# Kinetics of decomposition of erbium hydride

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## Abstract

Erbium was used as a model hydride-forming metal to study the possibility of applying thermal desorption spectroscopy (TDS) to research into hydride decomposition. The possibility of varying heating rates and final temperatures makes TDS acceptable for providing experimental information about the kinetics of decomposition. Discrimination of models and evaluation of rate constants were performed by fitting computer-simulation derived curves to experimental ones. The most probable models have boundary-value problems in which the rates of decomposition, desorption and migration of hydrogen are taken into account. The movement of an interface between hydride and solid solution of hydrogen is determined by all these reactions.
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## 1. Introduction

The formation of metal hydrides is studied much more than their decomposition. Some results are summarized, for instance, in reviews [1,2]. In experimental studies concerning decomposition, special attention is paid to the desorption processes; in particular, the influence of the size of hydride particles and activation of desorption using a catalytic metal are considered [3–7]. In one experimental work [8], a method to evaluate hydride formation/decomposition parameters based on a barometric approach is given, and a rather complete model of these processes is suggested. Most of the investigations in the area of hydride decomposition are theoretical. Different models are suggested and computer simulations are done considering different processes as limitative (see for example Refs. [9,10]).

Previously we used thermal desorption spectroscopy (TDS) to determine the mechanism of hydrogen desorption from nanoporous carbon [11] and to evaluate the rate constants of elementary processes which influence hydrogen transport. Probable models were constructed and the experimental curves were fit by model curves.

The aim of this paper is to examine the possibilities the TDS method provides to obtain experimental information sufficiently complete to discriminate the models which describe the mechanisms of hydrogen liberation from metal hydrides, as well as to evaluate the rate constants of elementary processes such as hydride decomposition, diffusion, desorption, etc. The TDS method seems acceptable as it allows both heating rate and the final temperature to be varied. A single desorption curve can evidently be successfully approximated by different models, but it is harder with a family of curves corresponding to different heating rates. A necessary (but not sufficient) criterion of model adequacy must be closeness of the parameter sets calculated for different TDS curves.

## 2. Experimental details

Erbium was chosen as a model material. The object of investigation was a powder with mean particle sizes of ~2 μm, obtained as a result of numerous cycles of sorption/desorption of hydrogen. When the drift of the experimental results disappeared, we assumed that the powder particles had stopped decreasing.

The powder was heated in a quartz crucible. Partial flows of desorbed gases were monitored by mass spectrometry. The sample was hydrogenated at pressures of 5–50 Torr and temperatures of 20–200 °C. Dehydrogenation occurred under continuous vacuum at linear heating from room temperature to 900 °C.

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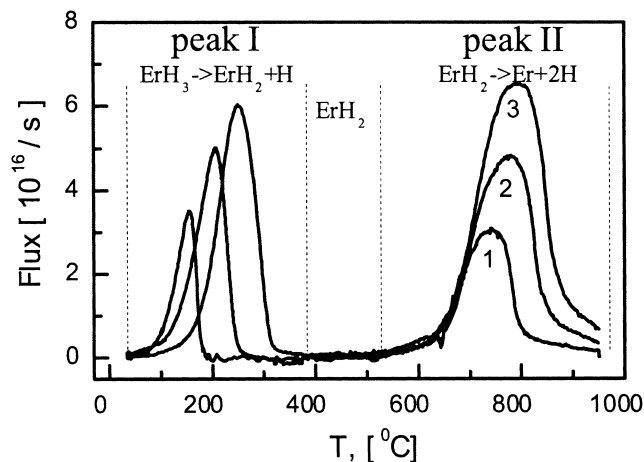*E-mail address:* igor.gabis@paloma.spbu.ru (I. Gabis).

Fig. 1. Family of TDS curves at heating rates: 1, 0.1 K/s; 2, 0.2 K/s; 3, 0.3 K/s.



Fig. 2. Family of TDS spectra at various final temperatures: 1, 900 °C (continuous heating); 2, 600 °C; 3, 550 °C.

