

## HYDROGEN-INDUCED DIFFUSION PHASE TRANSFORMATIONS IN $\text{Nd}_2\text{Fe}_{14}\text{B}$ AND $\text{Sm}_2\text{Fe}_{17}$ MAGNETICALLY HARD ALLOYS

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The  $\text{Nd}_2\text{Fe}_{14}\text{B}$  and  $\text{Sm}_2\text{Fe}_{17}$  magnetically hard alloys become thermodynamically unstable under the action of hydrogen and suffer hydrogen-induced direct and inverse phase transformations at elevated temperatures. The kinetics of these transformations is investigated. It is shown that they are diffusion-controlled and develop according to the mechanism of nucleation and growth.

The hydrogen treatment of materials is a new branch of materials science [1] based on the specific features of hydrogen and hydrogen-induced phase transformations.

In  $\text{Nd}_2\text{Fe}_{14}\text{B}$ - and  $\text{Sm}_2\text{Fe}_{17}$ -type magnetic materials, the hydrogen-induced diffusion phase transformations occur due to the different affinities of the atoms of different components of materials to hydrogen. Since the alloys consist of strong hydride- and nonhydride-forming elements, they lose their thermodynamic stability as a result of saturation with hydrogen. At low temperatures, these materials exist in the nonequilibrium (metastable) state. At elevated temperatures ( $T > (0.20-0.45)T_m$ , where  $T_m$  is the melting point), the diffusion of large atoms of the material becomes possible, and we observe the realization of hydrogen-induced diffusion phase transformations. The alloys decompose into rare-earth hydrides ( $\text{NdH}_x$  or  $\text{SmH}_x$ ) and the  $\alpha$ -phase of iron. In the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy, we also observe the formation of iron boride ( $\text{Fe}_2\text{B}$ ). The evacuation of hydrogen from the alloy after the direct transformation requires the thermodynamically inverse phase transformation resulting in the formation of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  or  $\text{Sm}_2\text{Fe}_{17}$  initial phase. As a result of the direct and inverse phase transformations, the microstructure is refined, which improves the magnetic properties of permanent magnets prepared from the alloys treated as indicated above [2].

In what follows, we generalize the results of investigations of the kinetics of hydrogen-induced direct and inverse diffusion phase transformations in the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  or  $\text{Sm}_2\text{Fe}_{17}$  alloys and discuss the nature of these transformations within the framework of solid-state physics.

### Direct and Inverse Diffusion Phase Transformations in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ Magnetically Hard Alloy

In the chemistry of solids, the decomposition of this type of alloys is regarded as the following solid-state chemical reaction [2]:



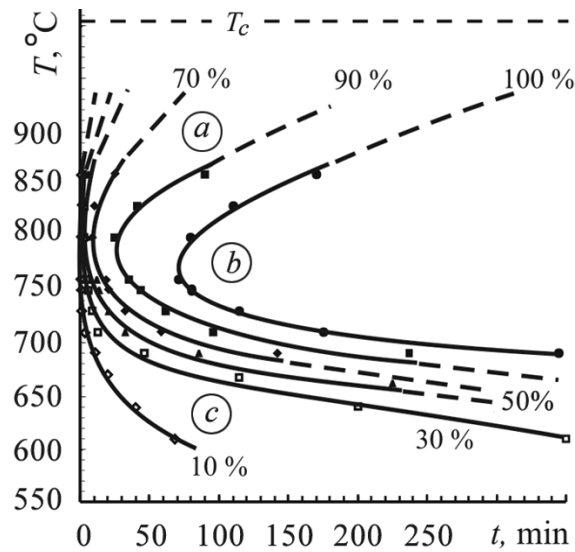
where  $\Delta H$  is the enthalpy of the reaction.

From the viewpoint of solid-state physics, the decomposition of alloys according to schemes (1) is a new type of phase transformations including hydrogen-induced diffusion phase transformations [1].

