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Thermal desorption spectroscopy (TDS) method for hydrogen desorption characterization (I): theoretical aspects

Facundo J. Castro[a,*,1], Gabriel Meyer[b,2]

[a]Centro Atómico Bariloche e Instituto Balseiro, (8400) S.C. de Bariloche, Argentina
[b]Centro Atómico Bariloche e Instituto Balseiro, (8400) S.C. de Bariloche, Argentina

Abstract

We present a theoretical study of thermal desorption spectroscopy applied to the characterization of hydrogen desorption kinetics from hydride forming materials. We propose a model that considers bulk and surface processes during desorption in the solid solution+hydride field of a metal–hydrogen system. We consider as possible rate limiting steps: diffusion, phase transformation, bulk to surface passage and two-atom recombination on the surface of the sample.

Keywords: Thermal desorption spectroscopy; Metal hydrogen systems; Mathematical model; Desorption kinetics of H_2; Diffusion of H_2; Surface effects

1. Introduction

Thermal desorption spectroscopy, a technique developed in the surface science area [1], was first used to study hydrogen desorption kinetics in bulk hydrides around 1980 [2]. Briefly, the technique consists in a non-isothermic study of desorption kinetics. A sample, previously charged with hydrogen, is continuously heated following a predefined temperature profile (usually a linear ramp) while the amount of gas desorbed from the material is recorded. The plot of the flow of gas desorbed as a function of temperature is a TDS spectrum. TDS spectra are usually composed of many desorption peaks, each of which can be associated with a different kinetic process. The main goal of a TDS experiment is to identify the rate limiting step and to determine the kinetic parameters associated with the process.

The analysis of TDS spectra of metal–hydrogen (MH) systems is a difficult task that must take into account surface processes, bulk processes and different thermodynamic phases. Previous work in the theoretical treatment of TDS of MH systems has mainly focused on desorption controlled by specific kinetic processes. Pick et al. [3] and Davenport et al. [4] have studied hydrogen desorption from the solid solution of a MH system. In their model, they considered hydrogen transfer between the gas and the surface, and between the surface and the bulk. They derived an expression for the desorption rate assuming fast diffusional equilibrium in the bulk and on the surface and quasiequilibrium for hydrogen transfer between the surface and the bulk. They have found an expression that describes desorption under surface controlled kinetics. Stern et al. [5] have presented a model that can be used to analyze desorption in the solid solution and in the hydride phases of a MH system. This model assumes fast bulk diffusion and quasiequilibrium for the hydride to solid solution phase transformation and for hydrogen transfer between the surface and the bulk. Mavrikakis et al. [6–8] have introduced a simultaneous treatment of bulk diffusion and surface processes without assuming quasiequilibrium or fast diffusion. This model involves the numerical resolution of a set of equations that consider hydrogen transfer between the gas and the surface, and between the surface and the bulk. They have not considered different thermodynamic phases in their treatment. Finally, Han et al. [9] have presented a theoretical analysis of TDS spectra assuming a desorption process controlled by the hydride to solid solution phase transformation.

In a recent paper [10], we presented a simple model devised to simultaneously treat desorption under non-equilibrium bulk diffusion and surface processes for a system in a single thermodynamic phase. In this work we extend this scheme to include desorption from a MH

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*Corresponding author.

E-mail address: fcastro@cab.cnea.gov.ar (F.J. Castro).

[1] Fellow of CONICET.

[2] Member of CNEA.

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system with two different thermodynamic phases: a solid solution and a hydride connected through a miscibility gap. We will focus on desorption during solid solution and hydride coexistence.

2. Model

We assume a simplified phase diagram for our hypothetical MH system. Irrespective of temperature, below a hydrogen concentration equal to $c_{\alpha,\mathrm{eq}}$ the system forms a solid solution (α phase), above $c_{\beta,\mathrm{eq}}$ a hydride phase (β phase) precipitates, and between $c_{\alpha,\mathrm{eq}}$ and $c_{\beta,\mathrm{eq}}$ the solid solution and the hydride coexist. This approximation should be valid as long as the temperature can be kept sufficiently below the critical temperature of the miscibility gap.