Fig. 1 shows a family of curves of hydrogen desorption from erbium after the same experiments corresponding to the $ErH_3$ concentration, but obtained at different heating rates. A low-temperature peak I corresponds to $ErH_3 \rightarrow ErH_2$ transformation, while a high-temperature peak II corresponds to $ErH_2 \rightarrow Er$ transformation. An advantage of erbium as the model material is that the peaks are not overlapped. The ratio of areas under peaks I and II was under continuous control. It showed the ratio of the amounts of desorbed hydrogen and was equal to 1/2.

The low-temperature and high-temperature phases behave differently while the heating rate is varied. Thus different hydrogen desorption models should be considered. Peak I moves toward the higher temperatures when the heating rate increases, but peak II has almost coincident initial parts of fronts, and only a tiny shift of maximum temperature can be noticed.

## 3. Results and discussion

### 3.1. 'Shrinking core' or 'nucleation and growth'?

The TDS method allows the model for hydride decomposition to be chosen: either a 'shrinking core' or 'nucleation and growth'. In the second case, when nucleation commences, the surface separating $ErH_2$ and the α-phase (or $ErH_3$ and $ErH_2$) grows monotonically until growing nuclei begin to intersect. Thus at initial stages of decomposition of hydride at *constant temperature* the amount of hydrogen moving from $ErH_2$ into the α-phase (or from $ErH_3$ to $ErH_2$) must grow, which results in increased concentration in the solution and finally in growth of the desorption flux. For the 'shrinking core' model, the monotonic decrease should be present due to monotonically decreasing boundary surface. Fig. 2 shows a family of desorption curves corresponding to peak II (curve 1). For curves 2 and 3 the heating was stopped at
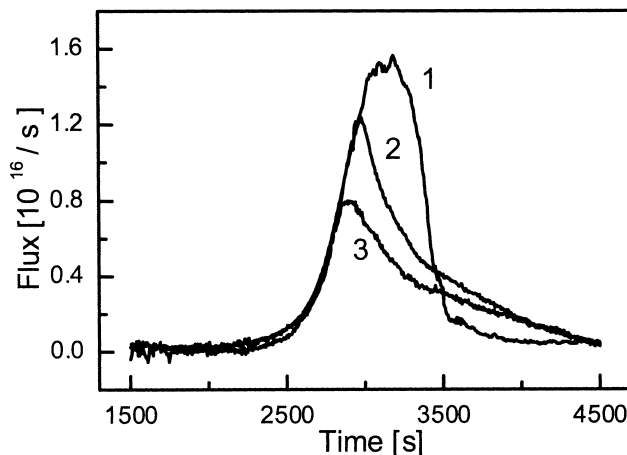
temperatures of 600 and 550 °C, respectively. Peak I reveals similar behavior. The flux has decreased, thus a 'shrinking core' model is more probable for erbium powder.

### 3.2. TDS spectra analysis: preliminary notes

The most complete model of hydrogen desorption from hydrides, from our point of view, is suggested in Ref. [10]. However it is hardly suitable for the inverse problem solution, i.e. determining the most probable dehydrogenation mechanism, for the authors tried to take every elementary process into consideration. Our aim is to separate those processes which influence hydrogen desorption from those that are hidden. Some of the elementary reactions, at least when erbium is studied, can be excluded from consideration a priori.

(i) According to pressure–composition isotherms [12], the concentration of the mobile hydrogen atoms, which are dissolved in hydride phases, is low compared to the concentration of the hydrogen bound in hydride and dissolved in erbium.

(ii) The capacity of the surface can be neglected compared to the total amount of accumulated hydrogen. The amount of hydrogen in the surface monolayer compared to its content in $ErH_2$ is lower than 0.1%, with size dispersion of the powder particles and their roughness taken into consideration. It is also obvious that at high temperatures the hydrogen concentration on the surface is far from being a monolayer.

(iii) It is doubtful whether hydride formation and decomposition, which imply lattice reconstruction (change of phase), can be considered as reversible reactions each having non-zero rate at the same time. An unavoidable hysteresis on the pressure–composition isotherms [13] is an argument for using theta-function in the expressions for the hydride decomposition ($k_1$) and formation ($k_2$) rate constants:

$$k_1 = k_{1_0} \exp(-E_{dec}/RT)\Theta((c_R - \delta)/c(t) - 1) \qquad (1)$$

$$k_2 = k_{2_0} \exp(-E_{cre}/RT)\Theta((c_R + \delta)/c(t) - 1) \qquad (2)$$

where $T$ is temperature, $t$ is time, $R$ is radius of hydride core, $c$ is concentration of mobile hydrogen and $E_{dec}$, $E_{cre}$ are activation energies of hydride decomposition and creation. Here $c_R$ is the concentration of mobile hydrogen atoms in equilibrium with hydride, $\delta << c_R$ is the half of the hysteresis width. In the TDS method when the hydrogen-filled sample is heated in vacuum, $k_2 = 0$.

