2.2. Heat of reaction

The hydrogen dissolved (absorbed) in the lattice is in atomic form. The heat of reaction of the gas that leaves the metal with oxygen can be calculated according to the first principle of thermodynamics [5], as illustrated in Fig. 1.

> The initial state is: H absorbed (dissolved) in the Pd lattice.
> The final state is: H_2O in the atmosphere surrounding the metal.

The overall reaction is sketched in Fig. 1 by the path 1. The path between these two states can be detailed along the paths 2 and 3:

Path 2:

- Adsorption of atomic H on the surface: $H_{abs} \rightarrow H_{ads}$.
- Recombination of molecules at the surface: $2H \rightarrow H_{2\,ads}$ (adsorbed on Pd surface).
- Desorption of the molecule into the air $H_{2\,ads} \rightarrow H_2$ (gas released in the atmosphere).

Path 3:

- Reaction with O_2: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ (vapor in air).

Each step is accompanied by an energy change. From the above reactions, the last one (path 3) is well known, because this is the combustion of hydrogen in air. The corresponding heat release is –242 kJ/mol H_2 or –249 kJ/mol D_2. In order to quantify the heat involved by the other steps, we can consider the reverse process that is following path 2 in reverse. When Pd is exposed to H_2, the following phenomena occur:

- adsorption of H_2 on the Pd surface,
- dissociation of the H_2 molecule into two atoms of H,
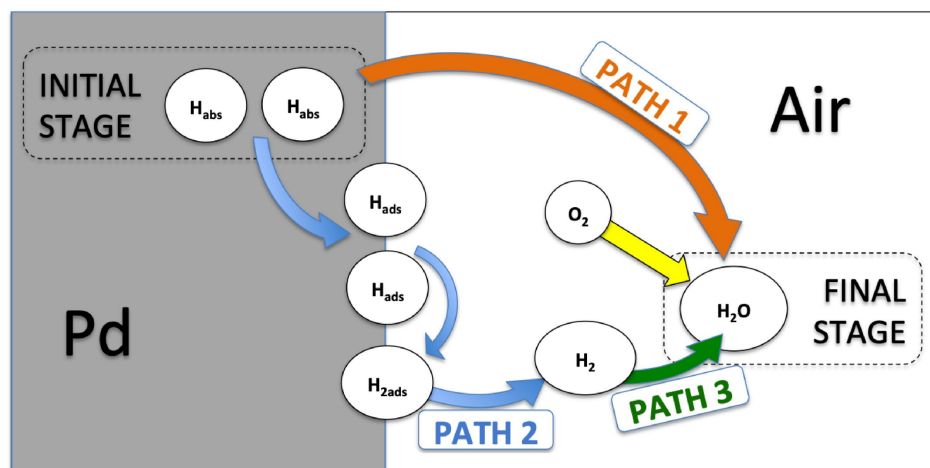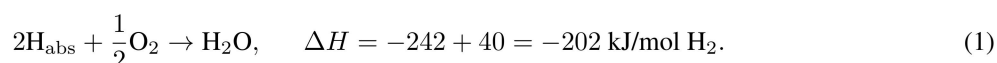- dissolution of the atomic H into the Pd.

Figure 1. Determination of the reaction energy involved in the formation of H_2O from H atoms dissolved in the metal according to the first principle of thermodynamics – The direct path 1 can be dissociated into the virtual paths 2 and 3.
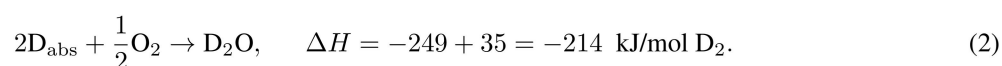
The dissociation of the H_2 molecule is highly endothermic (436 kJ/mol H_2). However, the dissolution is accompanied by a large energy release that more than compensates the energy required for the dissociation. The literature gives the enthalpy of the overall reaction: –40 kJ/mol H_2 (–35 kJ/mol D_2) [5].

The phenomena that take place during the dissolution of H_2 in Pd are exactly opposite to steps 1–3 discussed in the above (path 2). Therefore, the enthalpy associated to path 2 is the opposite of the enthalpy released during the dissolution. As a conclusion, the heat of reaction when the gas dissolved in the metal escapes and burns in air is:
Hydrogen:

$$2H_{abs} + \frac{1}{2}O_2 \to H_2O, \quad \Delta H = -242 + 40 = -202 \text{ kJ/mol } H_2. \tag{1}$$

Deuterium:

$$2D_{abs} + \frac{1}{2}O_2 \to D_2O, \quad \Delta H = -249 + 35 = -214 \text{ kJ/mol } D_2. \tag{2}$$

2.3. Diffusion of hydrogen in palladium

The coefficient of diffusion of hydrogen in palladium depends on the temperature but also on the hydrogen loading ratio. In this simplified model, the diffusion law is represented by the following relationships. According to [6] we have:

$$D_H = 2.5 \times 10^{-7} \exp(-21\,800/RT)(\text{m}^2\text{s}^{-1}), \tag{3}$$

$$D_D = 1.7 \times 10^{-7} \exp(-19\,900/RT)(\text{m}^2\text{s}^{-1}). \tag{4}$$

These values are for solid pieces of palladium.