We assume a sample with spherical shape and a desorption process that begins on the surface and proceeds towards the center of the sample. During desorption in the two-phase coexistence region, we suppose that there is a hydride core of radius r_i surrounded by an outer covering of solid solution. We also assume an initial concentration profile in the two-phase coexistence region with a uniform $c_{\beta,\mathrm{eq}}$ concentration in the β phase and a uniform $c_{\alpha,\mathrm{eq}}$ concentration in the α phase.

We propose the following set of equations to model desorption in the two-phase coexistence region. From the symmetry of the problem only the radial dependence of hydrogen concentration is considered

$$\begin{cases} \text{(a)}\ \dfrac{\partial c_\beta}{\partial t} = D_\beta(T)\nabla^2 c_\beta \\ \text{(b)}\ \left.\dfrac{\partial c_\beta}{\partial r}\right|_{r=0} = 0 \\ \text{(c)}\ c_\beta(r_\mathrm{i}) = c_{\beta,\mathrm{eq}} \end{cases} \tag{1}$$

$$\begin{cases} \text{(a)}\ \dfrac{\partial c_\alpha}{\partial t} = D_\alpha(T)\nabla^2 c_\alpha \\ \text{(b)}\ D_\alpha(T)\left.\dfrac{\partial c_\alpha}{\partial r}\right|_{r_\mathrm{i}} = -k_\mathrm{tf}(T)l_\mathrm{tf}c_{\beta,\mathrm{eq}}\left(\dfrac{c_{\alpha,\mathrm{eq}} - c_\alpha(r_\mathrm{i})}{c_{\alpha,\mathrm{eq}}}\right) \\ \text{(c)}\ D_\alpha(T)\left.\dfrac{\partial c_\alpha}{\partial r}\right|_{R} = -k_\rightarrow(T)l_\mathrm{c}c_\alpha(R)[1-c_\mathrm{s}] + k_\leftarrow(T)l_\mathrm{c}c_\mathrm{s}[1-c_\alpha(R)] \end{cases} \tag{2}$$

$$\frac{\mathrm{d}r_i}{\mathrm{d}t}\left[c_\beta(r_i) - c_\alpha(r_\mathrm{i})\right] = D_\alpha(T)\left.\frac{\partial c_\alpha}{\partial r}\right|_{r_\mathrm{i}} - D_\beta(T)\left.\frac{\partial c_\beta}{\partial r}\right|_{r_\mathrm{i}} \tag{3}$$

$$\frac{\mathrm{d}c_s}{\mathrm{d}t} = k_\rightarrow(T)c_\alpha(R)[1-c_\mathrm{s}] - k_\leftarrow(T)c_\mathrm{s}[1-c_\alpha(R)] - k_\mathrm{s}(T)c_\mathrm{s}^2 \tag{4}$$

c_β, c_α and c_s are hydrogen concentrations in the β phase, in the α phase and on the surface, respectively. $D_\beta(T)$ and $D_\alpha(T)$ are the corresponding diffusion coefficients, $k_\mathrm{tf}(T)$ is the β to α phase transformation rate constant, $k_\rightarrow(T)$ and $k_\leftarrow(T)$ are the rate constants for hydrogen transfer from the bulk to the surface and vice versa, respectively, and $k_\mathrm{s}(T)$ is the rate constant for desorption from the surface. These quantities are assumed to have a temperature dependence of Arrhenius form. l_c and l_tf are constants (characteristic lengths), r_i is the position of the interface between the α and β phases, and R is the radius of the sample.

Eq. (1) models diffusion in the β phase, Eq. (2) describes diffusion in the α phase, Eq. (3) is a Stefan condition that assures matter conservation at the α–β interface, and Eq. (4) models evolution on the surface. Eq. (2b) is a boundary condition at the α–β interface that models a hydride decomposition proportional to a phase transformation rate constant and to the difference between the hydrogen concentration at the interface and the equilibrium value [9]. Eq. (2c) is the boundary condition at the interface between bulk and surface; it takes into account hydrogen transfer between the surface and the bulk [6–8]. Finally, the processes considered on the surface are the transfer of hydrogen atoms to and from the bulk, and the desorption of two hydrogen atoms from the surface after recombination [3–4].

