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Hydride decomposition characterization by means of “morphological trajectory” method—Applied to AlH_3

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ABSTRACT

New approach to analyse hydride decomposition kinetics operating with integral morphological parameters as well as kinetic parameters of possible rate-limiting reactions (nucleation, desorption and reaction at interface) is proposed. Morphology of new phase growth in powder particle is described in terms of specific values of new phase volume, outer surface occupied by new phase, interface area and their interrelations (“morphological trajectories”). The approach describes H-release kinetics for free-form shape of particles and growing nuclei. The applicability of the approach is limited by the requirements of fast enough H-diffusivity in metal areas of powder particles and of nucleation at the outer surface of particles. Alane powder completely meets these requirements. It was found that the rate-limiting step is the reaction at the interface with activation energy 104 kJ/mol. Morphology of the transformation depends on experiment conditions: the higher is reaction temperature, the smaller is quantity of new phase nuclei.

1. Introduction

Design of hydrogen storage systems based on metal hydrides requires appropriate quantitative description of hydriding–dehydriding reactions. To get such a description for some material it is necessary to obtain reliable experimental data, formulate an adequate physical model of the process and carry out mathematical treatment to obtain estimations of kinetic parameters.

There is a wide variety of approaches for modeling kinetics of processes in hydride-metal systems [1,2]. In regard to hydride decomposition all methods can be roughly divided in two main groups tending to extremely generalized or extremely detailed description of the process. In the first group the most representative is Johnson–Mehl–Avrami–Erofeev (JMAE) approach. Its using is rather easy, and that is why it is very popular [3–5]. However, JMAE has serious drawbacks: it was developed originally for isothermal reactions and then was applied by force for thermal analysis; it operates with few extremely generalized parameters, which sometimes lose physical sense (for example fractional or too large values of fitted Avrami exponent normally used as a tracer for the dimensionality of reaction [2]); it often does not allow to determine rate-limiting stage unambiguously; due to its generalized character JMAE can account for a single rate-limiting reaction. In some studies [6] for overcoming last issue JMAE is used as a component of more complicated two-step models with switching of rate-limiting step.

On the contrary, in the second group of widespread approaches an attempt is made to account for many possible reactions: surface recombination (desorption), H-diffusion in metal and hydride phases, nucleation and new phase growth and so on. However simulation and multiparametric fitting for arbitrary shape of particle and interface is extremely resource-intensive. So in practice additional assumptions are usually made about the shape of hydride particle (usually sphere) and formation of continuous “skin” at the surface of the reacting particle at an early stage of the reaction [7–9]. This reduced form of the model (“shrinking core” [1]) remains very resource-intensive if diffusion is allowed.

This work was aimed to develop an approach for kinetics analysis which is not so simplified as JMAE and not so complicated as detailed description mentioned above. It should meet several requirements: (1) possibility of accounting for several simultaneous competing reactions; (2) absence of limitation on particle’s shape; (3) possibility of fitting of experimental data with acceptable computational resource.

2. Modeling details

One of the most limiting factors for developing a model for free shape particles/interfaces is accounting for H-diffusion. However we consider that in many important cases diffusion cannot be rate-limiting reaction. We have estimated characteristic time of H-diffusion in metal phase of 10–15 μm particles Al, Mg for TDS-experiments in temperature intervals according to remark-