2.4. Properties of palladium

The model supposes that the piece of metal behaves as if it were pure palladium. The presence of hydrogen in the lattice is not taken into account on the properties listed below [7]. The role of temperature is also disregarded.

Specific mass: $12\,030 \text{ kg m}^{-3}$,
Heat capacity: $c = 0.24 \text{ J g}^{-1}\text{ K}^{-1}$ or $2952\times 10^6 \text{ J m}^{-3}\text{ K}^{-1}$,
Thermal conductivity: $\lambda_{Pd} = 75 \text{ Wm}^{-1}\text{K}^{-1}$,
Normal spectral emissivity: $\varepsilon_{Pd} = 0.49$.

These values valid for Pd are also considered for PdH_x to simplify the problem. Hydrogen concentration: For a hydride corresponding to the formula PdH_x, the equivalent standard volume of molecular di-hydrogen contained in the metal is:

$$C_0 = x\,1294 \text{ Nm}^3\text{H}_2/\text{m}^3\text{Pd}. \tag{5}$$

For $x = 0.7$ we find $C_0 = 906$ volumes of gas per volume of metal, a value frequently noted in the literature.

3. Model of the Cylindrical Configuration (2D)

The numerical model uses a finite difference method and works as follows:

The cylindrical metal rod is subdivided into concentric layers (see Fig. 2). Initial temperature is $T_a = T$ ambient in the whole piece of metal. The initial H concentration is uniform along the radius and corresponds to the loading ratio PdH_x selected as input. H concentration at metal/air interface is considered zero at all time. There is therefore a concentration gradient that drives the H out of the metal. H_2O concentration on the surface is zero at all time. The model calculates by time steps, sufficiently small to guarantee the numerical stability.

All the hydrogen flowing out of the surface reacts with oxygen. Oxygen availability for the reaction is supposed sufficient without further analysis. The time constant of the reaction of the hydrogen adsorbed at the surface with oxygen is supposed to be negligible compared to the rate of diffusion of hydrogen towards the surface, so that the process is governed by the diffusion rate of hydrogen in the lattice. The heat of reaction Q_0 is split into several fluxes.

- Q_1: radiation loss to the environment,
- Q_2: convection in the surrounding air,
- Q_3: the balance modifies the temperature of the outermost metal layer.

The heat flow is computed in each layer to obtain the new temperature distribution. The coefficient of diffusion is recalculated at each step in each layer according to the new temperature.

The heat conductivities of palladium λ_{Pd} and air λ_{air} are constant, as well as the Pd heat capacity c. A more accurate model should revise these hypotheses, taking into account the influence of the temperature on the heat capacity and the heat conductivity. Another improvement would be to take into account the influence of the temperature and the hydrogen concentration on the heat of dissociation of the hydride, as shown for example in [8]. This sophistication is not introduced here.

This set of equations is introduced in the numerical model. The model gives the distribution of the temperature and hydrogen content in the rod at each time step. The evolution of the temperature along the time is also obtained.

The model is a finite difference explicit method written in Visual Basic. It is known that numerical errors introduced by this method are proportional to the time step and the square of the space step [9]. On the other hand, if the space step is diminished in an attempt to improve the accuracy, the time step must also be reduced, otherwise the numerical model is unstable. In our case a space step $\Delta x = 5 \times 10^{-4}$ m is sufficient to obtain a valuable result. The corresponding time step is $\Delta t = 10^{-3}$ s. Smaller space and time steps slightly increase the peak temperature calculated due to the chemical reaction but considerably increase the computing time. For example, for a 10 mm diameter rod with $\Delta x = 5 \times 10^{-4}$ m and $\Delta t = 10^{-3}$ s the peak temperature is 879°C. When Δx is divided by 2 and Δt by 4 the peak reaches 912°C. The difference is not considered essential in the present study because even the set of physical data used is an approximation. In any case, the exact behavior must depend on many parameters that are out of reach in such a model, like effective activity of the metal surface. The surface characteristics can be very different from one sample to another one. Assuming that all hydrogen atoms are immediately oxidized is a strong hypothesis. It may approximately correspond to the rare events when self-heating was observed. However, in most cases there is no heating, probably because the surface does not readily catalyze the hydrogen oxidation. This model is a simplified one that can only shed some light on the major phenomena that may occur. It cannot exactly predict the temperature evolution.

