Kinetics of first-order phase transitions initiated by diffusion of particles from the surface into the bulk

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The kinetic equations are formulated and solved to describe a first-order phase transition initiated by diffusion of particles from the surface into the bulk. The scenario of phase transformation is assumed to involve the following three stages. At first, the particles diffuse in the bulk almost freely because the grain concentration is low. Then, with increasing grain concentration, the particles are trapped predominantly near the interface and the space distribution of particles shifts to the interface. Finally, the dense phase formed near the interface blocks diffusion of particles from the interface into the bulk and prevents further uptake. General results are used to interpret the experimental data on the hydrogen uptake by Pd-coated Mg at low temperatures. In this system, the asymptotic hydrogen uptake as a function of time decreases with increasing hydrogen pressure. This unusual feature of the hydrogen uptake is shown to be qualitatively explained by hydride nucleation and growth near the Pd/Mg interface.

I. INTRODUCTION

The kinetics of first-order phase transitions in the bulk and on the surface of solids is well studied.[1-4] The classical result in this field has been derived by Lifshitz and Slyozov.[5] Their theory describes the size evolution of grains of the dense phase in a sea of the dilute phase. Larger islands are assumed to grow at the expense of smaller ones. The growth mechanism involves three-dimensional (3D) evaporation and condensation, and diffusion. The growth law predicted for the average grain radius is $R(t) \sim t^{1/3}$. The original Lifshitz-Slyozov treatment is applicable in the limit of small concentration of

grains (i.e., near the coexistence curve). There have been efforts[6] to extend the theory to finite concentration of grains (i.e., to the unstable spinodal region). There is agreement that the Lifshitz-Slyozov growth law is applicable to the latter case as well.

In the present paper, we will analyze another scenario of a first-order phase transition. In particular, we will assume the bulk phase transformation to be initiated by the flux of particles from the surface (see, e.g., Fig. 1). At the initial stage, the particles diffuse in the bulk almost freely because the grain concentration is low. At the intermediate stages, with increasing grain concentration, the particles are trapped predominantly near the interface, and the space distribution of particles shifts to the interface. At the late stage, the dense phase formed near the interface blocks diffusion of particles from the interface into the bulk and prevents further uptake. The detailed analysis of this scheme of phase transition by itself is a fundamental problem in physical kinetics. In addition, this analysis is also of practical interest.

II. HYDROGEN UPTAKE BY Pd-COATED Mg AT LOW TEMPERATURES

To motivate our study more deeply, we will consider the hydrogen uptake by magnesium. This process is important for technological applications connected with hydrogen storage.[7] At sufficiently high temperatures and pressures, magnesium reacts with hydrogen to form MgH_2 but at moderate temperatures the hydrogen uptake is slow because of an activation barrier for hydrogen dissociation, and partly due to the low mobility of hydrogen in magnesium hydride. In particular, temperatures higher than 500 K are customarily required to overcome the potential barrier that prevents hydrogenation.[8] However, the hydrogen uptake by Mg may occur effectively
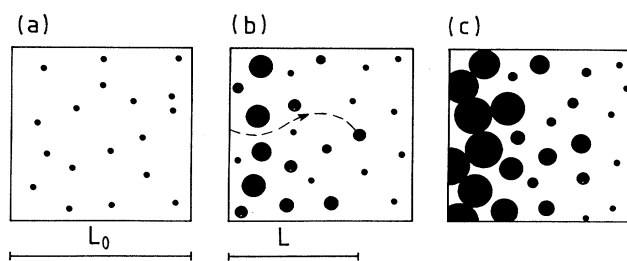
FIG. 1. Schematic picture of hydride formation initiated by hydrogen diffusion into Pd-coated Mg. Diffusion occurs from the left-hand side of the sample. At the initial stage (a) when the grain concentration is low, small hydride grains and hydrogen atoms are distributed randomly in the space. At the intermediate stage (b), the space distribution of hydride grains is shifted to the Pd/Mg interface (the dashed line shows diffusion of hydrogen atom from the Pd/Mg interface and trapping of this atom at the distance L). At the final stage (c), diffusion of hydrogen atoms from Pd to Mg is blocked by hydride grains located near the Pd/Mg interface.

