



THE HYDRIDING KINETICS OF MnNi_5 —I. DEVELOPMENT OF THE MODEL

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Abstract—The hydriding kinetics of hydrogen storage materials in the two-phase regions have been studied. It is believed that the hydriding process is best classified into three steps: dissolution of hydrogen into the alloy or its hydride; diffusion of hydrogen atoms through the alloy or its hydride phase; and nucleation and growth of β -hydride (hydride depositing from supersaturated α -solid solution). Kinetics equations have been derived for the cases when one of the three steps is the rate-determining step. Copyright © 1996 International Association for Hydrogen Energy

NOMENCLATURE

| | | | |
|------------------------------------|---|---|---|
| C_1 | Concentration of heterogeneous nucleation sites | K'_0 | Coefficient |
| $C_{\alpha\text{H}}$ | Hydrogen concentration of α phase equilibrating with P_0 | M | Mobility of the boundary |
| $C_{\beta\alpha}, C_{\alpha\beta}$ | The hydrogen concentration of the β - or α -hydrogen equilibrating with P_{eq} at the interface between the α - and β -phase | m | Number of particles |
| $C_{\beta\text{H}_i}$ | Concentration of hydrogen on the outer side of the surface | N_0 | Number of sites in unit volume |
| D_α, D_β | Diffusion coefficient of hydrogen atoms in α - and β -phase | n' | Constant, depending on the nucleation rate, the growth rate and the shape of the hydride |
| ΔG_n | Activation energy for atomic migration per alloy atom | P_{eq} | Equilibrium pressure |
| $\Delta G^*, P_a$ | Nucleation barrier | $P_{\text{H}_2, i}$ | Hydrogen pressure at the outside surface of sample |
| ΔG | Total free energy change in $\alpha \rightarrow \beta$ phase transformation | P_0, P_{H_2} | Applied hydrogen pressure |
| ΔG_m | Difference of free energy per mole between α - and β -phase | r_0 | Radius of the material particle |
| ΔG_n | Misfit strain energy per mole of β -phase | T_0 | Hydriding temperature |
| ΔG_d | Free energy released in the β -phase growth due to the destruction of a defect | t | Reaction time |
| K_1, K_2 | Reaction rate constants | X | Ratio of hydrogen concentration at any time to saturate hydrogen concentration equilibrating with P_0 |
| K_0 | Ratio of active area to the total area of the sample surface | X_β | β -phase transformed fraction |
| K_i | Constant, representing the degree of constraint in the hydrogen activity | a | Distance between two neighbouring atoms |
| K_s | Rate constant for hydrogen transition from the surface to the matrix | θ | Ratio of the area absorbing hydrogen to the active area |
| K_R | $= \frac{\sqrt{K_1}}{\sqrt{K_2} + \sqrt{K_1 P_{\text{H}_2, i}}}$ | ω | A factor including the vibration frequency of the atoms and the area of the critical nucleus |
| K' | constant $\left(= \frac{C_{\alpha\beta}}{C_{\beta\alpha}} \right)$ | $\frac{dn}{dt}, \frac{dX}{dt}, \frac{dX_\beta}{dt}$ | The hydriding rate |

1. INTRODUCTION

Many kinetics studies on hydrogen-hydrogen storage alloys system have been made in recent years. However, there are big disparities both in experimental results and in theoretical analyses. Rudman [1] proposed that hydriding was a phase transformation process which could be described by nucleation and a growth model (Johnson-Mehl-Avami equation). But Suda [2-4] and his coworkers regarded hydriding as a complex gas-solid chemical reaction and proposed a hydriding kinetic

