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АНАЛИЗ КИНЕТИКИ ПРЯМЫХ ФАЗОВЫХ ПРЕВРАЩЕНИЙ, ИНДУЦИРОВАННЫХ ВОДОРОДОМ, В СПЛАВАХ Y_2Fe_{17} В РАМКАХ МОДЕЛИ КОЛМОГОРОВА

Кинетика индуцированного водородом прямого фазового превращения в магнитотвердом сплаве Y_2Fe_{17} проанализирована в рамках кинетической модели Колмогорова. Установлено, что индуцированное водородом прямое фазовое превращение в магнитотвердом сплаве Y_2Fe_{17} классифицируется как диффузионно-контролируемое превращение, реализующееся по механизму зарождения и роста с убывающей скоростью зарождения центров новых фаз − α-Fe и YH_2. На основе кинетической теории фазовых превращений Колмогорова получено кинетическое уравнение, хорошо описывающее изотермические кинетические кривые фазового превращения в сплаве Y_2Fe_{17} в зависимости от температуры превращения.

Ключевые слова: кинетика, фазовые переходы, магнитные сплавы.

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ANALYSIS OF HYDROGEN-INDUCED DIRECT PHASE TRANSFORMATION KINETICS IN Y_2FE_{17} ALLOY ON THE BASE OF KOLMOGOROV'S MODEL

Kinetics of the hydrogen induced direct phase transformation in Y_2Fe_{17} hard magnetic alloy has been analyzed in framework of Kolmogorov's kinetic model. It is established that hydrogen induced direct phase transformation in Y_2Fe_{17} hard magnetic alloy classified as diffusion controlled transformation which occurs by mechanism of nucleation and growth with decreasing nucleation rate of new phases − α-Fe and YH_2. On the base of Kolmogorov's kinetic theory of the phase transformations has been obtained kinetic equation that well described the isothermal kinetic curves of phase transformation in Y_2Fe_{17} alloy depending on transformation temperature.

Keywords: kinetics, phase transitions, magnetic alloys.

R_2M_{17} compounds (R–Sm, Y, M–Fe, Co) demonstrate very interesting magnetic phenomenon during their interaction with interstitial atoms (H, N, C, B) [1–3]. 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 [4]. 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 [4]. 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.

In particular, at HDDR-treatment the Y_2Fe_{17} alloy undergoes the direct hydrogen-induced phase transformation at temperatures above 500 ^{o}C with decomposition of initial alloy on hydride YH_2 phase and α-phase of Fe that can be described by the following phase scheme [5]:

$$Y_2Fe_{17} + H_2 \rightarrow YH_2 + \alpha\text{-Fe}. \qquad (1)$$
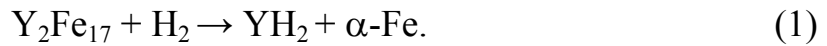
For Y_2Fe_{17} alloy above-mentioned kinetic peculiarities have been established earlier in work [5] and was established diffusive-controlled character of such transformations. In this study the main goal is analysis of transformation peculiarities in framework of the Kolmogorov–Johnson–Mehl–Avrami (KJMA) theory [6]. The results of studying a direct hydrogen-induced phase transformation in Y_2Fe_{17} alloy [5] are generalized in Figure 1a. As can be seen from Fig. 1a, with increasing of transformation temperature in narrow interval (140 ^{o}C) from 610 ^{o}C up to 750 ^{o}C the direct phase transformation lead to very strong acceleration of transformation in some order of magnitude.
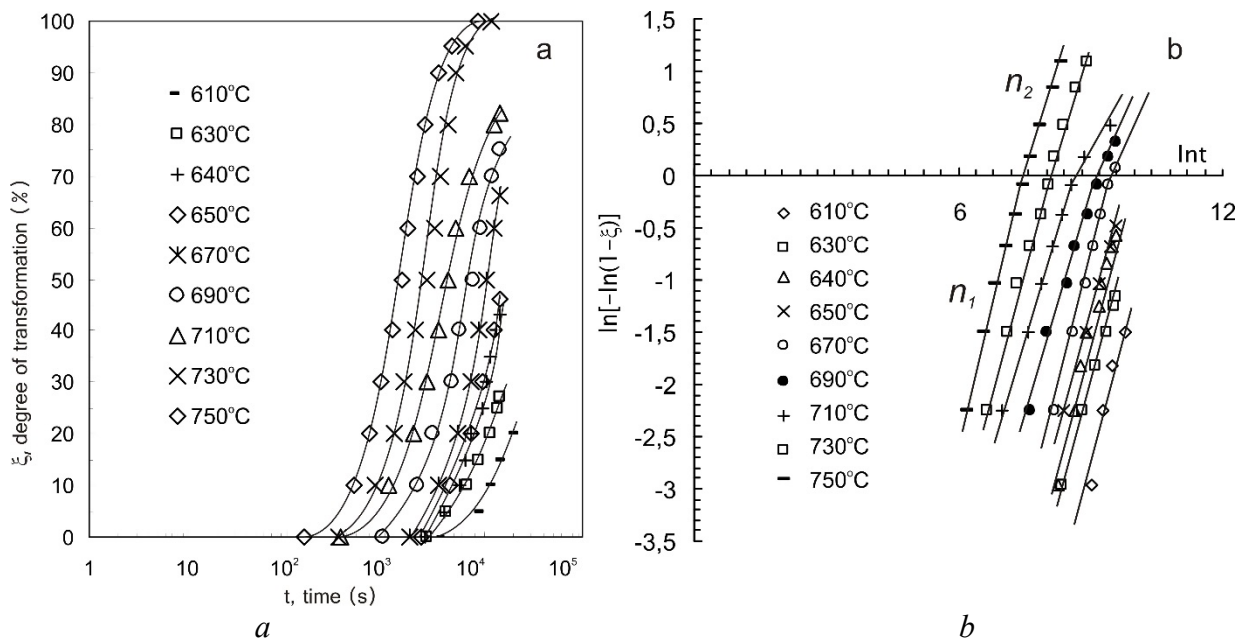