even at relatively low temperatures if the surface of the Mg film is modified by deposition of a thin palladium layer. Employing this procedure, we have produced[9–12] samples having the surface characteristics of palladium, i.e., a high dissociation rate and fast transport of hydrogen, but the bulk properties of magnesium (the thicknesses of the Pd and Mg layers were 5–20 and 380–910 nm, respectively). These samples made it possible to study[9–12] the hydrogen uptake by Mg in the temperature range 260–400 K and in the pressure range 0.03–30 Torr, i.e., at 10^3–10^5 times lower pressures than previously reported.[8]

In particular, Fig. 2 shows the saturation uptake as a function of temperature at two different pressures, 0.062 and 0.51 Torr. Each experimental point corresponds to saturation at constant temperature of a freshly deposited or a fully dehydrided sample. At low temperatures, the saturation uptake is much smaller than the expected equilibrium value and has the pressure dependence shown in Fig. 3. The uptake is seen to *decrease* with increasing pressure. This unusual behavior was attributed to nucleation and growth of a hydride at the Pd/Mg interface, which prevents further uptake, since hydrogen diffusion through the hydride is slow. The interface hydride formation has been verified and investigated by hydrogen depth profiling.[10]

As a function of temperature, the saturation uptake increases until a maximum is reached (Fig. 2), and then decreases rapidly. The maximum corresponds to the transition from kinetic to thermodynamic control. At temperatures above the maximum, an interface hydride is no longer formed and the equilibrium can be established between the gas and solid phases.[11]

An attempt to interpret the unusual pressure dependence of the hydrogen uptake by Mg at low temperatures has been made in Ref. 13. The model employed in Ref. 13 is based on the assumption that the hydrogen diffusion is slow at all hydrogen concentrations in Mg, i.e.,
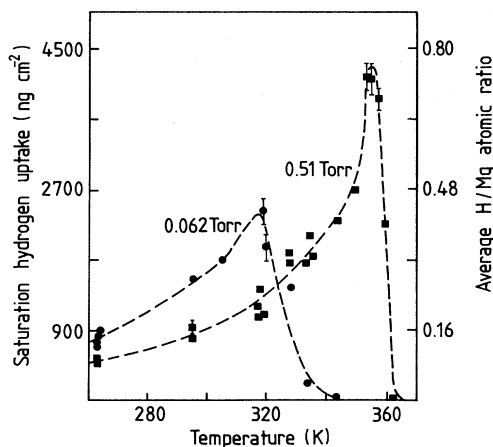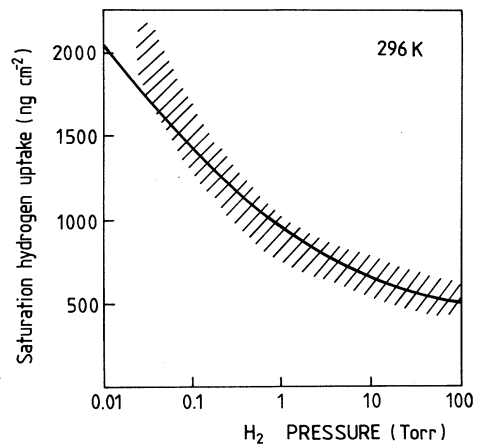

FIG. 3. Saturation hydrogen uptake as a function of pressure at $T = 296$ K. The hatched area, experimental data; the solid line, Eq. (28) [the parameters in Eq. (28) have been chosen so that $U_{tot} = 950$ ng/cm^2 at $P = 1$ Torr].