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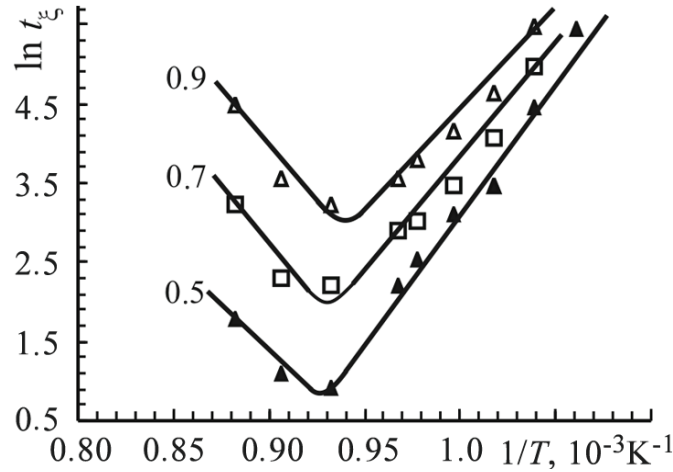


**Fig. 1.** Isothermal kinetic diagrams of direct hydrogen-induced phase transformations in  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy under a hydrogen pressure of 0.1 MPa within the following temperature ranges of transformation: (a) 800–900°C, (b) 700–800°C, (c) 600–700°C.

At temperatures higher than 600°C, Nd–Fe–B alloys readily absorb hydrogen and the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase undergoes a diffusion phase transformation according to scheme (1). If hydrogen is evacuated from the alloy after the direct transformation as a result of holding in a vacuum at elevated temperatures, then the decomposed alloy undergoes the inverse diffusion phase transformation, and the initial  $\text{Nd}_2\text{Fe}_{14}\text{B}$  matrix phase is restored but its structure becomes very fine [1].

The kinetics of hydrogen-induced direct and inverse phase transformations in the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy was systematically studied on the equipment designed and constructed at the Donetsk National Technical University on the basis of the Sadikov magnetometric method [3]. To record new phases formed in the course of transformations, this method uses the fact that, in the investigated temperature range (310–760°C), the initial  $\text{Nd}_2\text{Fe}_{14}\text{B}$  and  $\text{Sm}_2\text{Fe}_{17}$  alloys are paramagnetic, whereas the product of transformations, i.e., the  $\alpha$ -phase of iron, is ferromagnetic. Thus, the development of phase transformations was recorded by the increase or decrease in the amount of the ferromagnetic phase. The accumulated experimental data are used for the construction of kinetic curves and isothermal kinetic diagrams of hydrogen-induced phase transformations. The kinetics of direct hydrogen-induced transformations in this type of alloys within the temperature range 610–760°C under a hydrogen pressure of 0.15 MPa was studied in [4, 5]. Specifically, the isothermal kinetic diagram of hydrogen-induced direct phase transformations was constructed for the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy for the first time (Fig. 1). The  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy is stable for  $T > 1000^\circ\text{C}$  under a pressure  $P_{\text{H}_2} = 0.1$  MPa [6], and, hence, the critical temperature of direct phase transformation  $T_c$  is also recorded in the diagram.

The activation energy of the process was found from the dependence of  $\ln t_\xi$  on  $1/T$ , where  $t$  is the time of transformation,  $\xi$  is the degree of transformation, and  $T$  is the period of holding [7] (Fig. 2). The indicated dependence is plotted according to the data presented in Fig. 1 and has two linear segments. The range of activation energies 214–265 kJ/mole corresponds to the low-temperature interval (zone c in Fig. 1) in good agreement with the activation energy of the process of self-diffusion of iron atoms in the  $\alpha$ -phase ( $Q_{\alpha\text{-Fe}} = 251$  kJ/mole) [8, 9]. In the high-temperature interval (800–900°C) (zone a), the activation energy varies from –146 to –215 kJ/mole in good agreement with the heat of formation of the  $\text{NdH}_2$  rare-earth hydride ( $H_{\text{NdH}_2} = -187.7$  kJ/mole) [10].



**Fig. 2.** Dependences of  $\ln t_\xi$  on  $1/T$  for hydrogen-induced direct phase transformations in the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy for different degrees of transformation. Here, 0.5, 0.7, and 0.9 are degrees of transformation (corresponding to 50%, 70%, and 90%, respectively).