Fig. 1. Kinetic curves of direct hydrogen-induced phase transformation in Y_2Fe_{17} alloy (*a*); ln[-ln(1-ξ)] dependence on ln*t* for direct hydrogen-induced phase transformation in Y_2Fe_{17} alloy (*b*)

Then for further analyses has been used the KJMA theory. According to this theory [6], a degree of transformation ξ can be described by the following expression:

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

where t is a transformation time and k and n are kinetic variables.

It is known that if the experimental results reconstruct in coordinates $\ln[-\ln(1-\xi)]$ versus $\ln t$, it is possible to establish a kinetic constant n that gives us some important information about the most probable mechanisms of transformations. With this aim the experimental data from Fig. 1a were re-plotted in coordinates $\ln[-\ln(1-\xi)]$ versus $\ln t$ as it shown in Fig. 1b. As can be seen from Fig. 1b at temperatures interval of 670–750 $^{\circ}$C there are two linear parts – before of 50% of transformation (n_1) and after 50 % of transformation (n_2) as shown in Table 1.

According to Cahn's theory [6, 7], this is provoked by the saturation of nucleation sites. Before saturation of nucleation sites, the k coefficient in Equation (2) is proportional to the nucleation rate and growth and then it is proportional to the growth rate only.

Table 1

Kinetic constant n value in Eq. (2) for direct hydrogen-induced phase transformation in Y_2Fe_{17} alloy obtained from KJMA plot on Fig. 1b

T, $^{\circ}$C	610	630	640	650	670	690	710	730	750
n_1 ($\xi<50\%$)	1,88	1,46	1,83	1,53	1,71	1,51	1,37	1,67	1,74
n_2 ($\xi>50\%$)					1,52	1,11	0,83	1,58	1,29

Because of this, value of kinetic constant n that varying from ~1 up to ~1.9 corresponds to diffusion controlled growth with decreasing nucleation rate of new phases (α-Fe and YH_2) in accordance with KJMA theory [6].

On the other hand, in accordance with the Kolmogorov theory the kinetic constant $n = 4$ or $n = 3$ [8], but in case when the saturation of nucleation sites occurs at the initial stage of transformation in accordance with Cahn's approach kinetic constant value n can be decreased to 2 or 1 [6, 7]. In our case as follows from experimental data from Table 1 the kinetic constant value $n \approx 2$. Further, on the assumption that the kinetic constant $n = 2$ the kinetic coefficient k value was calculated from Eq. (2) with taking into account of experimental data from Fig. 1a for different of transformation temperature of direct hydrogen-induced phase transformation in Y_2Fe_{17} alloy that are presented in table 2.

