimental time. X-ray investigations done after the realisation of a direct transformation at 320°C confirmed by the magnetometric method results show that at this treatment temperature, a direct phase transformation does not develop during the experiment and the alloy phase composition does not change in comparison with the initial alloy. It should also be noted that as the treatment temperature decreases, an increase of the transformation incubation period takes place. For instance, at 750°C, 690°C and 650°C, this time is about 4–8 sec and with the decrease of temperature up to 400°C–330°C, this period increases to 10–30 min.

Figure 1 The kinetic curves of a direct hydrogen-induced phase transformation in the Sm$_2$Fe$_{17}$ alloy at temperatures from 750°C to 320°C and a hydrogen pressure of 0.1 MPa
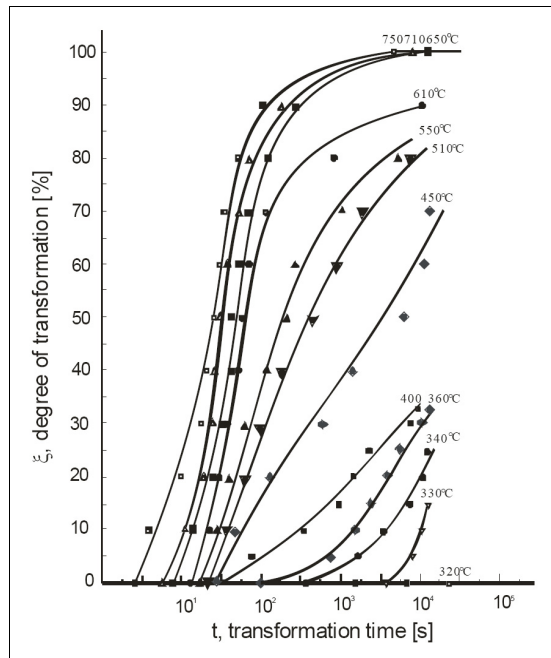
In Figure 2, the results of the X-ray analysis of the initial Sm_2Fe_{17} alloy are shown. As can be seen from Figure 2(a), in the initial state, the alloy consists of a basic phase Sm_2Fe_{17} with an insignificant amount of the Sm_2O_3 phase.

After a direct transformation is realised, a decomposed alloy consists of two phases: α-Fe and SmH_2 (Figure 2b).

Figure 2   The X-ray results of the analysis after the realisation of a direct hydrogen-induced phase transformation
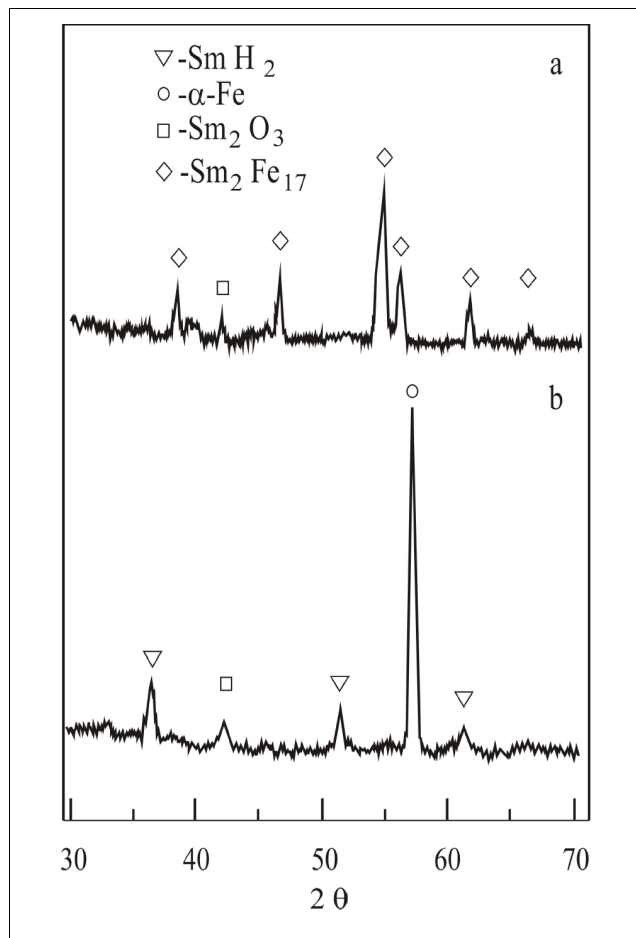

Notes: a – the initial alloy Sm_2Fe_{17}.
          b – after the realisation of a direct hydrogen-induced phase transformation.