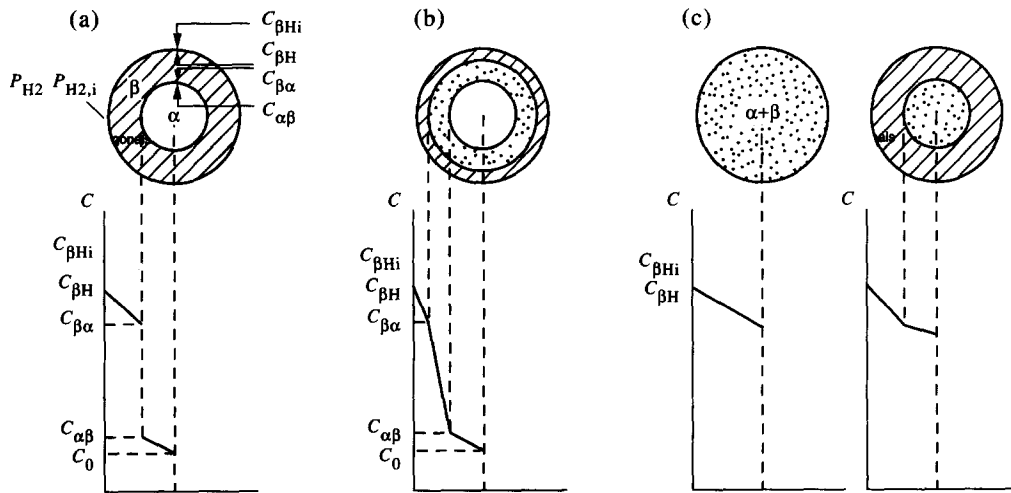


Fig. 1. Model of hydriding kinetics, (a) model with no two-phase ($\alpha + \beta$) region (continuous moving boundary), (b) model with a definite width of $\alpha + \beta$ two-phase region, (c) model of entirely two-phase ($\alpha + \beta$) region in its initial and later stages, respectively.

model derived from the chemical reaction kinetics. Based completely on reasoning and analysis, Park and Lee divided the process into six steps, which were simplified by Nahm [5] into three steps: the dissociative chemical absorption of hydrogen on the surface, the diffusion of the hydrogen atoms through the β -phase hydride and the chemical reaction of the hydrogen atoms with the α -phase at its interface between the β -hydride and unreacted core. He reported that the shrinking unreacted core model best fitted his kinetic study data. Two points in Nahm's three step model are worth discussing. (1) In his dissociative chemisorption, the diffusion of hydrogen from the outside of the surface to the inside of the hydride, i.e. the boundary transition, was not included in his three steps. When the hydrogen pressure is high, the rate of boundary transition is usually slower than the rate of dissociative chemisorption. So the boundary transition step should not be neglected in hydriding. The dissociative chemisorption together with the boundary transition is just the dissolution process of hydrogen. (2) $\alpha \rightarrow \beta$ is a phase transformation process. The hydriding rate must be described by phase transformation kinetics, not by chemical reaction kinetics. As the α -phase is one solid solution and β is another hydride-based solid solution, the $\alpha \rightarrow \beta$ phase transformation is actually deposition of the β -phase from supersaturated α -solid solution. In this paper, we propose a new hydriding kinetic model. In our model, the hydriding process is divided into: (1) the dissolution of hydrogen in the alloy (or its hydride); (2) hydrogen diffusion through the alloy (or its hydride); (3) phase transformation (β -hydride depositing from supersaturated α -solid solution).

2. HYDRIDING PROCESS

The hydriding process of the LaNi₅ system alloy is described as follows: First, hydrogen atoms are chemisorbed at the surface of the alloy under pressure,

and then transmitted from the surface to the matrix. As the hydrogen dissolution in the alloy proceeds, the α -solid solution is first formed and then gradually supersaturated with hydrogen in its surface region. The β -hydride starts to deposit from the supersaturated α -solid solution. Three cases may occur according to the readiness of β -phase nucleation in the α -matrix. (i) The nucleation of the β -phase in the α -matrix is easy and fast. When non-equilibrium defects such as excess vacancies, dislocations, grain boundaries, stacking faults and inclusions, all of which increase the total free energy, exist in the α -phase and when the volume expansion caused by phase transformation is low, a large amount of β -nuclei will occur at once on the outside of particles under low hydrogen supersaturation, then the β -phase grows and forms a continuous layer quickly. Here the β -phase with the most favorable orientation will grow slightly ahead of its neighbours. Thus it can be expected to encroach gradually on the domain of neighbours as its growth proceeds (Fig. 1a). In this case, the two-phase coexisting region is zero, it is similar to the case described by the continuous moving boundary model. The only difference is that the β -phase is considered as depositing from supersaturated α -solid solution in our phase transformation model, while the β -phase is considered as being formed by the chemical reaction of hydrogen atoms with the α -phase in a continuous moving boundary model (or shrinking unreacted core model). The increase in thickness of β -layers is the result of β -phase growth. (ii) The nucleation of the β -phase is difficult and slow, but the growth of the β -phase is fast. When the nucleation of the β -phase is difficult, the region of hydrogen supersaturation becomes wide in the matrix. When the amount of hydrogen supersaturation reaches the critical value, the β -phase deposits in the supersaturation region simultaneously. Because the growth rate of the β -phase is quick and the amount of its nuclei in the outer part of the particle, where the