$D \ll L_0^2/\tau$, where D is the hydrogen diffusion coefficient, L_0 the width of the Mg film, and τ the characteristic time of the hydrogen uptake. The latter condition does not correspond, however, to the H/Mg system, because hydrogen diffusion in the dilute α phase was found to be fast.[12,14] In the present paper we therefore propose a modified model to explain the pressure dependence of the hydrogen uptake by Mg. The latter model is based on a more realistic assumption that the hydrogen diffusion is rapid, i.e., $D \gg L_0^2/\tau$.

III. GENERAL EQUATIONS

The hydrogen uptake by Mg at relatively low temperatures is a rather complex phenomenon from a theoretical point of view because in this case the transient hydrogen diffusion is accompanied by hydride formation (Fig. 1). Nevertheless, employing reasonable physical assumptions and simplifications, it is possible to obtain an analytical solution to the problem. In particular, we will assume an equilibrium between hydrogen in the gas phase and in the Pd overlayer. In addition, the hydrogen diffusion from the Pd overlayer to the Mg film will be assumed to be irreversible and, consequently, the diffusion flux through the Pd/Mg interface to be proportional to the hydrogen concentration in Pd. Thus, at low pressures, the diffusion flux should be proportional to the square root of the gas-phase pressure, $\mathcal{J} \sim \sqrt{P}$. This dependence, however, does not hold with increasing pressure because of the hydrogen-hydrogen interactions in Pd. In particular, the analysis of the experimental data[10] shows that at $P \simeq 1$ Torr, the diffusion flux through the Pd/Mg interface is approximately proportional to the pressure:

$$\mathcal{J} = AP , \tag{1}$$

and, accordingly, the time dependence of the hydrogen uptake will be

$$U(t) = \mathcal{J}t = APt . \tag{2}$$

FIG. 2. Saturation hydrogen uptake by Pd-coated Mg as a function of temperature at $P = 0.062$ and 0.51 Torr. Near the maxima, the uptake changes from being kinetically limited due to the interface hydride formation to being in a thermodynamic equilibrium at temperatures above maxima.

Equation (2) is correct for the initial and intermediate stages of hydride formation, when the hydride grains in Mg do not significantly block the hydrogen diffusion from Pd to Mg [Figs. 1(a) and 1(b)]. These stages are of particular interest because they make up the dominant contribution to the total hydrogen uptake. The latter can be written as

$$U_{tot} = \mathcal{J}\tau = AP\tau \ , \tag{3}$$

where τ is the characteristic time of the hydrogen uptake.

To calculate τ, we should consider in detail the hydride formation in Mg which occurs via nucleation and grain growth. The kinetics of such first-order phase transitions is described by analyzing the time evolution of the grain-radius distribution due to the evaporation and condensation processes in analogy with the Lifshitz-Slyozov theory.[5,15] The latter is, however, rather cumbersome even if one has no diffusion flow from the surface to the bulk. To simplify our analysis, we will consider the simplest mechanism of nucleation, i.e., we will assume that nucleation is a result of two-particle "collisions" of hydrogen atoms. These "collisions" are affected by long-range hydrogen-hydrogen interactions arising from the deformation of the Mg lattice by hydrogen atoms. Thus the effective hydrogen radius characterizing "collisions" may be quite different compared to the geometric radius. In addition, we will assume that the grain formation is irreversible (i.e., evaporation of hydrogen atoms from grains is neglected). The latter assumption corresponds to the low-temperature limit and is supported by the phase diagram for the H/Mg system described in Ref. 12. (From the hysteresis in the plateau pressures for Mg-hydride formation and decomposition, respectively, it was deduced[12] that the enthalpy of hydride formation is more exothermic than the hydride decomposition enthalpy by about 11 kJ/mol H_2.)