For a practical application, it is convenient in many cases to use isothermal kinetic diagrams in which initial kinetic data are given in coordinates 'Temperature-Time -Transformation' (the so-called T-T-T diagrams) (Christian, 2002). Such a diagram for a direct hydrogen-induced phase transformation in the Sm_2Fe_{17} alloy is shown in Figure 3. As can be seen from this diagram, with a decrease of the temperature of the isothermal exposure in hydrogen, a direct phase transformation slows down for all degrees of transformation.

Figure 3   An isothermal kinetic diagram for a direct hydrogen-induced phase in the Sm_2Fe_{17} alloy at a hydrogen pressure of 0.1 MPa
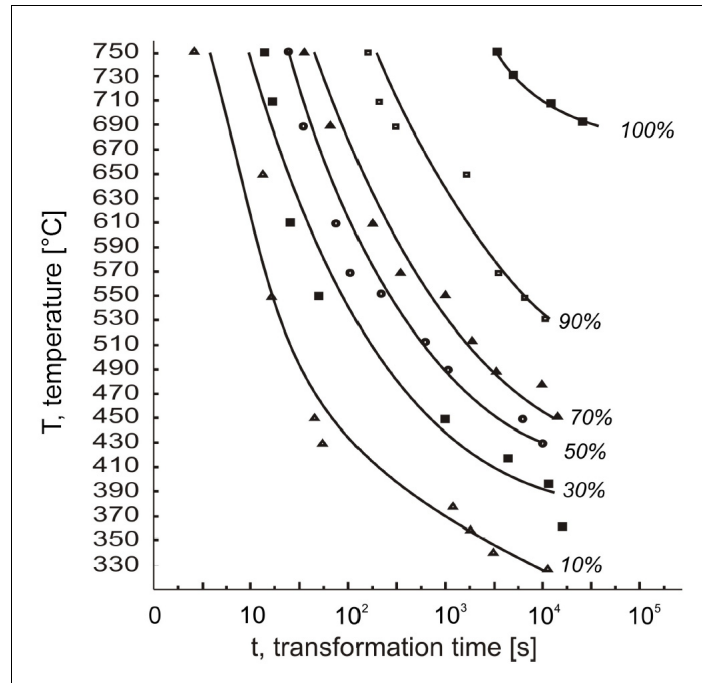
3.2   Reverse hydrogen-induced phase transformations in the Sm₂Fe₁₇ alloy

Thus, at hydrogen evacuation in a vacuum, the Sm_2Fe_{17} alloy undergoes a reverse phase transformation leading to the recombination of the decomposed phases SmH_{2+x} and α-Fe phase into an initial Sm_2Fe_{17} phase.

The results of studying a reverse hydrogen-induced phase transformation in an Sm_2Fe_{17} alloy are generalised in Figure 4. At 750°C, 730°C, 710°C and 650°C, a phase transformation is fully completed in 25, 95, 105 and 115 min, respectively. At a decrease of the temperature, the reverse phase transformation is not fully completed during the experiment. Thus, at 610°C, a transformation reaches 50% of completeness, at 590°C, 36%, at 570°C, 10% and at 550°C, only 5% of completeness. At 530°C, a phase transformation does not develop at all during the experiment. Thus, the temperature decrease from 750°C to 550°C leads to great slow down of the transformation evolution and at 530°C, the transformation does not develop during the experiment.

It is necessary to note that, as well as in the case of a direct transformation, an increase of the incubation period of the transformation takes place for reverse phase transformations too, with a decrease of the treatment temperature as seen in Figure 4.

X-ray analysis performed after the realisation of a reverse transformation has confirmed that if reverse phase transformations are fully completed, decomposed phases recombine in the initial Sm_2Fe_{17} phase with an insignificant amount of Sm_2O_3 oxide, as can be seen in Figure 5. It should be noted that the realisation of a reverse transformation leads to a decrease of the amount of the Sm_2O_3 oxide phase and that is a positive factor for manufacturing Sm_2Fe_{17} permanent magnets.

