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Decomposition kinetics of metal hydrides: Experiments and modeling

I.E. Gabis [a,*], I.A. Chernov [b], A.P. Voyt [a]

[a] Saint-Petersburg State University, Department of Physics, Saint-Petersburg 198504, Russia
[b] Institute of Applied Math Research, Karelian Research Centre, RAS, Petrozavodsk State University, 185910 Petrozavodsk, Russia

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ABSTRACT

The aim of the research was to understand decomposition of hydrides of metals and determine the most significant limiting reactions. We used functions that describe real physical processes, such as decomposition of hydride phase, desorption and diffusion of hydrogen, and morphology of phases. Dividing hydride materials to two classes depending on the type of bonding (metallic or non-metallic) allowed to explain details of kinetics of dehydriding. We show that for decomposition of non-metallic hydrides morphology of "nucleation and growth" is typical; while for metallic ones the "shrinking core" morphology is more common. In both cases hydrogen diffuses from the hydride-metal boundary to the outer surface through the metal phase rather quickly, so diffusion does not influence on the decomposition kinetics. The most probable limiting factor is the rate of hydrogen desorption from the metal phase. For the "shrinking core" morphology rate of hydride decomposition can also influence on the kinetics during the final stages of the process.

1. Introduction

Decomposition (as well as formation) of hydrides of metals is a complex process with numerous elementary reactions influencing on its rate. The aim of this paper is to reveal general facts about hydride decomposition and to determine which elementary reactions are most significant. Our approach is based on modeling of hydrogen evolution using physically reasonable processes, oppose to the Avrami–Erofeev approach.

Detailed models of hydriding and dehydriding that contain almost all possible elementary reactions exist, e.g. [1–3]. Although useful in general, they are hardly suitable for the stated problem, because it is difficult to estimate the role of each reaction by fitting experimental data. Complexity of models must conform that of experimental results, because models are tested by their ability to fit experimental curves well and to evaluate parameters that have physical meaning.

Additional difficulty is the diversity of properties of metal hydrides, including different chemical bonding (from metallic to ionic, including ion-covalent and covalent). Thus some hydrides are metals themselves, while other (called ion-covalent below) are semiconductors. We show that such conventional differentiation to metallic and non-metallic hydrides based on type of chemical bonding allows satisfactory systematization of various properties of hydrides decomposition. For all described models we evaluated their parameters. However, we do not discuss them here, focusing our attention on adequacy of the models themselves.

2. Hydrogen interaction with metals and semiconductors

Our study relies on the following statement: hydrogen diffusion in metals and desorption from metal's surface is much quicker compared to semiconductors. In 1980s and 1990s numerous studies showed that gas of free electrons is very important for adsorption and desorption of hydrogen, providing their high rates on metals (see e.g. [4,5]).

Hydrogen interaction with semiconductors is less studied due to low rates of adsorption and desorption naturally explained by low concentrations of free charge carriers. Articles [6,7] illustrate this: the barrier of dissociative adsorption for oxide is much higher (2.2 eV) compared to metal (0.7–0.8 eV). MgO is a semiconductor [8] with band gap about 8 eV [9,10].

Similarly, diffusion in metals is also quick due to, in particular, flexibility of the crystal structure also related to high concentration of free electrons. Experimental data are available in reference books, e.g. [11]. Diffusion in non-metals is less studied compared to metals. A few widely used materials are an exception; e.g. silicon, see the survey [12]. Diffusivity in silicon is 3–6 orders of magnitude less than in metals. Note that rate of diffusion increases as concentration of free charge carriers does.

The article [13] is the only one we know about that compares diffusion in metallic magnesium and its dihydride; it shows that diffusivity in the hydride is approximately three orders less, while its activation energy is significantly higher.

The third reaction that can potentially influence on kinetics of metal hydride decomposition, is decomposition itself at the metal-hydride boundary. We have no a priori information about its rate. In case of metallic hydrides two metals are contacting at

* Corresponding author.
E-mail address: igor.gabis@gmail.com (I.E. Gabis).

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the phase boundary; generally speaking, rate of hydrogen transport through it can be high and be accompanied by insignificant moves of metal ions (Bain deformation). Less is known about non-metallic hydrides; however, higher rate of hydride decomposition in this case seems unlikely.

So, the presented models contain up to three possibly limiting processes: diffusion, desorption, and hydride decomposition. Desorption flux density is described as $b(T)c^2$ where c is hydrogen concentration in the given phase near the surface. Diffusion is described by the Fick equations with diffusivity $D(T)$. There are no common dependencies for the hydride decomposition rate; constant $k(T)$ or linear function $k(T)(1-c/\bar{c})$ (with respect to hydrogen concentration c near the phase boundary) seem reasonable as the first approximation. The temperature dependencies are all Arrhenius.

3. Experiments and modeling

Experiments were held in the Sieverts-type apparatus with mass-spectrometric analysis of desorbing gases [14]. Special attention was paid to temperature control of the samples. Experiments were either with constant sample's temperature or under linear heating. Phase morphology was determined using metallography and SEM.

Mathematical models are based on the conservation laws and expressions for elementary reactions. We take into account a few (but generally more than one) most significant reactions. Models are tested by their ability to fit series of experimental curves; this also allows evaluation of the model parameters, including kinetic constants of elementary reactions. The same kinetic constants for different curves is an additional argument for the model.