For the initial stages, when the grain concentration is low [Fig. 1(a)], we will employ the following kinetic equations describing the hydride formation

$$dn/dt = \mathcal{J}/L_0 - 2k_0 n^2 - k_1 n_1 n \ , \tag{4}$$

$$dn_1/dt = k_0 n^2 \ , \tag{5}$$

where n is the concentration of hydrogen atoms in Mg, and n_1 the grain concentration. The first term in the right-hand part of Eq. (4) describes the flux of hydrogen atoms into the Mg bulk. This term is derived assuming the hydrogen diffusion to be rapid and hydrogen atoms to be distributed randomly in the space [Fig. 1(a)]. The second term in Eq. (4) takes into account the grain formation due to "collisions" of hydrogen atoms (k_0 is the corresponding rate constant). The third term describes trapping of hydrogen atoms by grains (k_1 is the average rate constant for this process).

With increasing time, the concentration of hydrogen atoms and the grain concentration will increase, and the probability will then be low for hydrogen atoms to diffuse from the Pd/Mg interface into the Mg bulk without being trapped. In other words, the space distribution of hydrogen atoms will not be random any more [Fig. 1(b)], but instead it will be shifted to the Pd/Mg interface. The

latter fact can be taken into account as follows.

Let us consider that a hydrogen atom starts to diffuse from the Pd/Mg interface. An average squared diffusion length during time δt is known to be

$$L^2 = D\delta t \ . \tag{6}$$

On the other hand, the average lifetime of hydrogen atoms is $\delta t = 1/(k_0 n + k_1 n_1)$. Substituting the latter expression into Eq. (6), we obtain an average diffusion length at given concentrations n and n_1

$$L = [D/(k_0 n + k_1 n_1)]^{1/2} \ . \tag{7}$$

If $L < L_0$, we can replace L_0 in Eq. (4) by L. Thus, we will have

$$dn/dt = \mathcal{J}/L - 2k_0 n^2 - k_1 n_1 n \ . \tag{8}$$

The latter equation is correct for $x \leq L$ ($x = 0$ corresponds to the Pd/Mg interface). In this region, hydrogen atoms are assumed to be distributed more or less randomly. The concentration of hydrogen atoms at $x > L$ is less than that at $x < L$. Note that L decreases with increasing time. Thus, as already pointed out, the distribution of hydrogen atoms will gradually shift towards the Pd/Mg interface.

With increasing time, hydrogen atoms will predominantly be trapped by grains, and consequently we will ignore the terms $k_0 n$ in Eq. (7) and $2k_0 n^2$ in Eq. (8), i.e.,

$$dn/dt \simeq \mathcal{J}(k_1 n_1/D)^{1/2} - k_1 n_1 n \ . \tag{9}$$

The lifetime of hydrogen atoms is short compared to the characteristic time of the hydrogen uptake. For this reason, we can solve Eq. (9) in the steady-state approximation, i.e.,

$$n^2 \simeq \mathcal{J}^2/k_1 n_1 D \ . \tag{10}$$

Substituting expression (10) into Eq. (5) yields

$$dn_1/dt = k_0 \mathcal{J}^2/k_1 n_1 D \ . \tag{11}$$

The average rate constant k_1 for trapping of hydrogen atoms by grains is time dependent because the grain size increases with increasing time. Thus, to solve Eq. (11), we must obtain the equations describing the time dependence of k_1. The form of these equations is dependent on the mechanism of hydride formation. We will assume that the grain formation and trapping are limited by hydrogen diffusion. In this case, the rate constants k_0 and k_1 can be represented as

$$k_0 = 4\pi D R_0 \tag{12}$$

and

$$k_1 = 4\pi D R_1 \ , \tag{13}$$

where R_0 is the effective radius of hydrogen atoms, and R_1 the average radius of grains.