Hence, in the low-temperature interval (600–700°C), the phase transformation is controlled by the diffusion of iron atoms and, in the high-temperature interval (800–900°C), it is controlled by the formation of the  $\text{NdH}_2$  hydride phase. The range 700–800°C (zone *b*) is characterized by the optimal combination of the growth rates of the  $\alpha$ -phase of iron and  $\text{NdH}_2$  and, hence, the rate of phase transformations is maximum. As temperature decreases, the process of transformation decelerates and does not develop for the kinetic causes. At temperatures above 800°C (zone *a*), the development of transformation is retarded because the  $\text{NdH}_2$  hydride becomes less thermodynamically stable at temperatures close to 900–1000°C. This is why the kinetic diagrams of direct phase transformations in  $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type alloys are similar.

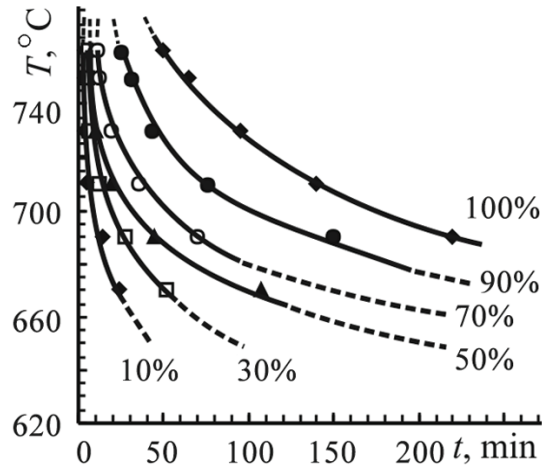
In the subsequent analyses [4, 5], we used the Johnson–Mehl–Avrami phenomenological kinetic theory according to which the degree of transformation  $\xi$  is described by the formula

$$\xi = 1 - \exp(-kt^n), \quad (2)$$

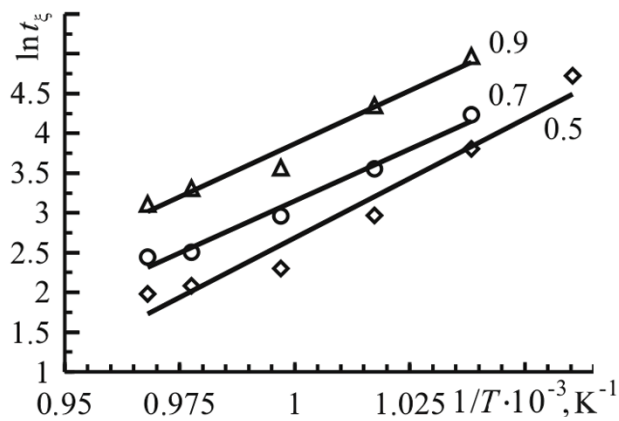
where  $t$  is the time of transformation, and  $k$  and  $n$  are kinetic constants.

For the direct transformations of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy, the value of  $n$  varies within the range 0.8–1. According to the above-mentioned theory, this corresponds to diffusion-controlled transformations running according to the mechanism of nucleation and growth [7].

The experimental investigations of the kinetics of hydrogen-induced inverse phase transformations in  $\text{Nd}_2\text{Fe}_{14}\text{B}$ -type alloys are described in [4, 5]. In approaching the thermodynamic equilibrium, the multiphase alloy obtained as a result of the direct phase transformation ( $\text{NdH}_2$ ,  $\alpha$ -Fe, and  $\text{Fe}_2\text{B}$ ) suffers the inverse phase transformation in the process of hydrogen release from the metal, and the  $\text{NdH}_2$ ,  $\alpha$ -Fe, and  $\text{Fe}_2\text{B}$  phases recombine into the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase. As a result of both transformations, the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase with fine grains (0.3  $\mu\text{m}$  [5]) is formed in the alloy. In its nature, the inverse transformation is also diffusive, and its rate is limited by the diffusion of atoms of the components of alloy (Nd, Fe, and B). The kinetics of the inverse phase transformations is well described by the Johnson–Mehl–Avrami phenomenological theory. In this case,  $n = 1.18$ –1.4, which corresponds to the diffusion-controlled transformations according to the mechanism of nucleation and growth [7].



**Fig. 3.** Isothermal kinetic diagrams of the inverse phase transformation in a vacuum of  $\sim 1$  Pa for  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy after the direct transformation carried out under an initial hydrogen pressure of 0.1 MPa: the numbers near the curves mark the degrees of transformation.