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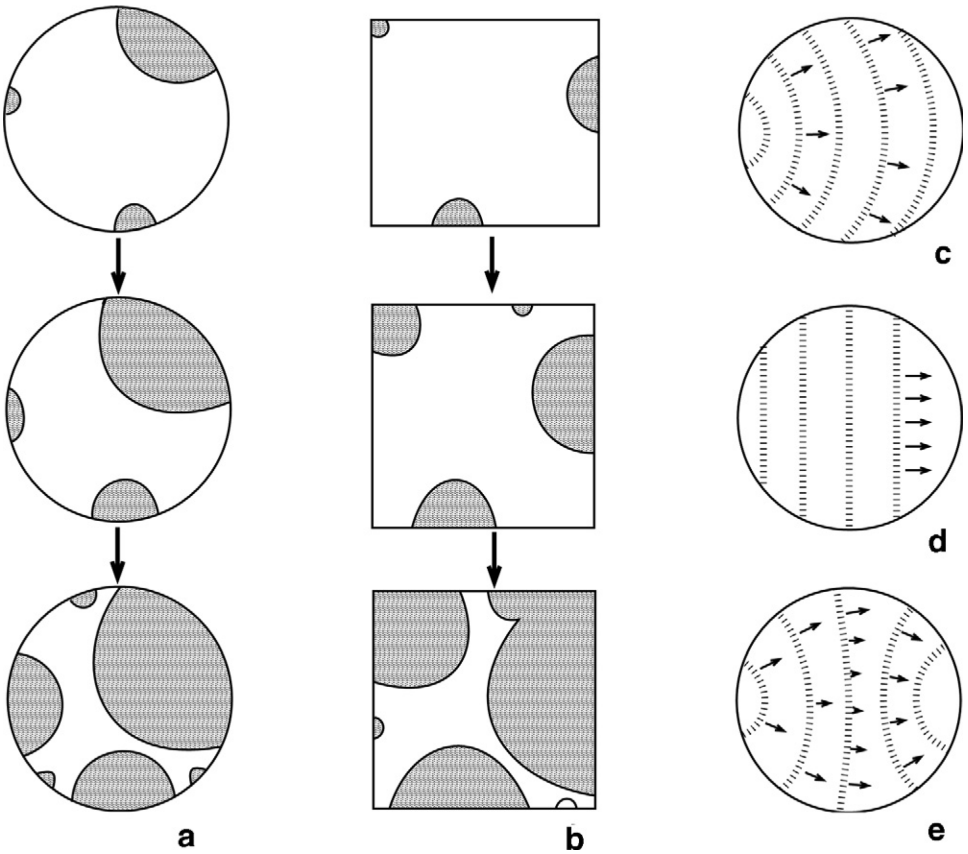

Fig. 1. Different shapes of particle (a – sphere; b – cube) and interface (c – sphere; d – flat; e – convex-concave) considered in the paper.

able H-desorption [10,11]. We have obtained that temperature of the samples changes by 1 K in a period much longer (10–20 times) compared to the characteristic time of hydrogen diffusion. So, we conclude that for fine powders of metal hydrides H-diffusion through metal phase cannot be rate-limiting step.

It is known that in many cases hydride decomposition (denoted here as β → α reaction) can be described as formation (instant or extended in the time) of new phase nuclei at the outer surface of the particles and their following growth into the bulk. However developing of only one nucleus could be analytically described in the framework of model accounting for desorption, interface reaction, or their concurrency.

We can overcome these limits considering the morphology of new phase growth in terms of specific values of new phase volume ($\tilde{V}_\alpha = V_\alpha/V_0$), outer surface occupied by new phase ($\tilde{S}_\alpha^{\text{out}} = S_\alpha^{\text{out}}/S_0$), interface area ($\tilde{S}_\alpha^{\text{int}} = S_\alpha^{\text{int}}/S_0$) and their interrelations ("morphological trajectories"), where V_0 and S_0 are the volume and outer surface of the particle. Values $\tilde{V}_\alpha$ and $\tilde{S}_\alpha^{\text{out}}$ always grow from 0 to 1, interface area $\tilde{S}_\alpha^{\text{int}}$ has maximum somewhere in the middle of the process and is equal to 0 at the beginning and at the end. Exact form of each dependency is determined by kinetic parameters of the reactions under consideration (nucleation, desorption, interface reaction). But all the variety of these dependencies can be reduced to trajectories

$$\begin{cases} \tilde{S}_\alpha^{\text{out}} = f(\tilde{V}_\alpha), \quad \tilde{S}_\alpha^{\text{out}}(0) = 0, \quad \tilde{S}_\alpha^{\text{out}}(1) = 1 \\ \tilde{S}_\alpha^{\text{int}} = g(\tilde{V}_\alpha), \quad \tilde{S}_\alpha^{\text{int}}(0) = 0, \quad \tilde{S}_\alpha^{\text{int}}(1) = 0 \end{cases} \tag{1}$$

and that is true for any shape of particles, any nucleation rate and shape of nucleus, and for a wide set of experiments: isothermal decomposition, TDS, barometry, etc.