In the sequel we assume that the original (parent) phase that contains more hydrogen is either metal or semiconductor, while the other, growing phase is metal.

4. Experimental and theoretical results and discussion

4.1. Nucleation and morphology

First of all, the type of chemical bonding can influence on the nucleation rate and thus on the morphology of the new phase growth. Due to Section 2, desorption from the entire surface of the metal parent phase is fast, so many nuclei of the new phase appear (we do not consider passivation layers here) and later form a solid skin of the new phase; then the process continues in the "shrinking core" morphology. On the contrary, in case of ion-covalent hydrides due to slow (compared to metals) hydrogen desorption only a few nuclei appear relatively slow and seldom form a skin (see e.g. Fig. 4 in [15]). Fig. 1 schematically describes these morphologies. However, formation of the skin is also possible for ion-covalent hydrides, especially if nuclei are numerous, e.g. due to surface activation of dehydriding [16].

4.2. Diffusion

Keeping in mind the shrinking core morphology for metallic hydrides (Fig. 1a) we can state that diffusion way of hydrogen from the phase boundary to the outer surface is through metal. For ion-covalent hydrides both ways (through metal or semiconductor) are possible; however, due to Section 2, diffusion of hydrogen in the new metallic phase is quicker compared to the parent hydride; so the main diffusion flux of hydrogen from the phase boundary to the outer surface is also through the metallic phase.

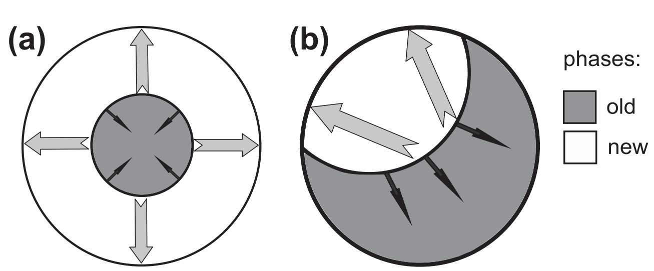

Fig. 1. "Shrinking core" (a) and "Nucleation and growth" (b) morphologies. Black arrows show the direction of growth, gray ones show the hydrogen diffusion path.

Hydrides of metals are fine powders with particles or fragments about 1–100 μm. Typical time of a TDS experiment or isothermal dehydriding is 10^3–10^5 s. If the mean diffusion path $L = 10$ μm, then the typical diffusion time $\tau = L^2/D$ for e.g. magnesium at 400 °C [11] is $\tau = 0.03$ s. This means that gradient of concentration of hydrogen dissolved in metallic magnesium is very low, while its diffusion is fast, so it hardly can significantly influence on the total rate of hydrogen evolution. Comparing models with and without diffusion applied to YH_3 decomposition showed that hydrogen diffusion in metal is quick and has no influence on the fitting. All this does not mean that diffusion in the metal phase can never influence, but its role seems negligible.

4.3. Desorption and/or hydride decomposition

The choice here is more difficult and sometimes hardly possible. Firstly we consider decomposition of non-metallic hydrides MgH_2 [15] and AlH_3 [17].

Decomposition of MgH_2 had the morphology of growth of a few separate nuclei, with no shrinking core. TDS curves for different heating rates against temperature have coinciding front parts; this means that hydride decomposition is limited by hydrogen desorption from the outer surface. The model [15] describes growth of a single round nucleus of metal in the spherical particle (Fig. 1b) with hydrogen desorption from metallic magnesium. Reacted fraction time dependence follows from the balance equation under the assumption of constant concentrations. Size distribution of the powder particles is taken into account.

In [17] devoted to AlH_3 decomposition, fitting by two models (with one of the limiting factors each) is compared. Experimental results for constant temperature and linear heating were fitted by the morphological trajectory method that describes growth of the new phase by dependence between its volume and surface area. Constant velocity of metal-hydride boundary at constant temperature is concluded. This shows that reaction of decomposition of AlH_3 is limiting; however another interpretation [18] is possible: as generated metallic aluminum is porous (Fig. 7b in [19]), hydrogen desorbs almost directly from the phase boundary (through the open pores). So total area of the desorbing surface is similar to that of the phase boundary and desorption from Al can be important. Final choice now is hardly possible.

For hydrides with metallic type of bonding shrinking core morphology is typical (see Fig. 1a).

Desorption as the limiting factor means that concentration in the solid solution is maintained equilibrium (with respect to hydride) due to hydride decomposition, so its rate completely depends on desorption. Conservation law yields the model (applied to ErH_2 in [20])

$$(c_h - c_m)\dot{V}_h = -b(T)c_m^2 S, \quad V_h > 0,$$
$$V\dot{c}_m = -b(T)c_m^2 S, \quad V_h \equiv 0.$$

Here and below V_h is the hydride phase volume, $\bar{c}_h, \bar{c}_m, c_h, c_m$ are equilibrium and current concentrations in hydride and metal, S and V are for surface area and volume of the particle, dot means d/dt. As soon as $V_h = 0$ (no hydride phase), the final degassing begins. Desorption flux density curves grow (if b does), then decrease, forming the special spike (e.g. curve 1 in Fig. 2a. Experimental curves (circles in Fig. 2a) have no spike; however, for a powder of particles of different sizes the curve is smooth. Note that the particles' shape does not affect the results, only the surface area does. However, in case of the shrinking core rate of hydrogen desorption