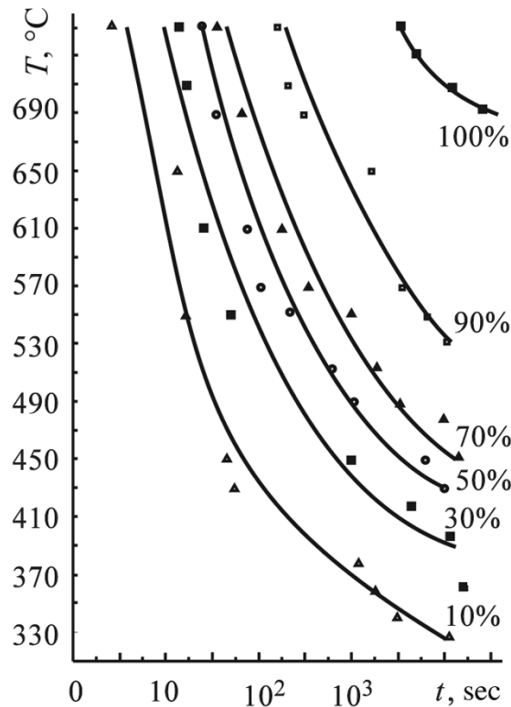


**Fig. 4.** Dependences of  $\ln t_\xi$  on  $1/T$  for the inverse phase transformations in  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy with different degrees of transformation. Here, 0.5, 0.7, and 0.9 are the degrees of transformation (corresponding to 50%, 70%, and 90%, respectively).

The kinetics of inverse transformations (Fig. 3) differs from the kinetics of direct transformations by the character of isothermal kinetic diagrams [5]. As the temperature of transformation increases, the development of the inverse phase transformation becomes more rapid (Fig. 3). The dependences of  $\ln t_\xi$  on  $1/T$  are plotted in Fig. 4. The activation energy of the process varies within the range 221–248 kJ/mole in good agreement with the activation energy of diffusion of iron atoms in the  $\alpha$ -phase of iron ( $Q_{\alpha\text{-Fe}} = 259.54$  kJ/mole) [8]. The experimental data on the structure of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy formed as a result of the direct and inverse transformations are presented in [10].

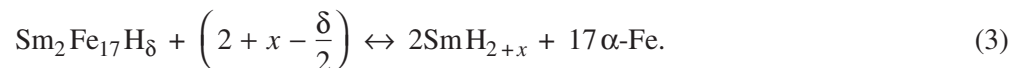
### Hydrogen-Induced Diffusion Phase Transformations in the $\text{Sm}_2\text{Fe}_{17}$ Alloy

The process of heating of the alloy in hydrogen leads to the formation of an  $\text{Sm}_2\text{Fe}_{17}\text{H}_\delta$  ( $\delta_{\text{max}} = 5$ ) interstitial solid solution in the initial stage [11, 12].



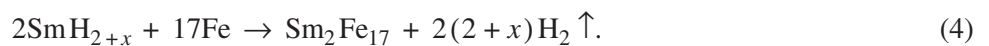
**Fig. 5.** Isothermal kinetic diagrams of the direct phase transformations in the  $\text{Sm}_2\text{Fe}_{17}$  alloy under a hydrogen pressure of 0.1 MPa: the numbers near the curves correspond to the degrees of transformation.

At temperatures higher than  $500^\circ\text{C}$ , this solution undergoes the following direct phase transformation [13]:



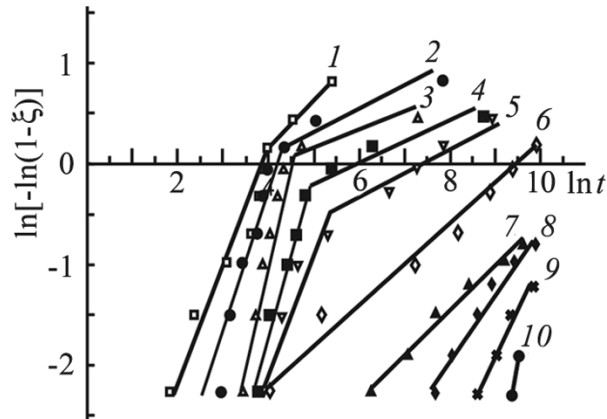
After this transformation, we observe the formation of particles of samarium hydride ( $\text{SmH}_{2+x}$ ) with diameters of several nanometers distributed in the matrix of  $\alpha$ -iron [13].