### 3.3. High-temperature peak

Let us first interpret peak II, for its mathematical description is simpler. We begin by considering a single particle, keeping in mind that hydride particles have some radius dispersion. Size dispersion influence will be discussed later.

The maximum radius of erbium particles is no more than 20 μm, therefore at temperatures of $T > 500$ °C diffusion transit time at $D > 10^{-6}$ cm$^2$/s [12] is below 5 s. So if low heating rates are used (0.1–0.3 K/s) the concentration of mobile hydrogen atoms can be considered independent of coordinate $c = c(t)$. Another important point is that the initial parts of all three curves (Fig. 1, peak II), obtained at different heating rates, coincide. Consequently at these temperatures the concentration of dissolved hydrogen atoms near the surface does not depend on the heating rate and this can be only if it is in equilibrium with hydride. The curves disperse when the hydride decomposition rate becomes limitative.

Let us consider the dehydrogenation model of a single spherical particle (a globule). The heating is linear: $T(t) = T_0 + qt$, where $q$ is heating rate. Let $L$ be the radius of a globule, $R(t)$ the radius of the hydride ErH$_2$ core, $V(r)$ the volume of a ball with radius $r$, and $S(r)$ its surface. In the spherical layer $r \in (R(t), L)$ with the moving boundary of phases, mobile hydrogen atoms are dissolved in erbium. Let the concentration of hydrogen bound in hydride core be $Q$.

Hydrogen desorption from the globule rate constant will be written in the Arrhenius form: $b(t) = b(T(t)) = b_0 \exp(-E_b/RT)$, where $E_b$ is activation energy of desorption and $b$ is desorption rate constant. Let us construct a balance equation for the amount of hydrogen in the initial state and at an arbitrary time:

$$QV(L) = QV(R) + c(t)(V(L) - V(R)) + S(L)\int_0^t b(\tau)c^2(\tau)d\tau \qquad (3)$$

Differentiating in time keeping in mind that $R = R(t)$ results in

$$\frac{dc}{dt}(L^3 - R^3)/3 = -bc^2L^2 - (Q - c)\frac{dR}{dt}R^2. \qquad (4)$$

Let us consider two temperature intervals.

(i) $bc_R^2L^2 \leq k_1QR^2$. This makes initial parts of fronts of the desorption curves coincide. This means that the rate of hydrogen desorption from the globule is lower than the possible rate of hydride core decomposition. Hydride could decompose more quickly, but that would mean that the concentration of dissolved hydrogen exceeds equilibrium, which is impossible. Thus the rate of decomposition is such that the concentration $c \cong c_R = \mathrm{const}(t)$ remains, i.e.

$$\frac{dc}{dt} = 0 \qquad (5)$$

The condition on the rate of movement of the boundary between hydride and solution follows from (4):

$$\frac{dR}{dt} = -\frac{bc_R^2L^2}{(Q - c_R)R^2} \qquad (6)$$

Thus the rate of decreasing of the hydride core radius is defined by desorption only, while it is slow.

(ii) $bc_R^2L^2 > k_1QR^2$. Now the concentration $c(t) < c_R$ and expression (1) for $k_1$ will look like $k_1 = k_{1_0}\exp(-E_{dec}/RT)$. One more equation for the moving boundary is necessary. In the period of time from $t$ to $t + dt$ a spherical layer with some dissolved hydrogen appears. Let $I(t)$ be the flux through a sphere of radius $R(t)$. Then

$$(Q - c(t + dt))(V(R(t)) - V(R(t + dt))) = S(R(t))\int_t^{t+dt} I(\tau)d\tau \qquad (7)$$

Dividing this equation on $dt$ and considering $dt \to 0$ we obtained $(Q - c(t))\frac{dR}{dt} = -I(t)$. Now the flux density $I(t)$, which is caused by hydride decomposition, must be calculated: $I(t) = k_1Q$. Finally the following model is obtained:

$$\frac{dc}{dt} = \frac{3}{(L^3 - R^3)}(-bc^2L^2 + k_1QR^2) \qquad (8)$$

$$\frac{dR}{dt} = -\frac{k_1Q}{Q - c(t)} \qquad (9)$$

At time $t*$ hydriding is finished, i.e. $R(t*) = 0$, and after that simply the outgassing of hydrogen dissolved in a globule occurs.