Taking into account that the diffusion flow to the grain with the radius R is $4\pi R D n$, we obtain the following equation for the grain radius

$$n_0 R \, dR/dt = Dn \ , \tag{14}$$

where n_0 is the concentration of hydrogen atoms in hydride. If a given grain starts to grow at time t', its radius at time t, according to Eq. (14), will be

$$R(t,t') = \left[\frac{2D}{n_0} \int_{t'}^{t} n(t'')dt'' \right]^{1/2} . \tag{15}$$

The number of grains formed during the time interval from t' to $t'+dt'$ is $k_0 n^2(t')dt'$ [see Eq. (5)], and consequently the average grain radius can be represented as

$$R_1(t) = \int_0^t R(t,t')k_0 n^2(t')dt'/n_1(t) . \tag{16}$$

Substituting expressions (12) and (13) into Eqs. (10) and (11), we have

$$n^2 \simeq \mathcal{F}^2/4\pi R_1 n_1 D^2 \tag{17}$$

and

$$dn_1/dt = R_0 \mathcal{F}^2/R_1 n_1 D . \tag{18}$$

Equations (15)–(18) form a basis for describing the hydride formation. To solve these equations, we will use the iteration method based on the fact that the time dependence of R_1 is rather weak. In the first step, we neglect the latter dependence, i.e., integrating Eq. (18) we assume $R_1(t) \simeq$ const. In this case Eq. (18) yields (to simplify designations, we omit all the numerical factors)

$$n_1 \simeq (R_0 \mathcal{F}^2 t/R_1 D)^{1/2} . \tag{19}$$

Substituting Eq. (19) into Eq. (17) yields

$$n^2 \simeq \mathcal{F}/(R_0 R_1 D^3 t)^{1/2} . \tag{20}$$

In the second step, we can approximately calculate the time dependence of R_1. In particular, substituting Eq. (20) into Eq. (15), we have

$$R(t,t') \simeq \left[\frac{\mathcal{F}^{1/2}D^{1/4}}{n_0(R_0 R_1)^{1/4}} (t^{3/4} - t'^{3/4}) \right]^{1/2} . \tag{21}$$

Then, substituting Eqs. (20) and (21) into Eq. (16) yields

$$R_1(t) \simeq \left[\frac{\mathcal{F}^{1/2}D^{1/4}t^{3/4}}{n_0(R_0 R_1)^{1/4}} \right]^{1/2}$$

or

$$R_1(t) \simeq \left[\frac{\mathcal{F}^2 D t^3}{n_0^4 R_0} \right]^{1/9} . \tag{22}$$

The total volume of grains is defined as (we omit the factor $4\pi/3$)

$$V(t) = n_1 R_1^3 . \tag{23}$$

Substituting Eqs. (19) and (22) into Eq. (23), we obtain

$$V(t) \simeq \left[\frac{\mathcal{F}^7 R_0 t^6}{D n_0^5} \right]^{2/9} . \tag{24}$$

The characteristic time of the hydrogen uptake may be estimated using the condition

$$V(\tau) \simeq 1 , \tag{25}$$

i.e., considering that the total volume defined by Eq. (24) is equal to the unit volume. Employing Eqs. (24) and (25), we obtain

$$\tau \simeq (D n_0^5/\mathcal{F}^7 R_0)^{1/6} . \tag{26}$$

Accordingly, the total hydrogen uptake [Eq. (3)] can be represented as

$$U_{\text{tot}} = (D n_0^5/\mathcal{F} R_0)^{1/6} , \tag{27}$$

or, taking into account expression (1),

$$U_{\text{tot}} = (D n_0^5/APR_0)^{1/6} . \tag{28}$$

The latter equation is the main result of our analysis.