For establishing interrelation of these values a number of computer modeling experiments was performed for different shapes of particles (sphere, cube) and interface (sphere, flat, convex-concave), different rates of nucleation NG and interface movement $\dot{r}$, changing of ratio $NG/\dot{r}$ during experiment. Part of considered configurations is shown in Fig. 1. After processing all massive of data we have fitted simple analytic formulae $\tilde{S}_\alpha^{\text{out}} = f(\tilde{V}_\alpha)$, $\tilde{S}_\alpha^{\text{int}} = g(\tilde{V}_\alpha)$ which depend on few parameters and satisfactorily describe all considered cases. Parameters of these functions reflect influence of nucleation rate. In particular, the greater is relation $NG/\dot{r}$, the faster is transition to extreme case of "shrinking core" (Fig. 2a). Changing of this relation towards lower values shifts the maximum position of $\tilde{S}_\alpha^{\text{int}}$ to the right (Fig. 2b).

It is assumed in further consideration that H-desorption from the hydride surface is negligible and that hydrogen concentration in the metal phase $C_\alpha(t)$ is controlled by the difference between the rate of hydrogen desorption from the outer surface of the metal phase and the rate of hydride decomposition at the interface.

Rate constants of desorption and movement of interface have Arrhenius dependencies on temperature. Overall desorption flux is proportional to squared concentration in the metal phase $C_\alpha(t)$ as associative H-desorption occurs. Besides this the rate of the movement of interface is assumed to be proportional to the deviation of $C_\alpha(t)$ from the equilibrium concentration C_α^{eq}. These considerations result in the following set of equations

$$\begin{cases} \dfrac{d}{dt}(C_\alpha V_\alpha + C_\beta V_\beta) = -b(T) C_\alpha^2 S_\alpha^{\text{out}}(V_\alpha) \\ \dfrac{d}{dt} V_\alpha = (1 - C_\alpha / C_\alpha^{\text{eq}}) \cdot k(T) S_\alpha^{\text{int}}(V_\alpha) \end{cases} \tag{2}$$

where $b(T) = b_0 \exp(-E_d/RT)$ and $k(T) = k_0 \exp(-E_{\text{int}}/RT)$ are desorption and interface's movement rate constants, model dependen-