Table 2

Kinetic coefficient k value calculated from Eq. (2) at kinetic constant $n = 2$

T (K)	923	943	963	983	1003	1023
k (c^{-2})	$2{,}97 \times 10^{-9}$	$5{,}88 \times 10^{-9}$	$1{,}31 \times 10^{-8}$	$3{,}2 \times 10^{-7}$	$0{,}97 \times 10^{-7}$	$2{,}79 \times 10^{-7}$

Then, was plotted dependence the kinetic coefficient k from transformation temperature T that is shown in Fig. 2a. In accordance with [9, 10] the kinetic coefficient k (that is proportional to the nucleation rate and growth) can be approximated in dependence on transformation temperature T by following equation:

$$k \approx aTe^{-\frac{U}{RT}}, \tag{3}$$

where T is a transformation temperature (K), $R = 8{,}31$ J/(mol·K) is the gas constant, $U=250$ kJ/mol is the activation energy of transformation and a is the constant. Approximation the data for kinetic coefficient k dependence on transformation temperature T in Fig. 2a give us the following expression:

$$k \approx 1.17 \times 10^3 \, Te^{-\frac{U}{RT}} \tag{4}$$

Then, substitute equation (4) into equation (2) we can obtain kinetic equation for volume of the transformed area ξ in dependence on transformation time t and temperature T:

$$\xi = 1 - \exp(-1.17 \times 10^3 \, Te^{-\frac{U}{RT}} t^2), \tag{5}$$

where t is a transformation time (s), T is a transformation temperature (K), $R = = 8{,}31$ J/(mol·K) is the gas constant, $U = 250$ kJ/mol is the activation energy of transformation [10] and kinetic constant $n = 2$. In Fig. 2b are generalized kinetic curves of direct hydrogen-induced phase transformation in Y_2Fe_{17} alloy calculated by Eq. (5) for various transformation temperature.
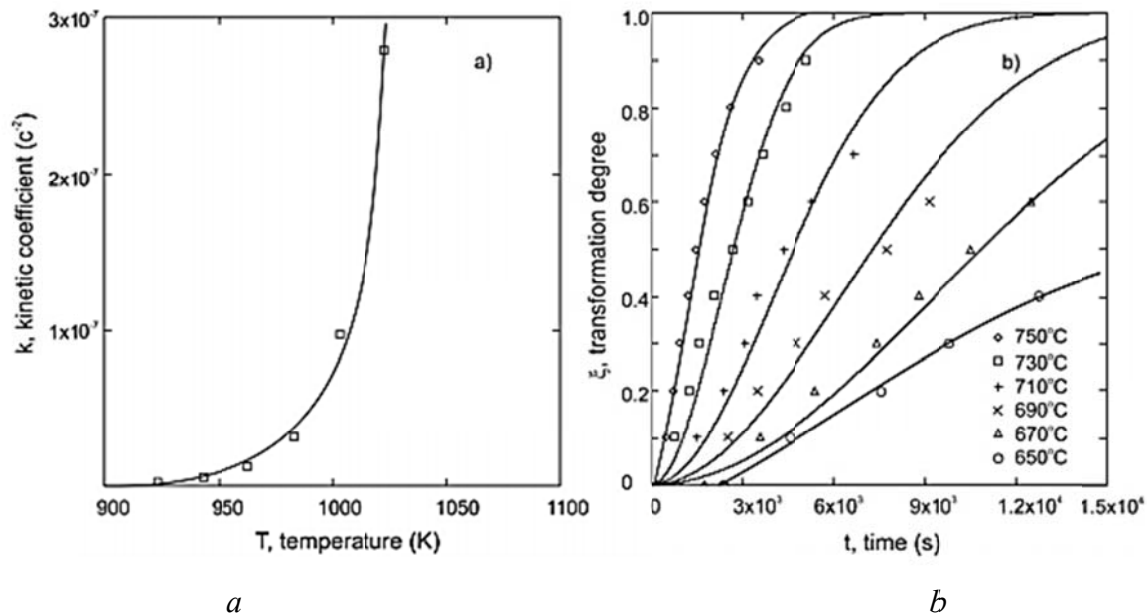

a   *b*

Fig. 2. (a) Kinetic coefficient k dependence on transformation temperature for direct hydrogen-induced phase transformation in Y_2Fe_{17} alloy; (b) kinetic curves of direct hydrogen-induced phase transformation in Y_2Fe_{17} alloy calculated by Eq. (5) for various transformation temperature (dots – experimental data)

As can be seen from this figure the calculated curves well approximate experimental kinetic data transformation from Fig. 1a [5]. Therefore, the kinetic equation of form Eq. (5) obtained on the base of Kolmogorov's kinetic theory of the phase transformations can be used for describing of the kinetics of hydrogen induced direct phase transformations in Y_2Fe_{17} alloy.

Finally, on the base of analysis in framework of Kolmogorov's theory the direct hydrogen-induced phase transformation in Y_2Fe_{17} alloy can be classified as diffusion controlled transformation which occurs by mechanism of nucleation and growth with decreasing nucleation rate of new phases (α-Fe and YH_2). In addition it is established that the kinetics of this transformation can be good approximated by kinetic equation of form Eq. (5).

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