



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.

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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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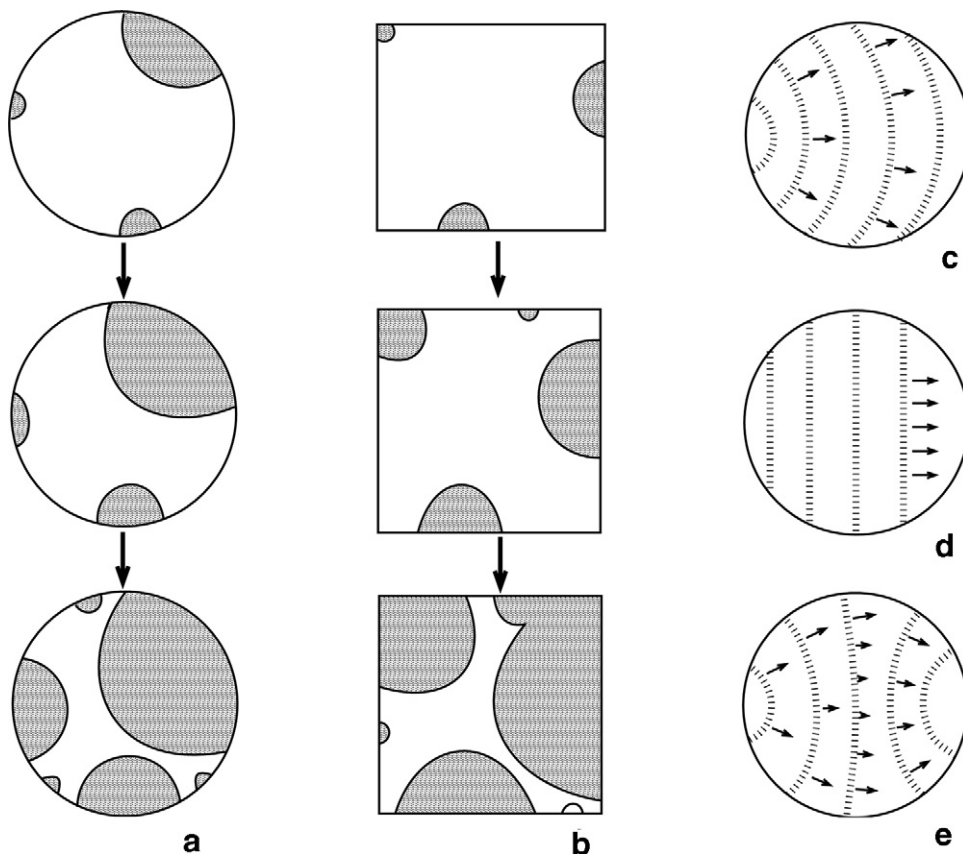


Fig. 1. Different shapes of particle (a – sphere; b – cube) and interface (c – sphere; d – flat; e – convex-concave) considered in the paper.

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 $\beta \rightarrow \alpha$ 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}_α 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

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

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

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

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-

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