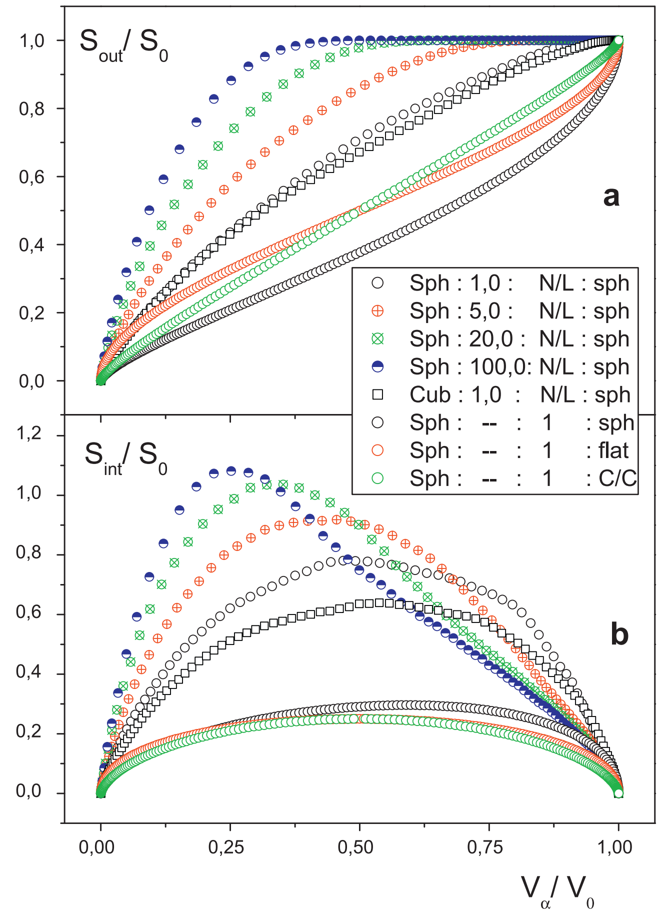

Fig. 2. Model dependencies of outer surface occupied by new phase (a) and interface area (b) upon reacted volume. Parameters of simulations are: shape of particle (sphere, cube), relation $NG/\dot{r}$ (dash means a single nucleus), maximal allowed quantity of nuclei (N/L means non limited), shape of interface of individual nucleus (spherical, flat, convex–concave).

cies $S_\alpha^{\mathrm{out}} = S_0 \cdot f(\tilde{V}_\alpha)$, $S_\alpha^{\mathrm{int}} = S_0 \cdot g(\tilde{V}_\alpha)$ incapsulate all the parameters of nucleation morphology and $NG/\dot{r}$ relation.

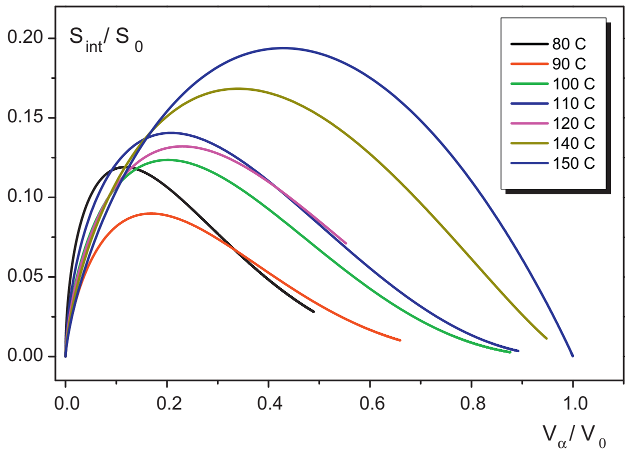

Fig. 4. Fitted dependency of the specific interface area on the reacted volume.

Obtained equations completely describe H-release kinetics under conditions of competing desorption and interface reaction with no restrictions on the rate of nucleation and shape of particles and growing nuclei. It means that we can apply this set of equations to any kind of hydride meeting the following conditions:

- H-diffusion is not the rate-limiting step (H-diffusivity is fast enough to rapidly set uniform concentration in metal areas of fine powder particle).
- H-desorption from the hydride surface is negligible compared to one from the surface of metal phase.
- Nucleation occurs at the outer surface of particles only.

The model can be modified easily to account for size distribution of powder in the manner described in [10]. Inverse problem solution (fitting of experimental data) allows estimating kinetic and morphological parameters. Obtained “morphological trajectory” for some experimental curve allows supposing character of nucleation. Fitted series of experiments (for instance, isothermal decomposition at different temperatures, TDS at different heating rate) can show a dependency of the morphological parameters upon experiment conditions. There are two main criteria of adequacy of method application: good fitting of the whole set of experimental curves and independent confirmation of nucleation nature by means of metallographic analysis, SEM, etc.