It is also of interest to calculate the concentration profile of hydrogen in Mg. According to our model, the time dependence of the total hydrogen concentration at distance x is described by [cf. Eq. (8)]

$$dn_{\text{tot}}/dt = \begin{cases} \mathcal{F}/L(t) & \text{at } x < L(t) , \tag{29} \\ 0 & \text{at } x > L(t) . \tag{30} \end{cases}$$

Ignoring the term $k_0 n$ in Eq. (7), we have $L(t) \sim 1/(k_1 n_1)^{1/2}$. In addition, according to Eqs. (19) and (22), we obtain $n_1(t) \sim t^{1/3}$. Taking also into account (13) and (22), we have $k_1(t) \sim R_1(t) \sim t^{1/3}$. Thus,

$$L(t) \sim 1/t^{1/3} . \tag{31}$$

Substituting Eq. (31) into Eq. (29) and integrating, we derive

$$n_{\text{tot}}(t) \sim t^{4/3} . \tag{32}$$

According to Eqs. (30) and (31), the increase in the total hydrogen concentration at distance x stops at $t \sim 1/x^3$. Substituting the latter relationship into Eq. (32), we get the concentration profile of hydrogen at $t \to \infty$,

$$n_{\text{tot}}(x) \sim 1/x^4 . \tag{33}$$

Above, we have assumed that the grain growth is limited by hydrogen diffusion. In principle, this process may be kinetically limited. In the latter case, the rate constant for trapping of hydrogen atoms by grains is proportional to the squared grain radius, $k_1 \sim R_1^2$ [cf. Eq. (13)]. Taking into account this fact and carrying out the same transformations as above, we have

$$U_{\text{tot}} \sim 1/\mathcal{F}^{1/9} , \tag{34}$$

or, employing (1),

$$U_{\text{tot}} \sim 1/P^{1/9} . \tag{35}$$

Equations (28) and (35) are derived assuming that nucleation is a result of two-particle "collisions" of hydrogen atoms. The same approach, however, can be used for analyzing the uptake kinetics in the case of many-particle nucleation. By increasing the order of nucleation, the pressure dependence of the total uptake will be stronger (we will not consider this problem in detail).

IV. CONCLUSION

We have formulated a model which takes into account the effect of hydride formation on the hydrogen uptake

by Pd-coated Mg. The model predicts that the total hydrogen uptake should be in inverse proportion to H_2 pressure to the power 1/6 [Eq. (28)]. This prediction is in good qualitative agreement with the experimental data (see Fig. 3). Quantitatively, however, Eq. (28) somewhat underestimates the decrease in the hydrogen uptake with increasing pressure.

According to Eq. (28), the dependence of the total hydrogen uptake on the temperature is connected with the temperature dependence of D and A (n_0 and R_0 are expected to be independent of temperature). The activation energy for hydrogen diffusion in Mg is low, $E_a \simeq 4.6$ kcal/mol. The decrease in the factor A with increasing temperature is not strong. In addition, the exponent in Eq. (28) is low. Thus, the temperature dependence of the total hydrogen uptake should be weak. This conclusion is in agreement with the low-temperature experimental data (the apparent activation energy of the hydrogen uptake at low temperatures is about 3.5 kcal/mol).

The concentration profile of hydrogen in Mg has been studied in detail in Ref. 10. Comparing the experimental data with Eq. (33), we can conclude that the latter equation describes rather accurately the decrease in the hydrogen concentration with increasing x.

Finally, it is reasonable to recall briefly the shortcomings of our model: (i) nucleation is assumed to be a result of two-particle "collisions" of hydrogen atoms. (ii) The grain formation and growth are assumed to be irreversible. (iii) The possible overlapping of grains is neglected. (iv) The reaction rate constants for grain formation and trapping near the Pd/Mg interface are assumed to be the same as in the bulk of Mg (in reality the grain formation near the interface may be thermodynamically more favorable than in the bulk due to differences in lattice strain, defect densities, etc.). A more advanced approach should of course take into account the above mentioned factors. We expect, however, that all these factors are not too important. At least, they do not change the main qualitative prediction obtained with the present model (a decrease of the total uptake with increasing pressure). The latter prediction may be important not only for the H/Mg system but also for other H/metal systems.

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