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KINETIC EQUATION FOR HYDROGEN-INDUCED DIRECT PHASE TRANSFORMATIONS IN Y_2FE_{17} MAGNETIC ALLOY

АННОТАЦИЯ

Предложена модель для развития индуцированного водородом прямого фазового превращения в магнитотвердом сплаве типа Y_2Fe_{17}. Показано что процесс развития индуцированного водородом прямого фазового превращения в магнитотвердом сплаве типа Y_2Fe_{17} в низкотемпературном интервале 330–750 ^oC контролируется процессами диффузии атомов Fe. На основе кинетической теории фазовых превращений Колмогорова и Любова получено кинетическое уравнение, хорошо описывающее изотермическую кинетическую диаграмму для превращения такого типа в сплаве типа Y_2Fe_{17}.

Ключевые слова: фазовые превращения, наводораживание, кинетика

ABSTRACT

Model for evolution of the hydrogen-induced direct phase transformation in Y_2Fe_{17} magnetic alloy has been proposed. It is shown that evolution process of hydrogen-induced direct phase transformation in Y_2Fe_{17} type hard magnetic alloy is controlled by diffusion process of Fe atoms in low temperatures interval of 330–750 ^oC. On the base of Kolmogorov and Lyubov kinetic theory has been obtained kinetic equation that well described the isothermal kinetic diagram for this type transformation in Y_2Fe_{17} alloy.

Keywords: phase transformations, kinetics, hydrogen absorption

As well known phase transformations studies have always been one of the main standpoint areas of condensed matter physics, metal science, theoretical and practical materials science. In particularly, R_2M_{17} compounds demonstrate very interesting magnetic phenomenon during their interaction with interstitial atoms (H, N, C, B) [1]. For instance, 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}, $Nd_2Fe_{14}B$ etc.) alloys for permanent magnets allows improve their structure and magnetic properties by hydrogen-induced reversible phase transformations [2]. 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 scheme:

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

Then, the reverse phase transformation takes place during hydrogen evacuation at higher temperatures with recombination decomposed phases into initial Y_2Fe_{17} matrix phase and after the completion of recombination stage the treated alloy as a rule consist of the nanocrystalline phase of Y_2Fe_{17}.

Earlier the obtained values of an activation energy determined for some degrees of transformation varying from 162 up to 242 kJ/mol for Y_2Fe_{17} alloy [3]. Obtained above values of effective activation energy in low temperature region (330–750 °C) have good agreement with an activation energy of data for diffusion of Fe atoms in Rare-Earth metals – Q = 250 kJ/mol and self-diffusion of Fe atoms in α-Fe phase of iron ~250.6 kJ/mol [4]. For instance, earlier it was established that for $Nd_2Fe_{14}B$ alloy in high temperature region (780–860 °C) effective energy activation is equal to the energy of NdH_2 hydride phase formation (ΔG_{NdH2}= – (187.7 ± 3.3) kJ/mol [5]). Therefore, it is really possible to consider that evolution process of direct phase transformation is controlled by diffusion process of Fe atoms in low temperatures interval of 330–750 °C and in high temperatures interval of 780–860 °C phase transformation process controlled by growth kinetics of rare-earth RH_2 hydride phase. On the other hand, as can be seen from scheme (1) there is a reason to believe that diffusion of hydrogen into R_2Fe_{17} alloy leads to nucleation and growth process of RH_2 hydride phase and then diffusion of Fe atoms leads to formation of α-Fe phase. Thus, in our case we can believe that evolution process of transformation is controlled by two main process, i.e. nucleation and growth process of the two main phases: RH_2 hydride phase and α-Fe phase.

In accordance with above described model let's obtain kinetic equations for direct hydrogen induced phase transformation in R_2Fe_{17} type alloys. As well known from the Kolmogorov kinetic theory of phase transformation in solid state [6], the volume of the transformed area ξ in dependence on t transformation time can be written as

$$\xi(t) = \frac{V(t)}{V_o} = 1 - \exp\left[-\int_0^t I(t)\varphi(t-\tau)dt \right], \quad (2)$$

where $V(t)$ is the transformed area volume at time t, V_o is the initial volume, $I(t)$ is the nucleation rate of centres of new phases at time t, $\varphi(t)$ is the volume of this nucleation centre at time t, τ is the nucleation moment of centre of a new phase. For the isothermal conditions as in our case it is believed that $I(t)=I$=const.