Figure 4   The kinetic curves of a reverse hydrogen-induced phase transformation in the Sm_2Fe_{17}
alloy at 750°C–530°C
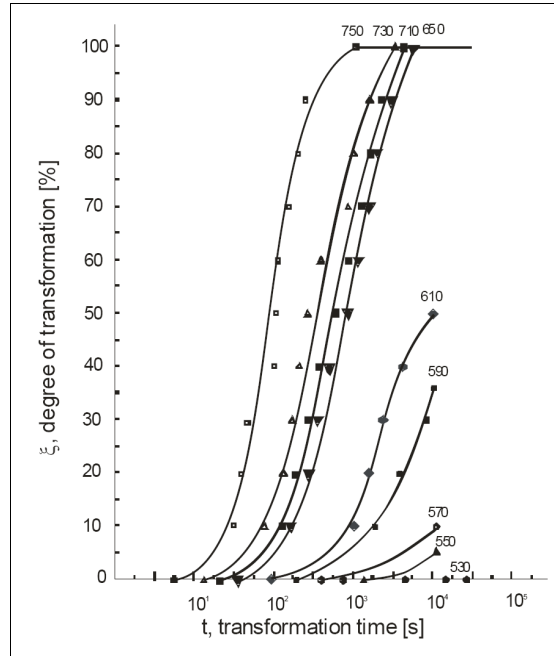
Figure 5   The X-ray results of the analysis after the realisation of a direct and reverse
hydrogen-induced phase transformation
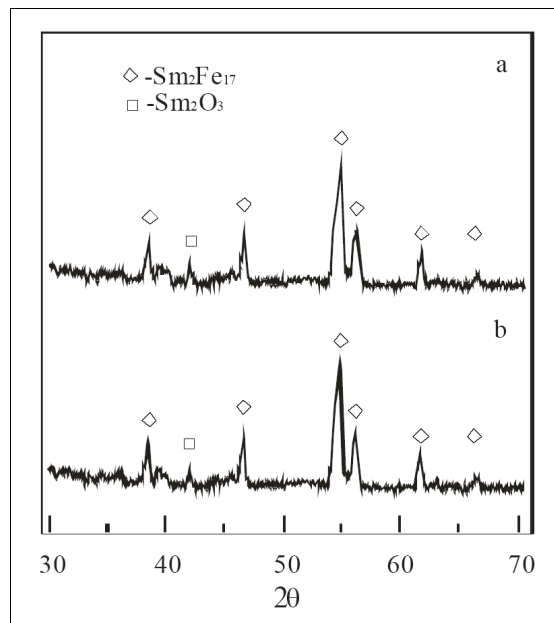
Notes: a – an initial alloy of Sm_2Fe_{17}.

b – after the realisation of direct and reverse phase transformations.

An isothermal kinetic diagram for a reverse hydrogen-induced phase transformation in the Sm_2Fe_{17} alloy is shown in Figure 6. As can be seen, as the temperature of isothermal exposure decreases, a reverse phase transformation slows down for all degrees of transformation.

Figure 6   An isothermal kinetic diagram for a reverse hydrogen-induced phase transformation in the Sm_2Fe_{17} alloy at an initial hydrogen pressure of 0.1 MPa and vacuum ~1 Pa
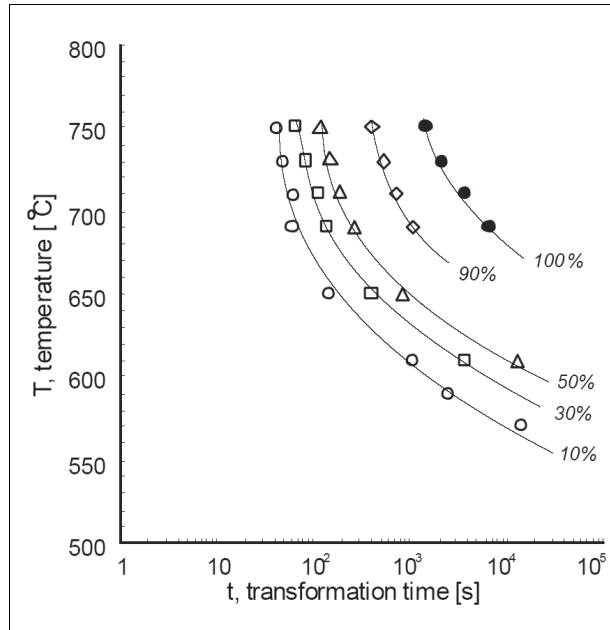
3.3   Discussions of hydrogen-induced phase transformations' kinetics in the Sm_2Fe_{17} alloy