4. Simulation Results

Figures 3 and 4 show the temperature of cylindrical rods for different parameters. The temperature rises slowly during the first minutes, then very rapidly until a peak is reached. The temperature progressively returns to the ambient. The calculation shows that the temperature at each moment is practically uniform between the axis and the surface. Figure 3
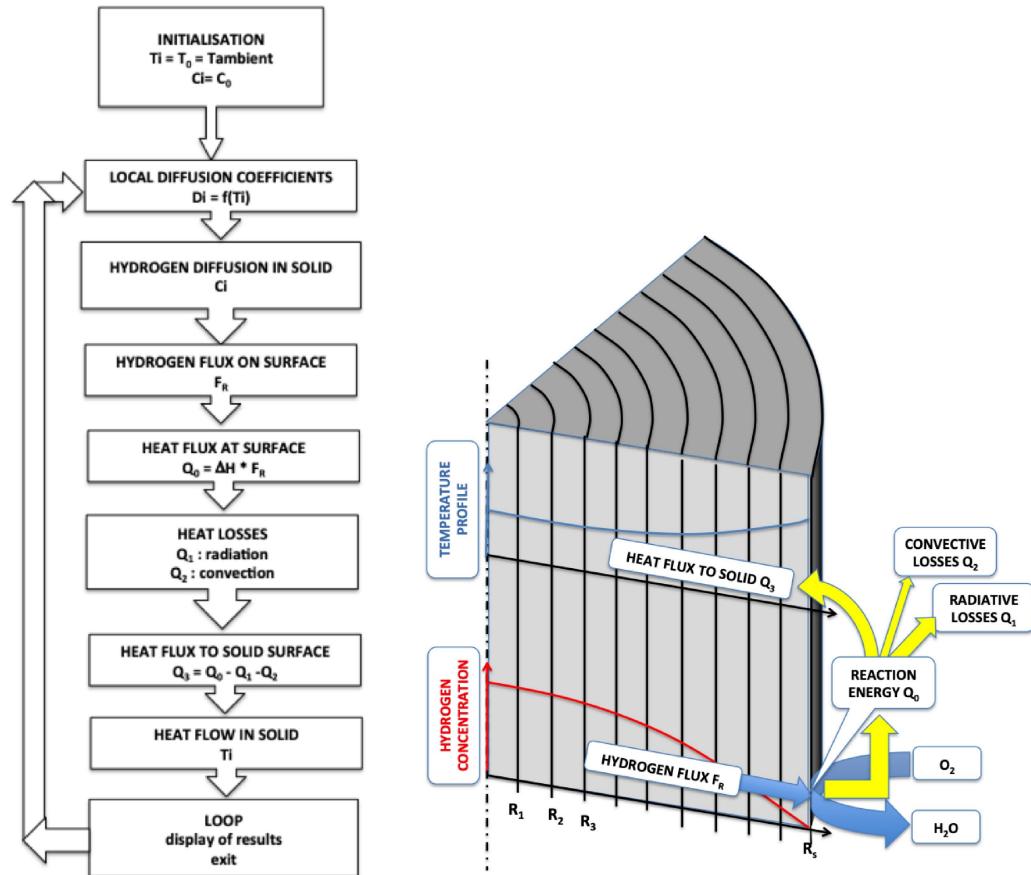
Figure 2. Flow chart of the model and schematic representation (figure for a 2D configuration).

shows that the surface peak temperature is higher in the case of a 5 mm diameter rod than a 10 mm rod, but the heat burst lasts longer in the larger sample. Figure 4 shows that the process is faster and the peak temperature higher when the initial loading increases. This reflects the major influence of the temperature on the hydrogen diffusion coefficient.

Figure 5 illustrates the evolution in a 10 mm diameter rod of the local deuterium content for an initial loading of 0.5. The initial diffusion flow is largest near the surface because of the sharp concentration slope. The reaction progressively increases the temperature. The high temperature accelerates the diffusion rate, so that most of the hydrogen flows out within a few minutes. Once most of the hydrogen is gone, the temperature drops, and so does the diffusion rate. The end of the de-loading is slow.

Figure 6 shows the variations of the deuterium inventory in the metal with time. When the loading ratio is high the large peak temperature accelerates the diffusion. As a result, the final content after cooling down is lower when the initial loading increases. The same figure displays the gas content when the metal surface is supposed to remain cold. This can be the case if the surface is non-reactive so that the hydrogen does not react with air. The desorption is slow.