hydrogen supersaturation is higher than that in the inner portion, is larger, the β -phase forms a continuous outer layer quickly. The β -layer exists in the outer portion of the particle, the $\alpha + \beta$ -two phase region exists in the middle and the α -single phase in the center, respectively (Fig. 1b). As the high gradient of hydrogen concentration in the $\alpha + \beta$ coexisting region is caused by the different fractions between the α - and β -phase, not by the difference of hydrogen concentration in the α -phase (or β -phase), the diffusion of hydrogen from α - to β -phase is easier than diffusion only in the α -phase because of the short diffusion distance and large concentration gradient. Hence, as the diffusion of hydrogen from the surface to the center proceeds, the width of the β -phase increases and the width of the $\alpha + \beta$ -two phase region decreases. Finally the $\alpha + \beta$ -phase disappears and the pattern changes to the one in the first case. (iii) The nucleation and growth of the β -phase is difficult and slow. In this case, the β -phase will distribute throughout the matrix (Fig. 1c). Now the nucleation and growth of β -phase is the rate controlling step. But at the later stage, β -phase forms in the outer layer as the result of hydrogen diffusion (Fig. 1c). For all three cases mentioned above, after the β -phase transformation is completed the hydrogen will be continuously dissolved into the β -phase and then diffused into the inside of the matrix until the equilibrium hydrogen pressure of the β -phase is equal to the applied hydrogen pressure. In the first case, the rate equation of β -phase growth derived is similar to the rate equation based on the chemical reaction deduced by Nahm [5] when the strain caused by volume expansion of phase transformation is small and the defects are negligible, see Section 3.3. below. But in the second or third case, the hydriding rate can not be described properly by the kinetics of chemical reactions.

3. HYDRIDING KINETIC EQUATIONS

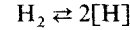
The hydriding process of the alloy in a single α -phase (or β -phase) can be divided into the following two steps: the dissolution of hydrogen in the α -phase (or β -phase) and the diffusion of hydrogen atoms through the α -phase (or β -phase). The same form of rate equation applies no matter whether the alloy is hydrided in a single α - or β -phase region. The only difference is that the coefficient depends on the physical properties, which change with the phase. However, for a hydriding process in the two-phase region, there are three steps, namely the dissolution of hydrogen, the diffusion of hydrogen and the nucleation and growth of β -phase. The process of hydriding of the hydrogen kinetics in a two-phase region is more general.

In order to develop the hydriding kinetic equation in a two-phase region, the following assumptions are made, (i) hydrogen storage particles are all of spherical shape with the same diameter, (ii) the number of spherical particles is m .

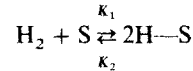
3.1. Dissolution of hydrogen into hydride

The dissolution of hydrogen into hydride can be

divided into two steps: (i) dissociative chemisorption of hydrogen, (ii) transition of hydrogen atoms through the surface boundary. The dissolution of hydrogen into hydride can be expressed as follows (see Fig. 1a):



(1) dissociative chemisorption of hydrogen on the outer surface:



(2) boundary transition: $\text{H} \rightleftharpoons [\text{H}]$.

The dissociative chemisorption rate can be written as [6]:

$$\frac{dn_c}{dt} = 4\pi r_0^2 m K_0 [K_1 P_{\text{H}_2} (1 - \theta)^2 - K_2 \theta^2]. \quad (1)$$

When P_{H_2} equals $P_{\text{H}_2, i}$, the rate of dissociative chemisorption $dn_c/dt = 0$. Therefore, when equilibrium is reached, θ becomes;

$$\theta = \frac{\sqrt{K_1 P_{\text{H}_2, i}}}{\sqrt{K_2} + \sqrt{K_1 P_{\text{H}_2, i}}}$$

Substitute θ into equation (1). The equation can be rewritten as,

$$\frac{dn_c}{dt} = \frac{4\pi r_0^2 m K_0 K_1 K_2}{[\sqrt{K_2} + \sqrt{K_1 P_{\text{H}_2, i}}]^2} (P_{\text{H}_2} - P_{\text{H}_2, i}). \quad (2)$$