The presented model even when a single particle is considered, gives a rather good coincidence with the experiment. Fig. 3 presents three experimental curves with fitted model curves. Discrepancy between experimental and model curves was minimized by varying activation energies and preexponential factors of decomposition of the hydride and of desorption. The total simulation flux
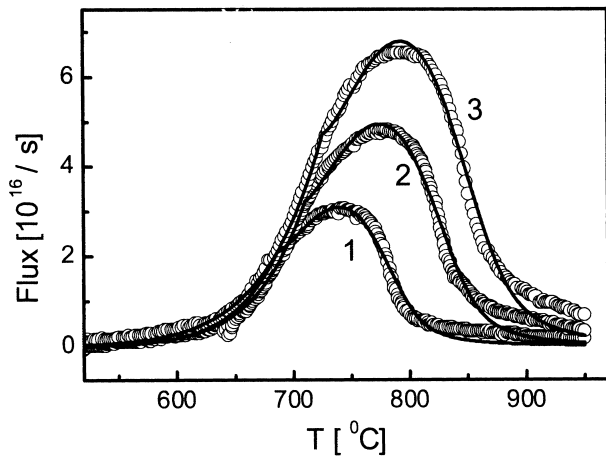
Fig. 3. Fitting of TDS curves (hollow circles) by model curves (solid lines) at heating rates: 1, 0.1 K/s; 2, 0.2 K/s; 3, 0.3 K/s.

was calculated using the formula $J_{\text{sim}}(t) = 4\pi L^2 N \chi b(t) c^2(t)$, where quantity of particles $N = 10^8$, radius $L = 1$ μm, and roughness coefficient $\chi = 5$. The concentration $c(t)$ was calculated from Eqs. (5) and (6) at $bc_R^2 L^2 > k_1 Q R^2$ and Eqs. (8) and (9) in opposite case. The energy parameters of fitting for different curves are rather close to each other and may be evaluated in the following way: $E_{\text{dec}} = 145 \pm 20$ kJ/mol, $E_b = 184 \pm 20$ kJ/mol. Preexponential factors differ by two orders of magnitude: $k_{1_0} = 0.3$–7.0 cm/s, $b_0 = (0.3\text{–}40) \cdot 10^{-20}$ cm$^4$/s.

The good quality of the fitting and the closeness of parameters are arguments for the adequacy of the considered model. Some doubts are caused by the low rate of desorption that can be hardly limitative for *pure* metal at temperatures of ~600°C. The reaction of transfer of hydrogen atoms from the solution in the bulk of erbium to its surface having limitative influence must also result in $c \cong c_R$ at the initial parts of TDS curves. Such a model, where the desorption rate $bc^2$ was replaced by the rate of hydrogen transition from the solution in the bulk of the material to its surface $k_{\text{b}\to\text{s}} c$, was also used for fitting. The result was a bit worse than that with limited desorption rate. Thus the model with the low desorption rate is more probable, but actually the alternative mechanism cannot be definitely rejected. The low rate of desorption at such high temperatures can be explained by the surface passivation effect caused by an admixture of other atoms, mainly by carbon.

### 3.4. Particle size distribution

To determine the influence of the size distribution of the powder particles on the results of the fitting, the total hydrogen desorption from a group of particles of different sizes was computer simulated. We used Gaussian distribution with main radius 1 μm and standard deviation 0.5 μm. Kinetic parameters were $E_{\text{dec}} = 130$ kJ/mol, $E_b = 170$

kJ/mol, $k_{1_0} = 0.15$ cm/s, and $b_0 = 0.6 \cdot 10^{-20}$ cm$^4$/s. The simulation curve was then fitted as an experimental curve. Results of the fitting are: $E_{\text{dec}} = 135$ kJ/mol, $E_b = 171$ kJ/mol, $k_{1_0} = 0.39$ cm/s, and $b_0 = 0.8 \cdot 10^{-20}$ cm$^4$/s. One can see that the resulting activation energies are in good agreement with the initial ones, preexponential factors differing by less than three-fold. Thus fitting considering a single particle gives an acceptable result.