In the process of evacuation of hydrogen in a vacuum at elevated temperatures, the alloy suffers the inverse phase transformation promoting the recombination of phases of the products of decomposition into the initial phase ( $\text{Sm}_2\text{Fe}_{17}$ ):

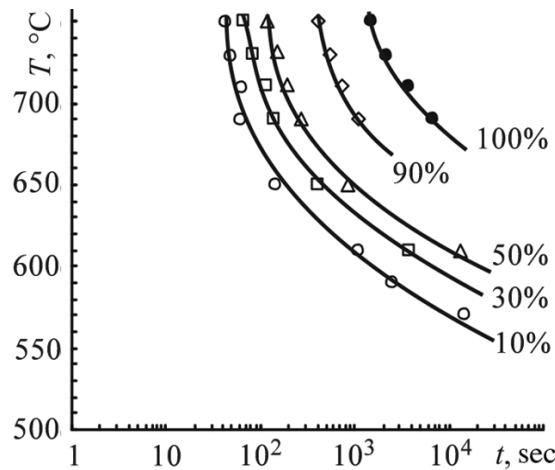


The reformed microstructure appearing in the alloys as a result of the direct and inverse transformations improves the magnetic properties of permanent magnets made from these alloys.

The kinetics of the direct and inverse transformations in the alloy is studied by using the same procedure as for the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy [3]. The isothermal kinetic diagrams of hydrogen-induced direct phase transformations in the  $\text{Sm}_2\text{Fe}_{17}$  alloy are plotted according to the experimental data (Fig. 5). It is easy to see that, as the temperature of isothermal holding in hydrogen increases, the direct phase transformation becomes much faster in good agreement with the data obtained for the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy. It should be especially emphasized that the direct phase transformations in the  $\text{Sm}_2\text{Fe}_{17}$  alloy also develop at relatively low temperatures ( $310^\circ\text{C}$ ) (Fig. 5) as compared with the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  alloy in which these transformations run only at temperatures higher than  $600^\circ\text{C}$ .



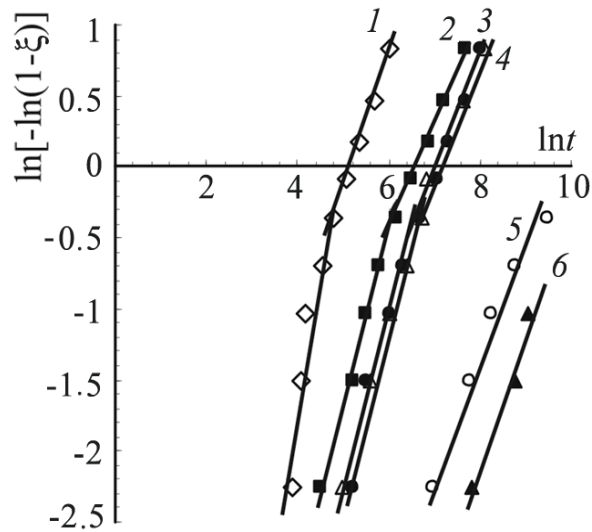
**Fig. 6.** Dependences of  $\ln[-\ln(1-\xi)]$  on  $\ln t$  for the hydrogen-induced direct phase transformations in the  $\text{Sm}_2\text{Fe}_{17}$  alloy at temperatures of ( $^{\circ}\text{C}$ ): (1) 750, (2) 650, (3) 610, (4) 570, (5) 510, (6) 450, (7) 400, (8) 360, (9) 340, (10) 330.



**Fig. 7.** Isothermal kinetic diagrams of the inverse phase transformations in the  $\text{Sm}_2\text{Fe}_{17}$  alloy in a vacuum of  $\sim 1$  Pa after the direct transformation carried out for an initial hydrogen pressure of 0.1 MPa; the numbers near the curves mark the degrees of transformation.