Hydrogen-induced phase transformations in metals and alloys can be conditionally divided into the following main classes according to the classification first proposed in Goltsov (2001):

- Hydride (diffusive-cooperative) phase transformations – The phase transformations of this class usually take place in materials at low temperatures: $T < (0.20–0.45)T_m$ (T_m – melting temperature) (Goltsov, 2001).

- Hydrogen-induced intermediate phase and structural transformations – The transformations of this class proceed in materials at moderate temperatures ($T \approx (0.2–0.45)\ T_m$) (Goltsov, 2001).

- High-temperature hydrogen-induced phase transformations (Goltsov, 2001; Rybalka *et al*., 2003) – These take place at increased temperatures: $T > 0.45T_m$. Transformations of the given type are (as a rule) diffusive-controllable transformations and the speed of their development is essentially slowed down by temperature reduction because of the diffusion speed delay of alloy component atoms.

Let us estimate a temperature interval when direct and reverse hydrogen-induced phase transformations in the Sm_2Fe_{17} alloy are realised. As can be seen in Figures 1 and 3, transformations are fully completed at 650°C–750°C. The melting temperature for the Sm_2Fe_{17} alloy is 1450°C. Thus, in our case, the temperature interval is $(0.44–0.51)T_m$. This interval corresponds to a case of the abovementioned high-temperature hydrogen-induced phase transformations.

Then, as mentioned above, hydrogen-induced phase transformations proceed in accordance with Equations (1) and (2) and in this case, for transformations to evolve, atoms of the alloy components (Sm, Fe) are to transport needs to new centres of the growing phases.

There are two types of diffusion phase transformations: spinodal decay and transformations by the mechanism of nucleation and growth. Transformations by the mechanism of spinodal decay develop by the diffusion of alloy components at very small distances and, therefore, they can proceed at rather low temperatures when an alloy is within an absolute thermodynamic instability. Spinodal decay develops at relatively large rates. Phase transformations by the mechanism of nucleation and growth require the diffusion of component atoms at large distances (in comparison with the atomic ones); they proceed at relatively high temperatures and their completion takes longer time.

As can be seen in Figures 1 and 4, the shape of the kinetic curves with a gradual slowdown of the transformation rate and dependence of the incubation period on the temperature let us suggest (Christian, 2002) that phase transformations develop by the mechanism of nucleation and growth.

It is necessary to note that the results obtained in this work are similar to the data in Goltsov (2001) and Rybalka *et al.* (2003), where the kinetics of hydrogen-induced phase transformations in $Nd_2Fe_{14}B$ alloys was studied; direct and reverse phase transformations in these alloys greatly slow down as the temperature decreases within 750°C–610°C, too.

For a further analysis, the Mehl-Johnson-Avrami phenomenological theory of phase transformations was used (Christian, 2002). According to this theory, a degree of transformation ξ can be described by the following expression:

$$\xi = 1 - \exp(-kt^n), \tag{3}$$

where t is a transformation time and k and n are constants.

It is known that if the experimental results reconstruct in coordinates $\ln[-\ln(1 - \xi)]$ versus $\ln t_\xi$, it is possible to establish a kinetic constant n that gives us some important information about the most probable mechanisms of transformations (Christian, 2002).

In Figure 7, such dependencies for hydrogen-induced phase direct phase transformations in the Sm_2Fe_{17} alloy are plotted. It is shown that at every temperature, there are two linear parts and n values varying from 0.39 up to 2.4 (see Table 1). According to Kahn's theory (Christian, 2002), this is provoked by the exhaustion of nucleation sites. Before exhaustion, at initial stage the transformation evolution rate is proportional to the nucleation rate and growth of new phases and then it is proportional to the growth rate of new phases only (Christian, 2002).

