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КИНЕТИКА ОБРАТНЫХ ФАЗОВЫХ ПРЕВРАЩЕНИЙ, ИНДУЦИРОВАННЫХ ВОДОРОДОМ, В СПЛАВЕ Y_2Fe_{17} В РАМКАХ МОДЕЛИ КОЛМОГОРОВА

Кинетика индуцированного водородом обратного фазового превращения в магнитотвердом сплаве Y_2Fe_{17} проанализирована в рамках кинетической модели Колмогорова. На основе кинетической теории фазовых превращений Колмогорова получено кинетическое уравнение, хорошо описывающее изотермические кинетические кривые обратного фазового превращения в сплаве Y_2Fe_{17} в зависимости от температуры превращения.
Ключевые слова: кинетика, фазовые переходы, магнитные сплавы.

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KINETICS OF HYDROGEN-INDUCED REVERSE PHASE TRANSFORMATION IN Y_2Fe_{17} ALLOY ON THE BASIS OF KOLMOGOROV'S MODEL

Kinetics of the hydrogen induced reverse phase transformation in Y_2Fe_{17} hard magnetic alloy has been analyzed in framework of Kolmogorov's kinetic model. On the basis of Kolmogorov's kinetic theory of the phase transformations has been obtained kinetic equation that well described the isothermal kinetic curves of reverse phase transformation in Y_2Fe_{17} alloy in dependence on transformation temperature.
Key words: kinetics, phase transitions, magnetic alloys.

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 [1]. In particular, at HDDR-treatment the Y_2Fe_{17} alloy undergoes the direct hydrogen-induced phase transformation at temperatures above 500 °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 [1]

$$Y_2Fe_{17} + H_2 \rightarrow YH_2 + \alpha\text{-}Fe$$

Then in vacuum (~10^{-2} torr) take place the reverse transformation with recombination process of decomposed phases into initial Y_2Fe_{17} phase [1, 2]

$$YH_2 + \alpha\text{-}Fe \rightarrow H_2 \rightarrow Y_2Fe_{17} \quad (1)$$

For Y_2Fe_{17} alloy the reverse transformation kinetic peculiarities have been established earlier in work [2] 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 [3–5]. The results of studying a reverse hydrogen-induced phase transformation in Y_2Fe_{17} alloy [2] are generalized in fig. 1, *a*. As can be seen from fig. 1, *a*, with increasing of transformation temperature in narrow interval (80 °C) from 670 °C up to 750 °C the reverse phase transformation lead to very strong acceleration of transformation in some order of magnitude.

a *b*

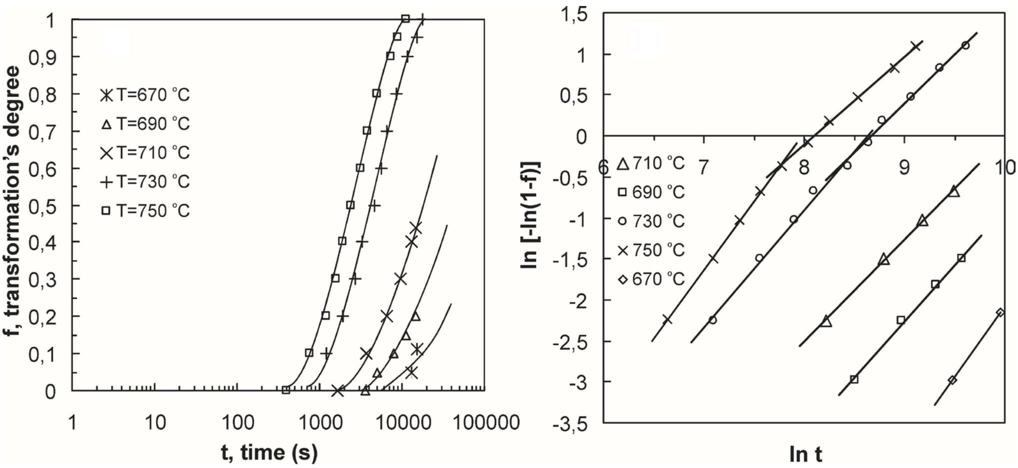

Fig. 1. Kinetic curves of reverse hydrogen-induced phase transformation in Y_2Fe_{17} alloy (*a*) [2]; ln[-ln(1-f)] dependence on ln*t* for reverse hydrogen-induced phase transformation in Y_2Fe_{17} alloy (*b*)

Then for further analyses has been used the KJMA theory. According to this theory [3–5], a degree of transformation *f* can be described by the following expression