3. Results and discussion

We analyze below the shape and main characteristics of TDS spectra obtained under different rate limiting mechanisms. We consider desorption controlled by: diffusion (in α and β phases), β to α phase transformation, bulk to surface passage, and two-atom recombination on the surface of the sample.

We assume that when a process controls desorption the other processes are in a quasiequilibrium state. Quasiequilbrium states in the bulk are characterized by uniform hydrogen concentrations. Quasiequilibrium states on the surface are characterized by a null hydrogen concentration.

3.1. Desorption controlled by diffusion in the β phase

When hydrogen desorption is controlled by diffusion in the β phase, we assume a quasiequilibrium state in the α phase and on the surface characterized by null hydrogen concentrations in both regions and a non-uniform concentration in the β region. Eqs. (1)–(4) reduce in this case to

$$\begin{cases} \text{(a)}\ \dfrac{\partial c_\beta}{\partial t} = D_\beta(T)\nabla^2 c_\beta \\ \text{(b)}\ \left.\dfrac{\partial c_\beta}{\partial r}\right|_{r=0} = 0 \\ \text{(c)}\ c_\beta(r_i) = c_{\beta,\mathrm{eq}} \end{cases} \tag{7}$$

with the Stefan condition

$$\frac{\mathrm{d}r_i}{\mathrm{d}t}c_{\beta,\mathrm{eq}} = -k_\mathrm{ttf}(T)l_\mathrm{tf}c_{\beta,\mathrm{eq}} - D_\beta(T)\left.\frac{\partial c_\beta}{\partial r}\right|_{r_i} \tag{8}$$

Taking into account Eqs. (7) and (8), the flow desorbed can be written as

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -3k_{\mathrm{tf}}(T)l_{\mathrm{tf}}\frac{r_i^2(T)}{R^3} \tag{9}$$

The TDS spectra of Fig. 1 correspond to the numerical resolution of Eqs. (7) and (8) for different initial hydrogen concentrations (c_0) in the hydride phase.

Each spectrum has only one desorption peak that rises very steeply and decreases smoothly. As higher c_0 values are considered the peak shifts towards higher temperatures. An average hydrogen concentration as a function of temperature can be obtained by integrating each spectrum. With this data we can construct a desorption path that can be plotted together with the phase diagram. Using this procedure we observed that the steep rise of each peak coincides with the entrance of the system into the coexistence region. Before this, the desorption of hydrogen dissolved in the β phase takes place, but the desorbed flow is so small that it cannot be appreciated in Fig. 1. The steep rise of desorbed flow in the spectra marks the beginning of hydride decomposition. At this particular point Eq. (9) takes a simplified form because the interface is located immediately below the surface

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -3k_{\mathrm{tf}}(T)\frac{l_{\mathrm{tf}}}{R} \tag{10}$$

This is the maximum desorption flow, that is entirely determined by the phase transformation rate constant. The maximum flow predicted by Eq. (10) is shown in dotted line in Fig. 1.

The shift of the spectra towards higher temperatures when higher c_0 values are considered occurs because more time (temperature) is needed to desorb higher amounts of hydrogen dissolved in excess in the β phase before hydride decomposition begins.

3.2. Desorption controlled by the β to α phase transformation

When desorption is controlled by the β to α phase transformation, we assume a quasiequilibrium state characterized by null hydrogen concentration on the surface and in the α phase, and a uniform $c_{\beta,\mathrm{eq}}$ concentration throughout the β phase. The desorbed flow can be written as

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -3k_{\mathrm{tf}}(T)l_{\mathrm{tf}}\frac{r_{\mathrm{i}}^2(T)}{R^3} \tag{11}$$

An analytical expression for the position of the interface $r_{\mathrm{i}}(\mathrm{T})$ can be found from the Stefan condition Eq. (3)

$$r_i(T) = r_i(T_0) - \frac{k_{\mathrm{tf}}^0 l_{\mathrm{tf}} E_{\mathrm{tf}}}{\alpha}\left[\Theta\left(\frac{E_{\mathrm{tf}}}{T}\right) - \Theta\left(\frac{E_{tf}}{T_0}\right)\right] \tag{12}$$

The TDS spectra obtained from Eqs. (11) and (12) for different c_0 values in the coexistence region are shown in Fig. 2.