3.3.1. *Boundary transition rate in hydride.* The concentration of hydrogen on the outer side of the surface can be expressed as

$$C_{\beta\text{H}_i} = K_0 \theta.$$

As the hydrogen storage alloy is a surface active material for hydrogen, some hydrogen atoms are held tightly by the alloy, only those hydrogen atoms with higher energy levels can diffuse into the interior. So the active hydrogen atoms participating in the boundary diffusion are only

$$C_{\beta\text{H}_{i\text{act}}} = K_1 K_0 \theta.$$

The boundary transition rate can thus be written as

$$\frac{dn_s}{dt} = 4\pi r_0^2 m K_s (K_1 K_0 \theta - C_{\beta\text{H}_i}).$$

Let

$$K_R = \frac{\sqrt{K_1}}{\sqrt{K_1 P_{\text{H}_2, i}} + \sqrt{K_2}},$$

and k_R can be expressed approximately as

$$K_R \approx \frac{\sqrt{K_1}}{\sqrt{K_2 + \sqrt{K_1 P_{eq}}}}$$

Now θ can be written as $\theta = K_R \sqrt{P_{H_2,i}}$.

$$C_{\beta H_{iact}} = K \sqrt{P_{H_2,i}}$$

where $K = K_0 K_1 K_R$. From this, we know that the hydrogen concentration of the β -phase changes with the pressure. The equilibrium pressure of the $\alpha \rightarrow \beta$ phase transformation is P_{eq} , so $C_{\beta\alpha}$, which is the hydrogen concentration of the β -hydride equilibrating with P_{eq} at the interface between the α - and the β -phase, can be written as

$$C_{\beta\alpha} = K \sqrt{P_{eq}}$$

When the dissolution is the rate controlling step of hydriding, that is, the diffusion of hydrogen and the $\alpha \rightarrow \beta$ phase transformation are quick, the concentration gradient of hydrogen within α and β can be ignored, then

$$C_{\beta H} = C_{\beta\alpha} = K \sqrt{P_{eq}}$$

So the boundary transition rate is

$$\frac{dn_s}{dt} = 4\pi r_0^2 m K_s K (\sqrt{P_{H_2,i}} - \sqrt{P_{eq}}) \quad (3)$$

Equation (2) can be written as follows:

$$\sqrt{P_{H_2,i}} = \sqrt{P_{H_2}} - \frac{dn_c}{dt} \frac{4\pi r_0^2 m K_0 K_1 K_2}{[\sqrt{K_2 + \sqrt{K_1 P_{H_2,i}}}]^2} \times (\sqrt{P_{H_2,i}} + \sqrt{P_{H_2}})$$

When the dissolution keeps a quasi-steady state,

$$2 \frac{dn_c}{dt} = \frac{dn_s}{dt} = \frac{dn}{dt} \quad (4)$$

Substituting $\sqrt{P_{H_2,i}}$ from equation (4) into equation (3), we obtain the dissolution rate of m spherical samples

$$\frac{dn}{dt} = 4\pi r_0^2 m K (\sqrt{P_{H_2}} - \sqrt{P_{eq}}) \left[\frac{1}{K_s} + \frac{K_1}{2K_2 K_R (\sqrt{P_{H_2}} + \sqrt{P_{H_2,i}})} \right] \quad (5)$$

$$X = \frac{n}{n_t}, \quad n_t = \frac{4}{3} \pi r_0^3 m K \sqrt{P_{H_2}}$$

Substituting these equations into equation (5), we obtain,

$$\frac{dX}{dt} = 3 \left(1 - \sqrt{\frac{P_{eq}}{P_0}} \right) / r_0 \left[\frac{1}{K_s} + \frac{K_1}{2K_2 K_R (\sqrt{P_{H_2}} + \sqrt{P_{H_2,i}})} \right]$$

Denoting

$$X_\beta = \frac{V_\beta}{V_\alpha + V_\beta} = \frac{n}{n_\beta},$$

where

$$n_\beta = \frac{4}{3} \pi r_0^3 m K \sqrt{P_{eq}}$$

we arrive at

$$\frac{dX_\beta}{dt} = 3 \left(\sqrt{\frac{P_0}{P_{eq}}} - 1 \right) / r_0 \left[\frac{1}{K_s} + \frac{K_1}{2K_2 K_R (\sqrt{P_{H_2}} + \sqrt{P_{H_2,i}})} \right]$$