### 3.5. Low-temperature peak

Peak I is more complex than peak II. One can see that at different heating rates there is no coincidence even on the fronts of the desorption curves (Fig. 1). So none of the surface processes is limitative (desorption or transfer from the bulk state to the surface). If the hydride decomposition rate influences the initial parts of the curves, when $L - R < < L$, they must also approximately coincide. Therefore we assumed that the influence of the diffusion transfer in the ErH$_2$ is significant.

The following distributed model was used. A diffusion equation in spherical coordinates at $t > 0$ is:

$$\frac{\partial c}{\partial t} = D(t)\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right), \quad t \in (0, t^*),$$
$$r \in (R(t), L), \quad D(t) = D_0 \exp(-E_D/RT) \tag{10}$$

On the external boundary of the ball the desorption flux density is equal to the rate of desorption:

$$D(t)\frac{\partial c}{\partial r}\bigg|_L = -b(t)c^2(t, L) \tag{11}$$

It is assumed that the rate of ErH$_3$ transformation to ErH$_2$ is high enough to maintain the quasistationary (and independent of temperature and time) concentration of hydrogen dissolved in ErH$_2$ near the border with ErH$_3$: $c(t, R(t)) = \eta Q$, where $\eta$ is hydride-solution equilibrium constant ($\eta \cong 0.15$ from Ref. [12]). Then the Stefan [14] condition is in the form:

$$Q(1 - \eta)\frac{\mathrm{d}R}{\mathrm{d}t} = D(t)\frac{\partial c}{\partial r}\bigg|_{R(t)} \tag{12}$$

Using this model, we have achieved only qualitative similarity of TDS spectra. Simulation curves are presented in Fig. 4. Similar to the experimental family in Fig. 1, they move towards the right when the heating rate increases, but the form of the peaks is distorted. The problem is to improve the discrepancy minimization algorithm for the Stefan problem, which actually requires too much computer time. It is also possible that the model itself needs improvement.

## 4. Summary

(i) The TDS method is shown to be appropriate for investigation of hydride decomposition. It allows the most
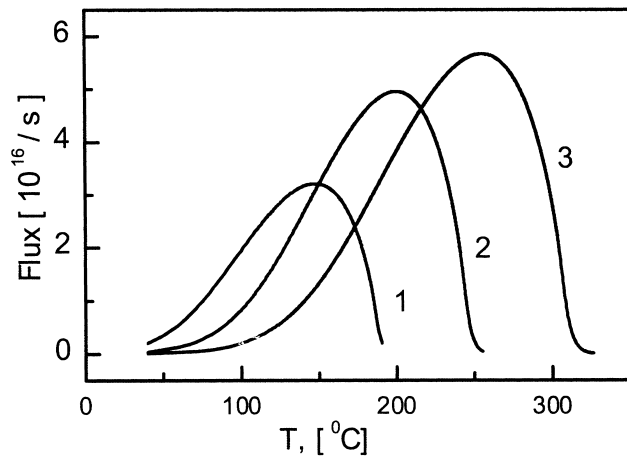
Fig. 4. Simulation curves for distributed model at heating rates: 1, 0.1 K/s; 2, 0.2 K/s; 3, 0.3 K/s.

probable model to be chosen and the rate constants of reactions that influence the overall process to be evaluated. The specific characteristics of TDS, which allow informative experimental data to be obtained, are heating at different rates, achieving a family of curves, and the possibility to stop heating at different temperatures.

(ii) Heating that was stopped at the fronts of the desorption curves showed that for the erbium powder with stable size distribution a 'shrinking core' model is more probable than a 'nucleation and growth' model.

(iii) The analysis of decomposition of erbium dihydride (peak II) was done using models which consider hydride desorption and decomposition rates, transfer from the bulk to the surface, and hydride decomposition rates. The first case seems to fit the experimental data best.

(iv) Activation energies and preexponential factors for the rates of $ErH_2$ decomposition and hydrogen desorption have been evaluated.

## Acknowledgements

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