Each spectrum has only one peak with smooth ascending and descending edges. As higher c_0 values are considered, the temperature of maximum flow (T_{m}) increases.

3.3. Desorption controlled by diffusion in the α phase

When desorption is controlled by diffusion in the α phase, the quasiequilibrium state is characterized by a

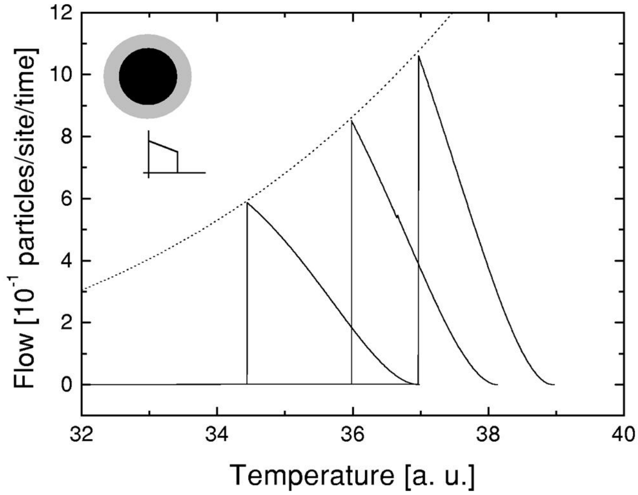

Fig. 1. TDS spectra of a desorption process controlled by diffusion in the hydride phase for different hydrogen initial concentrations (increasing from left to right). The diagram in the upper left corner schematizes the concentration profile in the sample.

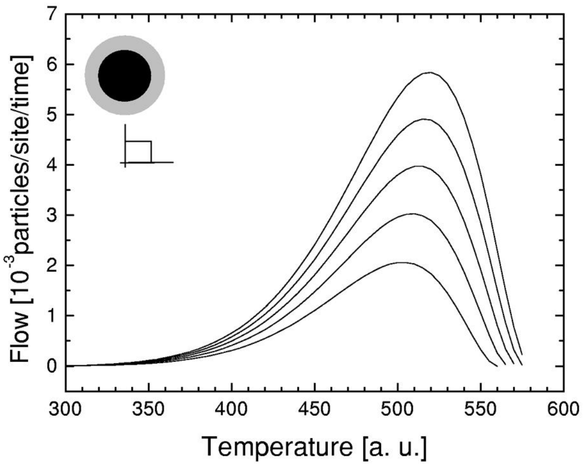

Fig. 2. TDS spectra of a desorption process controlled by the hydride to solid solution phase transformation for different hydrogen initial concentrations (proportional to the area below the spectra). The diagram in the upper left corner schematizes the concentration profile in the sample.

uniform concentration $c_{\beta,\mathrm{eq}}$ in the β phase, a null concentration on the surface, and a non-uniform concentration in the α phase. Hydrogen concentration in the α phase is $c_{\alpha,\mathrm{eq}}$ at the α–β interface and zero at the interface with the surface. According to this, the evolution can be described by the following set of equations

$$\left\{ \begin{array}{l} \text{(a)}\ \dfrac{\partial c_\alpha}{\partial t} = D_\alpha(T)\nabla^2 c_\alpha \\ \text{(b)}\ D_\alpha(T)\dfrac{\partial c_\alpha}{\partial r}\Big|_{r_i} = -k_{\mathrm{tf}}(T) l_{\mathrm{tf}} c_{\beta,\mathrm{eq}} \left(\dfrac{c_{\alpha,\mathrm{eq}} - c_\alpha(r_i)}{c_{\alpha,\mathrm{eq}}} \right) \\ \text{(c)}\ c_\alpha(R,t) = 0 \end{array} \right. \quad (13)$$

With a Stefan condition given by

$$\frac{\mathrm{d}r_i}{\mathrm{d}t}\left[c_{\beta,\mathrm{eq}} - c_\alpha(r_i)\right] = D_\alpha(T)\frac{\partial c_\alpha}{\partial r}\Big|_{r_i} \quad (14)$$

The desorption spectra of Fig. 3 correspond to the numerical resolution of Eqs. (13) and (14) for different c_0 values in the coexistence region.