From equation (5), we know,

(1) When applied hydrogen P_{H_2} is low, $P_{H_2,i}$ must also be low, and the value of

$$\frac{K_1}{2K_2 K_R (\sqrt{P_{H_2}} + \sqrt{P_{H_2,i}})}$$

is much bigger than the value of $1/K_s$. In this case, the dissolution rate is controlled by the dissociative chemisorption rate, hence

$$P_{H_2,i} = P_{eq}$$

From equation (5) or (2), the dissociative chemisorption rate of m spherical samples is

$$\frac{dn_c}{dt} = 4\pi r_0^2 m K_R^2 K_2 K_0 (P_0 - P_{eq}) \quad (6)$$

$$\frac{dX_c}{dt} = \frac{3K_R K_2}{r_0 K_1} \left(\sqrt{P_0} - \sqrt{\frac{P_{eq}}{P_0}} \right) \quad (7)$$

$$\frac{dX_{\beta c}}{dt} = \frac{3K_R K_2}{r_0 K_1 \sqrt{P_{eq}}} (P_0 - P_{eq}) \quad (8)$$

(2) When the applied hydrogen pressure is high,

$$\frac{K_1}{2K_2 K_R (\sqrt{P_{H_2}} + \sqrt{P_{H_2,i}})} \approx 0$$

and the boundary transition is the rate-controlling step of the dissolution.

$$P_0 = P_{H_2,i}$$

From equation (5) or (3),

$$\frac{dn_s}{dt} = 4\pi r_0^2 m K_s K (\sqrt{P_0} - \sqrt{P_{eq}})$$

$$\frac{dX_s}{dt} = \frac{3K_s}{r_0} \left(1 - \sqrt{\frac{P_{eq}}{P_0}}\right) n \quad (10)$$

$$\frac{dX_{\beta s}}{dt} = \frac{3K_s}{r_0} \left(\sqrt{\frac{P_0}{P_{eq}}} - 1\right). \quad (11)$$

(3) When the applied hydrogen pressure is comparatively high, both the dissociative chemisorption and boundary transition control the dissolution rate. The kinetics can be expressed by equation (5).

Letting $\sqrt{P_{H_2, i}} = \frac{1}{2}(\sqrt{P_0} + \sqrt{P_{eq}})$, we can write equation (5) as follows:

$$\frac{dn}{dt} = 4\pi r_0^2 m K (\sqrt{P_0} - \sqrt{P_{eq}}) \left/ \left[\frac{1}{K_s} + \frac{K_t}{K_2 K_R (3\sqrt{P_0} + \sqrt{P_{eq}})} \right] \right. \quad (12)$$

$$\frac{dX}{dt} = 3 \left(1 - \sqrt{\frac{P_{eq}}{P_0}}\right) / r_0 \left[\frac{1}{K_s} + \frac{K_t}{K_2 K_R (3\sqrt{P_0} + \sqrt{P_{eq}})} \right] \quad (13)$$

$$\frac{dX_{\beta}}{dt} = 3 \left(\sqrt{\frac{P_{eq}}{P_0}} - 1\right) / r_0 \left[\frac{1}{K_s} + \frac{K_t}{K_2 K_R (3\sqrt{P_0} + \sqrt{P_{eq}})} \right] \quad (14)$$

3.2. Diffusion of the hydrogen atoms

When diffusion of the hydrogen atoms is the rate-controlling step, the width of the two-phase region will be zero and the continuous moving spherical surface model fits well (see Fig. 1a). Neglecting the difference of concentration within the α -phase, the hydriding rate of m spherical samples is

$$\frac{dn}{dt} = 4\pi r_0 m D_{\beta} (C_{\beta H} - C_{\beta a}) \left/ \left(\frac{r_0}{r} - 1 \right) \right. \quad (15)$$

Since X_{β} is equal to $1 - (r/r_0)^3$, then

$$\frac{dn}{dt} = 4\pi r_0 m D_{\beta} K (\sqrt{P_0} - \sqrt{P_{eq}}) / [(1 - X_{\beta})^{-1/3} - 1] \quad (16)$$

$$\frac{dX}{dt} = 3D_{\beta} \left(1 - \sqrt{\frac{P_{eq}}{P_0}}\right) / r_0^2 [(1 - X_{\beta})^{-1/3} - 1] \quad (17)$$

$$\frac{dX_{\beta}}{dt} = 3D_{\beta} \left(\sqrt{\frac{P_0}{P_{eq}}} - 1\right) / r_0^2 [(1 - X_{\beta})^{-1/3} - 1] (1 - K). \quad (18)$$