Then, it is possible to calculate transformation activation energy (Christian, 2002) by plotting the dependence of $\ln t_\xi$ (where t_ξ is time t that needs some degree of transformation completion ξ (in our case ξ corresponds to 50%, 70% and 90% transformation degree)) versus $1/T$, as presented in Figure 8. The values of an activation

energy determined for some transformation degrees vary from 120 kJ/mol up to 160 kJ/mol. Thus, the values of the obtained activation energy correspond to the values of the activation energy of iron atom diffusion in R–T alloys (where R is a rare earth metal and T is a transition metal) (~250 kJ/mol) (Coey, 1996).

Figure 7   The dependence of $\ln[-\ln(1-\xi)]$ on $\ln t_\xi$ for hydrogen-induced phase direct phase transformations in the Sm_2Fe_{17} alloy
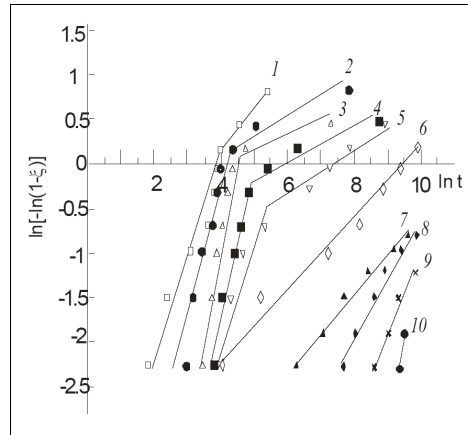

Note: Dependence at the following temperatures of transformation: 1 – 750, 2 – 650,
3 – 610, 4 – 570, 5 – 510, 6 –450, 7 – 400, 8 – 360, 9 – 340, 10 – 330°C, respectively.

Table 1   The values of n in Equation (3) at various temperatures for hydrogen-induced direct phase transformations in the Sm_2Fe_{17} alloy

T, °C	750	650	610	570	510	450	400	360	340	330
n_1	1,06	1,23	2,02	2,00	2,4	0,77	0,69	0,74	0,89	0,95
n_2	0,39	0,11	0,29	0,11	0,34					

Notes: n_1 – the value for 10%–60% of transformation.

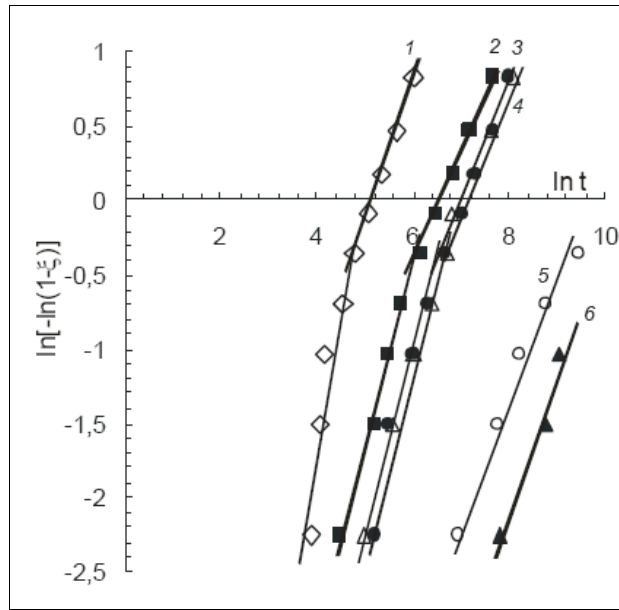n_2 – the value for 60%–90% of transformation.

Figure 8   The dependence of $\ln t_\xi$ on $1/T$ for direct phase transformations in the Sm_2Fe_{17} alloy for 50%, 70% and 90% of the transformation
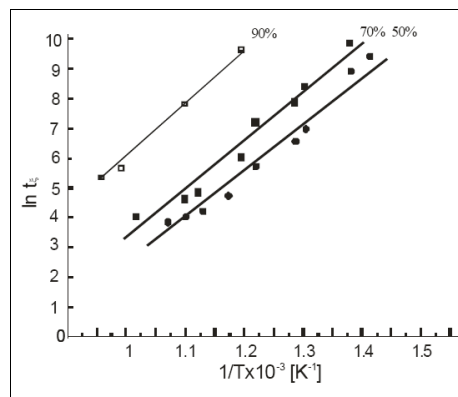
Let us carry out a similar analysis for hydrogen-induced reverse phase transformations in the Sm_2Fe_{17} alloy.