The full line spectra (c_0 in the α–β coexistence region) have a low temperature shoulder and a high temperature peak. The dotted line spectrum ($c_0 = c_{\alpha,\mathrm{eq}}$) has only a small peak that coincides with the shoulder in its ascending edge. The shoulder (and the small peak) correspond to desorption of hydrogen dissolved in the α phase. The high temperature peak corresponds to hydrogen desorption during hydride decomposition (phase transformation). The spectra start with the shoulder that corresponds to desorption of hydrogen dissolved in the α phase and continues with the high temperature peak associated with the phase transformation that begins when concentration gradients reach the α–β interface. The dependence of T_m with c_0 is not monotonic, as c_0 decreases T_m shifts first towards higher temperatures and then towards lower temperatures.

3.4. Desorption controlled by hydrogen transfer from the bulk to the surface

When desorption is controlled by hydrogen transfer from the bulk to the surface we assume a quasiequilibrium state with a uniform $c_{\beta,\mathrm{eq}}$ concentration in the β phase, a uniform $c_{\alpha,\mathrm{eq}}$ concentration in the α phase, and a null concentration on the surface. The desorbed flow can be written as

$$\frac{\mathrm{d}c}{\mathrm{d}t}(T) = -\frac{3}{R} l_\mathrm{c} c_{\alpha,\mathrm{eq}} k_{\rightarrow}(T) \quad (15)$$

Eq. (15) is independent of hydrogen concentration (zero order desorption process) and depends on temperature only through the rate constant. The TDS spectra obtained from Eq. (15) for different c_0 values in the coexistence region are shown in Fig. 4.

The spectra show the characteristics of a zero order desorption process: a common leading edge and a sudden fall when the desorbing material is exhausted.

3.5. Desorption controlled by recombination on the surface

When desorption is controlled by the recombination of two hydrogen atoms on the surface we assume a quasiequilibrium state characterized by uniform concentrations $c_{\beta,\mathrm{eq}}$ and $c_{\alpha,\mathrm{eq}}$ in the β and α phases, respectively, and by a concentration c_s on the surface that is related to $c_{\alpha,\mathrm{eq}}$ by the expression

$$c_\mathrm{s} = \frac{k_{\rightarrow}(T)}{k_{\leftarrow}(T) + [k_{\rightarrow}(T) - k_{\leftarrow}(T)]c_{\alpha,\mathrm{eq}}} c_{\alpha,\mathrm{eq}} \approx \frac{k_{\rightarrow}(T)}{k_{\leftarrow}(T)} c_{\alpha,\mathrm{eq}} \quad (16)$$

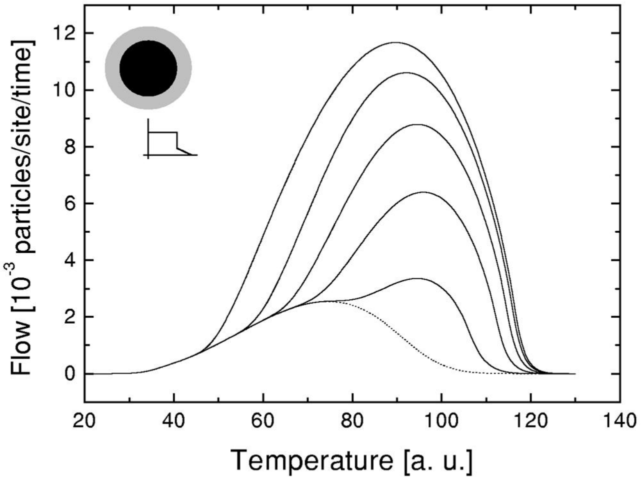

Fig. 3. TDS spectra of a desorption process controlled by diffusion in the solid solution for different hydrogen initial concentrations (proportional to the area below the spectra). The diagram in the upper left corner schematizes the concentration profile in the sample.