3.3. Phase transformation

The phase transformation process is actually the process of nucleation and growth of a new phase. When the nucleation of the β -phase is fast, (see Fig. 1a), the hydriding process in the two-phase region is the growth of the β -phase. But if the nucleation of the β -phase is difficult and slow, the $\alpha + \beta$ coexisting region would exist within the matrix. The width of the two-phase region depends on the ease of nucleation and growth of the β -phase (see Fig. 1b and c). The hydriding rate can be described by the JMA equation.

3.3.1. *Heterogeneous nucleation.* Porter [7] gives the relation of heterogeneous nucleation rate to ΔG^* :

$$\begin{aligned} N_{\text{het}} &= \omega C_1 \exp(-\Delta G_n/KT) \exp(-\Delta G^*/KT^*) \\ &= N_0 \exp(-\Delta G_n/KT). \end{aligned}$$

Because the existence of defects, such as vacancies, dislocations, stacking faults, grain boundaries and inter-phase boundaries, increase in ΔG_n , and decrease in ΔG^* , the rate of heterogeneous nucleation will be increased.

3.3.2. *Growth of the β -phase.* When the β -phase deposits from supersaturated α -solid solution and the two phases have different compositions, the β -phase growth requires long-range diffusion of metal atoms. If the interfacial reaction is fast, i.e. the transfer of atoms across the interface is an easy process, the rate at which the β -phase grows will be governed by the rate at which lattice diffusion can remove the excess atoms from the interface ahead. This is known as diffusion-controlled growth. This case has been discussed in Section 3.2. However, if for some reason the interfacial reaction is much slower than the rate of lattice diffusion, the growth rate will be governed by the interface reaction kinetics. Under these circumstances growth is said to be interface controlled. It is also possible that both the interface reaction and the diffusion process proceed at comparable rates. In this case the reaction is said to be mixed controlled. Now, we try to analyse interface-controlled growth. In this case, the β -phase can grow like continuous growth or lateral growth, which further depends on the properties of the boundary and driving force. If the β -phase is incoherent with the matrix, the boundary layer between the β -phase and matrix will be a diffused interface. If the two phases are structurally coherent, the interface migrates in quite different ways. In a continuous growth process, atoms migrate in such a way as to create a rough interface. In a lateral growth process, where leagues and jogs are formed by spiral growth or twin boundaries, atoms migrate in such a way as to create a flat interface. When the driving force increases, the lateral

growth would change to a continuous growth. In general, the interface between the α - and β -phase is incoherent, so the growth rate of the β -phase is [7]:

$$\frac{dr}{dt} = -M\Delta G = -\frac{D_\alpha \Delta G}{aT_0}$$

Since

$$X_\beta = 1 - \left(\frac{r}{r_0}\right)^3,$$

$$\frac{dX_\beta}{dt} = \frac{3D_\alpha \Delta G}{ar_0 RT_0} (1 - X_\beta)^{2/3}.$$

Since $\Delta G = \Delta G_m - \Delta G'_s + \Delta G_d$, it can easily be shown that for a dilute or ideal solution, the driving force ΔG_m is given by [7]

$$\Delta G_m = \frac{RT_0}{C_{\alpha\beta}} (C_{\alpha H} - C_{\alpha\beta}).$$

Since $C_{\alpha H} = K_\alpha \sqrt{P_0}$ and $C_{\alpha\beta} = K_\alpha \sqrt{P_{eq}}$

$$\begin{aligned} \frac{dX_\beta}{dt} = & \frac{3D_\alpha}{ar_0 \sqrt{P_{eq}}} (\sqrt{P_0} - \sqrt{P_{eq}})(1 - X_\beta)^{2/3} \\ & - \frac{3D_\alpha}{ar_0 RT_0} (\Delta G'_s - \Delta G_d)(1 - X_\beta)^{2/3} \end{aligned} \quad (19)$$

which is quite similar to Nahm's rate equation for a chemical reaction [5]:

$$\frac{dX_\beta}{dt} = \frac{3M_H K_s}{r_0 \rho_0 (RT_0)^{1/2}} (\sqrt{P_0} - \sqrt{P_{eq}})(1 - X_\beta)^{2/3}.$$

When the volume expansion at phase transformation is zero and no defect exists in the α -phase, the difference of the two equations is only the coefficient. Some experimental results, which show that the chemical reaction is the rate-controlling step, prove that the growth of the β -phase is actually the rate-controlling step. If the α -phase is coherent with the β -phase and the interface migrates by spiral growth, the rate of β growth would be proportional to the square of the driving force ΔG . In this case, the hydriding rate can not be described by kinetics of chemical reactions.