In general case, according to the Lyubov kinetic theory approach [7] we can obtain kinetic equation for volume of the transformed area ξ in dependence on t transformation time and temperature T:

$$\xi(t)=1-\exp\left[-\frac{\pi^4 d^{12}\Delta g^3 RT\gamma}{3^7 h^4}e^{-\frac{W+4U}{RT}}t^4{}_{cr.}-\frac{64\pi RT\gamma}{15h}\beta^3 D_o^{\frac{3}{2}}e^{-\frac{W+U+\frac{3}{2}Q}{RT}}\left(t^{5/2}-\tau^{5/2}\right)\right] \qquad (3)$$

For practical application phase transformation kinetics as a rule describes by curves showing time transformation t needs for reaching some degree of transformation ξ dependence on transformation temperature T. Finally, for direct hydrogen-induced phase transformations in R_2Fe_{17} type alloys in low temperature region (330–750 °C) we can obtain the following equation:

$$t(\xi,T)=\left[\frac{15h\ln\left(\frac{1}{1-\xi}\right)}{64\pi RT\gamma\beta^3 D_o{}^{3/2}}\right]^{\frac{2}{5}}e^{\frac{\frac{2}{5}(W+U)+\frac{3}{5}Q}{RT}}. \qquad (4)$$

Thus, in further analysis we can believed that above determined earlier effective activation energies (see Fig. 1) $Q_{ef.}$ equal correspondently $Q_{ef.}\cong\frac{2}{5}(W+U)+\frac{3}{5}Q$, where W is the free energy of critical nucleus of α-Fe phase formation, Q is the activation energy of Fe atoms diffusion (in our case we can take on following data for diffusion of Fe atoms in Rare-Earth metals – Q = 250 kJ/mol, D_o=1 mm^2/s [8]), U is the activation energy of hydrogen atoms at transition of atoms through interface of RH_2 phases which is equal to energy of RH_2 hydride phase formation nucleus, $\beta\approx10^{-3}\div10^{-5}$[7].

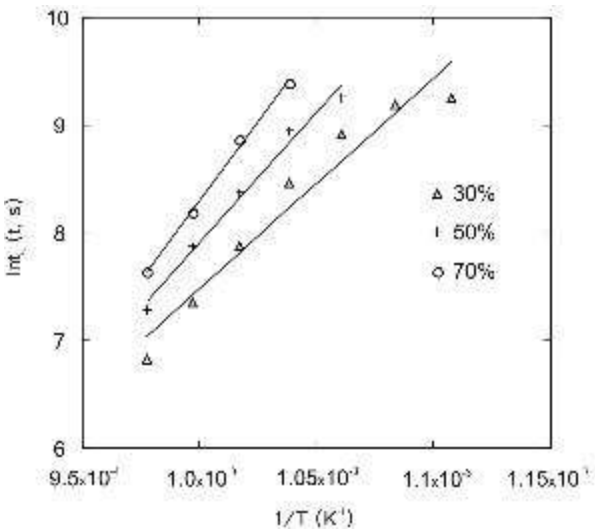

Fig. 1. Dependence Int$_\xi$ on 1/T for hydrogen-induced direct phase transformation in Y_2Fe_{17} alloy [4]

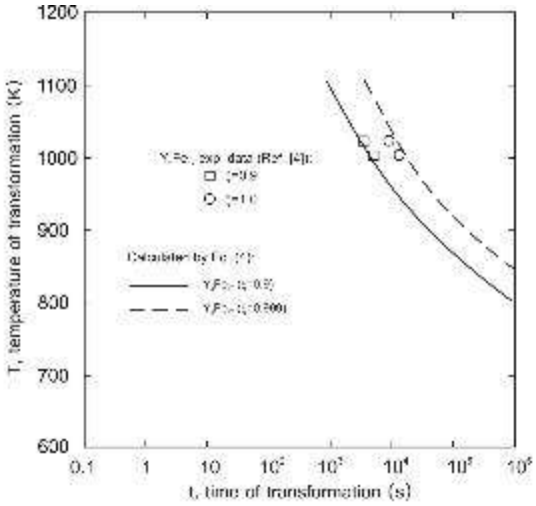

Fig. 2. The isothermal kinetic diagrams of hydrogen-induced direct phase transformation in Y_2Fe_{17} alloy calculated by Eq. (4)

Then, using obtained effective activation energies and above-mentioned data were obtained all unknown parameters in Eq. (4). Then was calculated isothermal kinetic diagram for direct hydrogen-induced phase transformation in Y_2Fe_{17} alloy which are shown in Fig. 2.

Finally, as follows from Fig. 2 equation (4) that was obtained on the base of Kolmogorov and Lyubov kinetic theory well describes the isothermal kinetic diagram for this type transformation in Y_2Fe_{17} alloy.

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