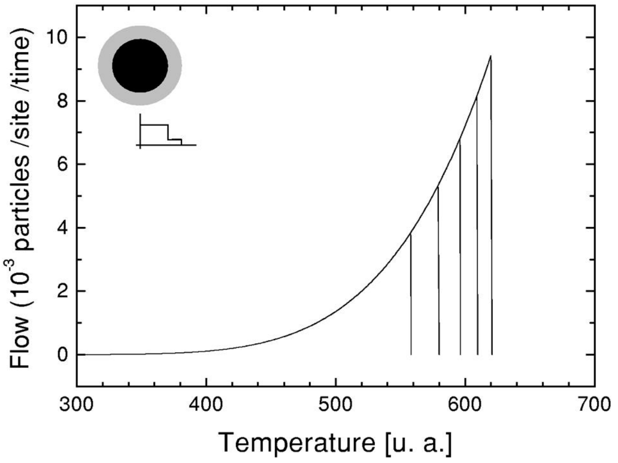

Fig. 4. TDS spectra of a desorption process controlled by hydrogen transfer from the bulk to the surface or by the recombination of two atoms on the surface. The spectra differ on the hydrogen initial concentration (proportional to the area below the spectra). The diagram in the upper left corner schematizes the concentration profile in the sample.

that characterizes a quasiequilibrium transfer of hydrogen atoms between the bulk and the surface.

The desorbed flow can be written as

$$\frac{\mathrm{d}c}{\mathrm{d}t}(T) \approx -\frac{3}{R} l_c k_s(T) \left[\frac{k_{\rightarrow}(T)}{k_{\leftarrow}(T)} \right]^2 c_{\alpha,\mathrm{eq}}^2 = -\frac{3}{R} l_c k_{\mathrm{ef}}(T) c_{\alpha,\mathrm{eq}}^2 \qquad (17)$$

Eq. (17) also describes a zero order desorption process. The corresponding spectra are similar to those shown in Fig. 4. As a consequence of this, desorption processes controlled by the surface, either by bulk to surface transfer or by recombination on the surface, produce TDS spectra with identical characteristics. Thus, we cannot distinguish a kinetic process controlled by bulk to surface transfer from a process controlled by surface recombination.

The model presented above can also be used to analyze desorption in the α or in the β phases. In these cases the possible rate limiting processes are hydrogen diffusion in the bulk, hydrogen transfer from the bulk to the surface and recombination of two hydrogen atoms on the surface. The restriction of the model to these cases coincides with a model that we presented elsewhere [10].

4. Summary

We presented a model that describes hydrogen desorption from a metal hydrogen system. The model assumes a simplified phase diagram that includes a solid solution, a hydride phase and a coexistence region. We studied specifically the hydrogen desorption behavior when the system is in the two phase region of the phase diagram. We propose different approximations that allowed us to obtain TDS spectra that characterize the desorption process when distinct rate limiting processes are assumed. In particular, we considered desorption controlled by: hydrogen diffusion in the hydride phase, phase transformation from the hydride to the solid solution, diffusion in the solid solution, hydrogen transfer from the bulk to the surface, and two hydrogen atom recombination on the surface.

When diffusion in the hydride phase limits desorption, the desorption spectra are characterized by a peak with a steep ascending edge that shifts towards higher temperatures when c_0 increases. When the phase transformation controls desorption, smooth peaks that also shift towards higher temperatures when c_0 is increased compose the spectra. When diffusion in the solid solution limits desorption, the spectra have a low temperature shoulder and a peak. The shoulder corresponds to desorption of hydrogen dissolved in the solid solution and the peak to desorption of hydrogen released during the decomposition of the hydride. The peak shifts first towards higher temperatures and then towards lower temperatures when c_0 is increased. Finally, when a surface process controls desorption (the transfer of hydrogen from the bulk to the surface or the recombination of two hydrogen atoms on the surface) the TDS spectra have the characteristics of a zero order desorption process. These spectra are composed of only one peak with a common leading edge (for different c_0 values) and an abrupt descending edge. The peaks shift towards lower temperatures as c_0 increases.

The different peak shapes and the change of the temperature of maximum flow with c_0 can be used to identify the rate controlling step dominating H desorption and to obtain the kinetic parameters associated with the process.

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