3.3.3. Nucleation and growth. In Fig. 1b and c, the hydriding rate is controlled by nucleation and growth. The rate equation for nucleation and growth is known as the Johnson-Mehl-Avami equation. The fraction of the β -phase is given by:

$$X_\beta = 1 - \exp[-(K_p t)]^{n'}, \quad n' \geq 0.5 \quad (20)$$

where $K_p = K'_0 \text{Ln}(P_0 - P_a/P_{eq})$ [9]. The hydriding rate is given by:

$$\frac{dX_\beta}{dt} = n' K'_0 (1 - X_\beta) \text{Ln} \frac{P_0 - P_a}{P_{eq}} [-\text{Ln}(1 - X_\beta)]^{\frac{n'-1}{n'}}. \quad (21)$$

The amount of absorbed hydrogen,

$$n = \frac{4}{3} \pi r_0^3 X_\beta m K \sqrt{P_{eq}}$$

$$\begin{aligned} \frac{dn}{dn} = & \frac{4}{3} \pi r_0^3 m n' K K'_0 \sqrt{P_{eq}} (1 - X_\beta) \\ & \times \text{Ln} \frac{P_0 - P_a}{P_{eq}} [-\text{Ln}(1 - X_\beta)]^{\frac{n'-1}{n'}} \end{aligned} \quad (22)$$

$$\begin{aligned} \frac{dX}{dt} = & n' K'_0 \sqrt{\frac{P_{eq}}{P_0}} (1 - X_\beta) \text{Ln} \frac{P_0 - P_a}{P_{eq}} \\ & \times [-\text{Ln}(1 - X_\beta)]^{\frac{n'-1}{n'}}. \end{aligned} \quad (23)$$

The n' value in Fig. 1b is smaller than that in Fig. 1c, when the activation proceeds, P_a in the above equations decreases and become close to zero after activation.

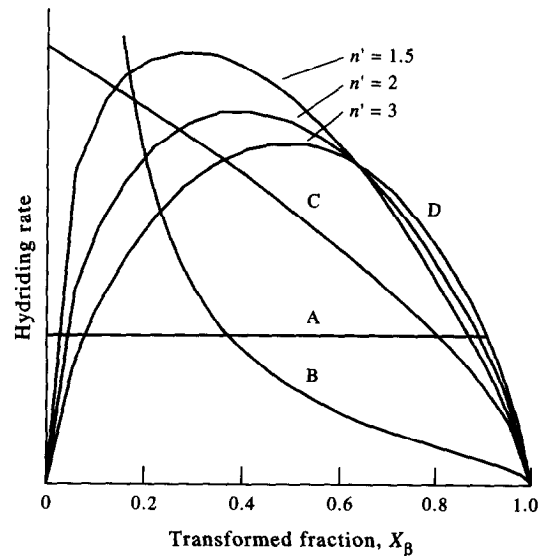


Fig. 2. Schematic diagram of various types of hydrogen absorption rate depending on the transformed fraction, X_β . (A) Dissolution of hydrogen molecules in the matrix. (B) Hydrogen diffusion through the hydride phase (or matrix). (C) The growth of the β -phase. (D) Time-dependent nucleation and growth.

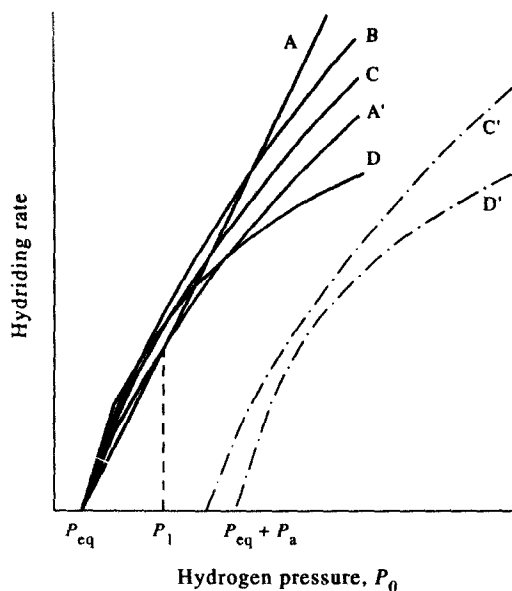


Fig. 3. Schematic diagram of hydrating rate versus the applied hydrogen pressure. (A) Chemisorption. (A') Boundary transition. (B) hydrogen diffusion. (C, C') Growth of β -phase after and before activation. (D, D') Nucleation and growth after and before activation.