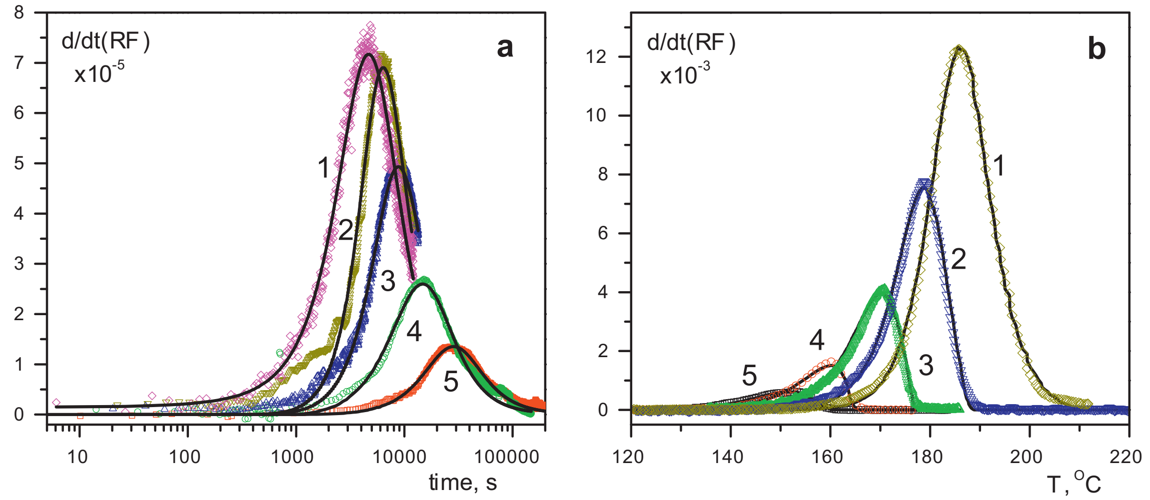

Fig. 3. Experimental curves of alane decomposition and fitting. (a) Isothermal decomposition at temperatures 1–125, 2–120, 3–115, 4–110, 5–100 °C; (b) TDS at heating rates 1–0.2, 2–0.1, 3–0.05, 4–0.02, 5–0.01 K/s. Hollow symbols – experimental data; solid lines – fitting.

3. Application for AlH_3

The approach described was applied to study AlH_3 under conditions of isothermal decomposition (353–423 K) and TDS (heat rates 0.01–0.2 K/s; decomposition temperatures 390–470 K). Experimental setup and obtained dependencies are described in detail in [10] and [11] accordingly. SEM study showed that studied alane has very narrow size and shape distribution [11]. This let us apply the single "morphological trajectory" to alane powder.

The application of proposed model in the general form results in large number of fitted parameters. Some of them may become ill-conditioned. Therefore at first we used reduced forms of the model accounting for (1) nucleation and desorption and (2) nucleation and reaction at the interface as rate-limiting stages.

Data processing showed that the first option does not give acceptable fitting for any set of parameters. On the contrary second option gave us excellent fitting of isothermal and TDS-curves (Fig. 3a and b). Activation energy of the reaction at interface was estimated as 104 kJ/mol and pre-exponential factor $k_0 = (0.3 \div 4.8) \times 10^7$ cm/s. It was found also that transformation morphology depends on experiment conditions (Fig. 4): the higher is reaction temperature, the smaller quantity of new phase nuclei has time to appear. In TDS-experiments high temperature is reached quickly so it is typical for them 1–2 nuclei to form. Estimation of nuclei quantity was made by qualitative comparison of fitted "morphological trajectories" with model trajectories illustrated in Fig. 2b.

Obtained kinetic parameters were applied successfully to fitting TDS-traces of thermally activated [11] alane and ball-milled alane. In both cases E_{int} and k_0 were fixed, morphological parameters were being varied. For the BM alane we have taken into account size distribution in the manner described in [10].

4. Summary

- New approach of analysis of hydride decomposition kinetics is proposed operating integral morphological parameters as well as kinetic parameters.
- The limiting stage of alane decomposition is shown to be the reaction at interface with activation energy 104 kJ/mol.
- Transformation morphology depends on experiment conditions: the higher is reaction temperature, the smaller is quantity of new phase nuclei.
- Obtained parameters give also excellent fitting of
  - thermally activated alane and
  - ball-milled alane (taking into account size distribution).

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