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

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

It is known [3] that if the experimental results reconstruct in coordinates ln[–ln(1–*f*)] 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. 1, *a* were replotted in coordinates ln[–ln(1–*f*)] versus ln*t* as it shown in fig. 1, *b*. As can be seen from fig. 1, *b* at temperatures interval of 730–750 °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 [3, 6], this is provoked by the saturation of nucleation sites. Before saturation of nucleation sites, the *k* coefficient in eq. (1) 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 reverse hydrogen-induced phase transformation in Y_2Fe_{17} alloy obtained from KJMA plot on fig. 1, *b*

T, °C	670	690	710	730	750
n_1 ($f < 50\,\%$)	1,34	1,37	1,25	1,42	1,67
n_2 ($f > 50\,\%$)	–	–	–	1,19	1,08

When the one hand in accordance with the Kolmogorov theory the kinetic constant $n = 4$ or $n = 3$ [3, 5, 6], 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. In our case as follows from experimental data from table 1 the kinetic constant value $n \approx 2$. In accordance with [3–6] 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

$$k \approx a(T)e^{-\frac{U}{RT}}, \tag{3}$$

where $a(T)$ is the constant that depends on transformation temperature; *U* is the activation energy of transformation; *R* is the gas constant; *T* is a transformation temperature (K). Then, substitute eq. (3) into eq. (2) we can obtain kinetic equation for volume of the transformed area ξ in dependence on transformation time *t* and temperature *T*

$$f = 1 - \exp\left(a(T)e^{-\frac{U}{RT}}t^2\right), \tag{4}$$

where *T* is a transformation temperature (K); *U* is the activation energy of transformation, $U = 250$ kJ/mol; *R* is the gas constant, $R = 8{,}31$ J/(mol·K); *t* is a transformation time (s) [7]. Further, on the assumption that the kinetic constant $n = 2$ the kinetic coefficient $a(T)$ value was calculated from eq. (4) with taking into account of experimental data from fig. 1, *a* for different of transformation temperature of reverse hydrogen-induced phase transformation in Y_2Fe_{17} alloy that are presented in table and then plotted in fig. 2.

Kinetic coefficient *a*(*T*) value calculated from eq. (4) at kinetic constant *n* = 2

T, K	943	963	983	1003	1023
a(*T*), c^{-2}	0,42·10^5	0,49·10^5	0,79·10^5	3,17·10^5	5,72·10^5

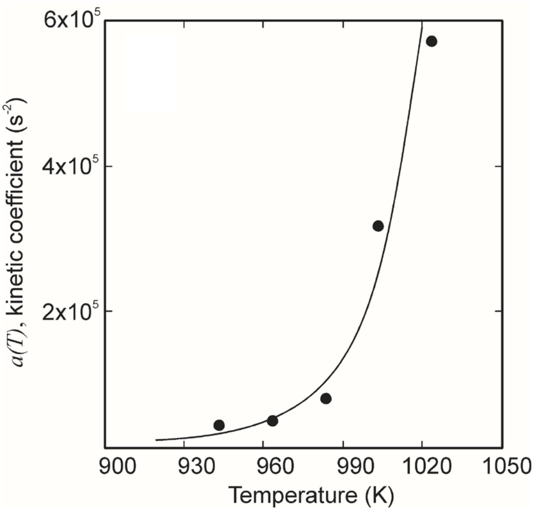

Fig. 2. Kinetic coefficient *a* (*T*) dependence on transformation temperature for reverse hydrogen-induced phase transformation in Y_2Fe_{17} alloy

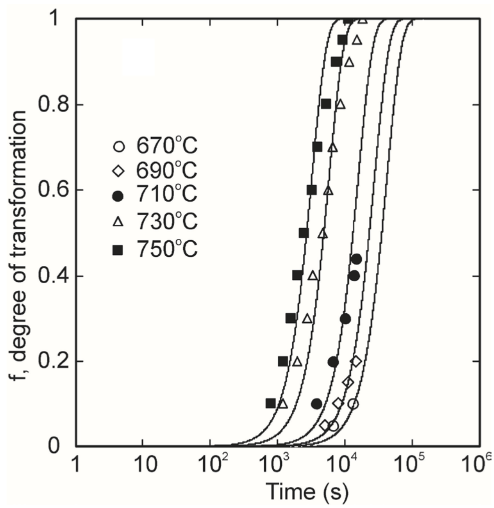

Fig. 3. Kinetic curves of reverse hydrogen-induced phase transformation in Y_2Fe_{17} alloy calculated by eq. (4) for various transformation temperature (dots — experimental data)

As can be seen from fig. 3 the calculated by eq. (4) and data from table (p. 71) curves well approximate experimental kinetic data transformation from fig. 1, *a* [2]. Therefore, the kinetic equation of form eq. (4) obtained on the base of Kolmogorov's kinetic theory can be used for describing of the kinetics of hydrogen induced reverse phase transformations in Y_2Fe_{17} alloy.

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