Figure 9 shows a dependence of $\ln[-\ln(1 - \xi)]$ on $\ln t_\xi$ for hydrogen-induced reverse phase transformations in the Sm_2Fe_{17} alloy. It is evident that at all temperatures, there are two linear parts and n values varying from 0.78 up to 1.89 (as can be seen in Table 2).

Figure 9   The dependence of $\ln[-\ln(1 - \xi)]$ on $\ln t_\xi$ for hydrogen-induced reverse phase transformations in the Sm_2Fe_{17} alloy

Note: Dependence at the following temperatures of transformation: 1 – 750°C, 2 – 730°C, 3 – 710°C, 4 – 650°C, 5 – 610°C, 6 – 590°C, respectively.

Table 2   The values of n in Equation (3) at various temperatures for hydrogen-induced reverse phase transformations in the Sm_2Fe_{17} alloy

| T, °C	750	730	710	650	610	590
n_1 (10%–50%)	1,89	1,16	1,21	1,06	0,76	0,93
n_2 (50%–90%)	0,93	0,78	0,88	0,81		

Notes: n_1 – value for 10%–60% of transformation.
         n_2 – value for 60%–90% of transformation.

The activation energy of hydrogen-induced reverse phase transformations has been obtained by plotting the dependence of $\ln t_\xi$ versus $1/T$, as presented in Figure 10. The values of activation energy determined for some degrees of transformation vary from 118 kJ/mol up to 199 kJ/mol. Thus, the values of the obtained activation energy correspond to the values of activation energy of iron atom diffusion in the α-Fe matrix (Hertsriken and Dekhtyar, 1960).

One can believe that the investigated hydrogen-induced phase transformations in an Sm_2Fe_{17} alloy are controlled by a mutual diffusion of the alloy's components.

Figure 10 The dependence of lnt_ξ on 1/T for reverse phase transformations in the Sm$_2$Fe$_{17}$ alloy for 50%, 70% and 90% of the transformation
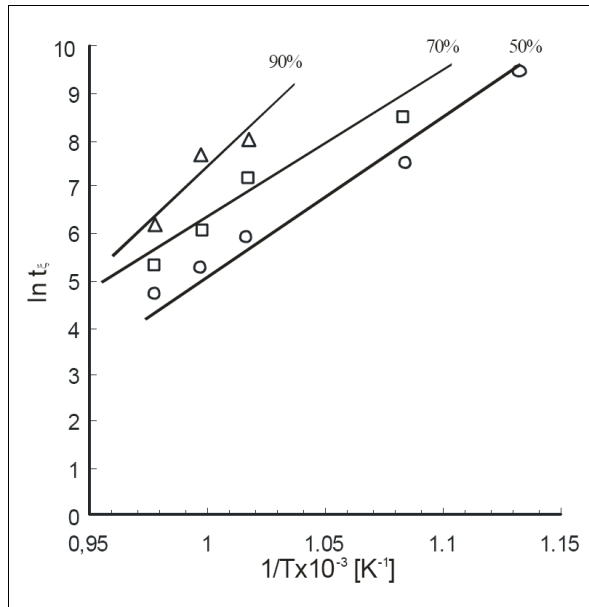
4   Conclusions

- It has been experimentally established that with an increase in the temperature, the development of direct and reverse hydrogen-induced phase transformations in the Sm$_2$Fe$_{17}$ alloy greatly slows down. At temperatures below the critical ones (320°C for direct and 530°C for reverse transformations), phase transformations do not develop during the experiment.

- On the basis of the analysis carried out in terms of the kinetic theory of phase transformations, it has been established that hydrogen-induced phase transformations in the Sm$_2$Fe$_{17}$ alloy develop by the mechanism of nucleation and growth.

- It has been shown that phase transformation kinetics in the investigated interval of temperatures is controlled by a mutual diffusion of the alloy's components.

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