Then the diffusion phase transformations run in the  $\text{Sm}_2\text{Fe}_{17}$  alloy according to schemes (3) and (4) and require the diffusion transport of the atoms of its components (Sm and Fe). These transformations can be of two types, namely, spinodal decompositions and transformations by the mechanism of nucleation and growth. The spinodal decomposition requires the diffusion transport of atoms of the components for distances comparable with interatomic distances and, hence, the phase transformations may proceed at relatively low temperatures and high rates. Since the phase transformations of nucleation and growth occur as a result of diffusion for large (as compared with interatomic) distances, they usually develop at relatively high temperatures and for longer periods of time. These transformations are also characterized by the presence of an incubation period preceding the onset of their development. Thus, it is possible to assume that the phase transitions in the analyzed alloy develop according to the mechanism of nucleation and growth.

For the subsequent analysis of the mechanism of transformations, we use the Johnson–Mehl–Avrami theory [7]. The processed experimental data (for the degrees of transformation from 10 to 90%) (Fig. 6) are well approximated by straight lines.



**Fig. 8.** Dependences of  $\ln[-\ln(1-\xi)]$  on  $\ln t$  for hydrogen-induced inverse phase transformations in the  $\text{Sm}_2\text{Fe}_{17}$  alloy at temperatures of ( $^{\circ}\text{C}$ ): (1) 750, (2) 730, (3) 710, (4) 650, (5) 610, (6) 590.

The kinetic constant  $n_1$  (the slope of the dependence for the degrees of transformation varying from 10 to 60%) take values within the range 0.69–2.4, whereas the constant  $n_2$  (the slope of the dependence for the degrees of transformation varying from 60 to 90%) takes values within the range 0.11–0.39. According to the Christian classification [7], the obtained values of  $n$  are typical of the transformations with diffusion-controlled rate of growth of the centers of new phase. This confirms the assumption that the investigated transformations are transformations of nucleation and growth. At temperatures of 750–510 $^{\circ}\text{C}$  (Fig. 6), the plots have kinks corresponding to the transition to new values of  $n$ . According to the Cahn theory, this is connected with the formation of the centers of nucleation [8]. Prior to the termination of nucleation (in our case, up to 60% transformation), the kinetic coefficient  $k$  in Eq. (2) is proportional to the rates of nucleation and growth. After termination, the indicated coefficient depends only on the growth rate.

The values of the effective activation energy computed for different degrees of transformation vary within the range 120–160 kJ/mole in qualitative agreement with the values of the activation energy of diffusion of iron atoms in the matrix of  $\alpha$ -iron (196–306 kJ/mole) [9]. Thus, in the investigated temperature range, the direct phase transformation is evidently controlled by the diffusion of iron atoms.

The inverse phase transformations are analyzed similarly. The results of this investigation are generalized in Fig. 7. It is easy to see that, as the temperature of isothermal holding in hydrogen increases, the inverse transformation accelerates in agreement with the data presented in [4, 5].

The dependences of  $[-\ln(1-\xi)]$  on  $\ln t$  for the hydrogen-induced inverse phase transformations are plotted in (Fig. 8). Note that, in this case,  $n_1 = 0.76$ –1.89 and  $n_2 = 0.78$ –0.93, which is typical of the transformations with diffusion-controlled rate of growth of the centers of new phase. In this case, the nucleation centers are not formed for large degrees of transformation.

The computed values of the activation energy are equal to 118–199 kJ/mole, which also qualitatively agrees with the values of the activation energy of diffusion of iron atoms in the matrix of  $\alpha$ -iron (196–306 kJ/mole) [9]. Thus, the inverse phase transformation is, most likely, also controlled by the diffusion of iron atoms. Hence, the hydrogen-induced phase transformations in the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  and  $\text{Sm}_2\text{Fe}_{17}$  alloys are diffusion-controlled and develop according to the mechanism of nucleation and growth.

## CONCLUSIONS

Under the influence of hydrogen,  $\text{Nd}_2\text{Fe}_{14}\text{B}$ - and  $\text{Sm}_2\text{Fe}_{17}$ -type magnetically hard alloys become thermodynamically unstable and undergo direct and inverse phase transformations at elevated temperatures. The kinetics of these transformations is investigated, and it is shown that they are diffusion-controlled and develop according to the mechanism of nucleation and growth.

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