4. THE DEPENDENCE OF THE HYDROGEN ABSORPTION RATE ON THE HYDROGEN PRESSURE AND TRANSFORMED FRACTION

From equations (14), (18), (19), (21), and (8), (11), (18), (19), (21), the theoretical rate-transformed fraction relation of an alloy and rate-hydrogen pressure relation for each type of rate limitation are plotted in Figs 2 and 3, respectively.

5. DISCUSSION

It is generally accepted that the first hydrogenation process of a metal hydrogen storage alloy is a phase transformation process and the nucleation and growth of the β -phase is the hydrating rate-controlling step, because there exist fewer defects in the matrix before activation, and this makes the nucleation and growth of the β -phase difficult. In this case, the hydrating rate equation can be described by the JMA equation and the dependence of the hydrating rate on the reacted fraction and applied hydrogen pressure are shown in Figs 2 (curve D) and 3 (curve D'), respectively. In Fig. 3 and equation (20), P_a is the nucleation barrier. In the first several hydrating and dehydrating cycles, P_a will decrease and finally become close to zero after activation. Simultaneously, $(\Delta G'_s - \Delta G_d)$ in equation (19) has the same variation tendency as P_a . This means that the rate curves

D' and C' in Fig. 3 will move in parallel toward the low pressure side and finally coincide with curves D and C, respectively. It is for this reason that the defects caused by the volume expansion in the hydrogenation process make the nucleation and growth of the β -phase fast and easy. If curve D' moves faster than curve C', growth of the β -phase may become the hydrating rate-controlling step in the activation process.

After activation, the rate-controlling step may be the dissolution or diffusion of hydrogen, or the nucleation and growth of the β -phase, because the relative positions of lines A, B, C, and D in Figs 2 and 3 will vary with the experimental conditions and the tested materials. Figures 2 and 3 show a typical case, the rate-controlling step varies with the reacted fraction and applied hydrogen pressure according to the rule that the step with the slowest rate governs the hydrating process. At the former stage, the rate-controlling step will change from dissolution of hydrogen to nucleation and growth of the β -phase with increasing applied hydrogen pressure. If the dissolution of hydrogen is the rate-controlling step, then at low pressure ($P < P_1$), and the dissociative chemical absorption controls the dissolution of hydrogen. But at higher pressure ($P > P_1$) the dissolution of hydrogen changes to the boundary transition. In this case the hydrating rate does not change with the transformation fraction as shown in Fig. 2 (curve A). When the growth of the β -phase or hydrogen diffusion is the controlling step, the hydrating rate varies with the transformation fraction as curves B or C in Fig. 2, respectively, but at higher pressure the nucleation and growth is still the rate-controlling step. However, as the hydrogenation proceeds, curves C and D in Fig. 3 will move downward around point $P = P_{eq}$ according to equations (19) and (21), and curve C moves most quickly. Therefore, at the later stage, the hydrating process may become a hydrogen-diffusion-limited process as shown in Fig. 2. In the middle stage, there exists the possibility that growth of the β -phase or the nucleation and growth of the β -phase governs the hydrating process.

6. CONCLUSIONS

1. The hydrating process can be divided into three steps, (i) dissolution of hydrogen atoms on the surface of the α -phase (or β -phase); (ii) diffusion of hydrogen atoms through the α -phase (or β -phase); (iii) phase transformation (hydride depositing from supersaturated α -solid solution), or nucleation and growth of hydride. The dissolution can be divided further into dissociative chemisorption and boundary transition.
2. For the hydrating process, at first the nucleation and growth of β -phase is the controlling step. After activation, the hydrating rate-controlling step varies with the experimental conditions and the tested material. At low applied hydrogen pressure, the rate-controlling step may be hydrogen dissociation or hydrogen diffusion or growth of β -phase. At higher pressures nucleation and growth is the controlling step.

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