PHYSICAL MODELLING OF THERMAL DESORPTION ANALYSIS AND HYDROGEN PERMEATION TESTS

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Abstract

A physical model describing the diffusion of interstitial atoms was developed and has been repeatedly used to study the redistribution of hydrogen, as well as predicting the risk of hydrogen damage during various real manufacturing processes.

A particular advantage of this model is that, contrary to some simplified commercial and academic models, it contemplates diffusion in its most comprehensive description, *i.e.*, with the driving force for atom diffusion being the gradient in chemical activation (and not simply occurring down a composition gradient). As the model also incorporates thermal history, microstructure, matrix solubility, multiple trapping distributions, interaction with the atmosphere and others, that is especially suitable to study of real manufacturing processes.

In this case, two applications of interest both to academia and industry are presented. Fist, the model is applied to simulate a Thermal Desorption Analysis (TDA) test. By using the model, it is possible to relate desorption fluxes with the redistribution between different trapping sites within the metal.

Then hydrogen permeation is considered. In the case studied hydrogen is transported through a metal wall separating one volume with high hydrogen pressure and temperature from another volume with low hydrogen pressure and temperature. By using such comprehensive physical model, it is possible to study the effects of hydrogen pressure and temperature gradient, wall thickness, metal microstructure and trap distribution on the flux across the wall and on the accumulation of hydrogen within the metal. Furthermore, it makes possible to estimate the embrittlement risk and when necessary the time to fracture.

Keywords: Hydrogen, steel, permeation, Thermal Desorption Analysis, physical model

1. INTRODUCTION

Hydrogen diffusion and its effects in high performance alloys have become a hot research topic in recent years. While it was first identified as a cause of embrittlement over a century ago, our understanding of the phenomena involved is still superficial [1-7]. Our contribution to deepen this understanding is based on the use of a recent physical model of hydrogen redistribution, and its application to various real industrial processes [8, 9]. In this case, two new applications of interest both to academia and industry are presented. Fist, the model is applied to simulate a Thermal Desorption Analysis (TDA) test. Then hydrogen permeation though a metal wall is considered.

2. MODELLING HYDROGEN REDISTRIBUTION

2.1. Brief description of the model

The physical model used to study redistribution of hydrogen in steel has already been extensively described elsewhere and therefore, only a brief overview is presented here [8, 9].

The model is based in the fact that diffusion, in its more general description, does not occur in order to reduce the composition gradient but to reduce the chemical potential gradient, promoting a reduction of the Gibb’s energy of the system. Diffusion of hydrogen is described in the model as a random walk of interstitial elements, consequence of the thermal activation and atom mobility of such elements and governed by the differences in partial saturation distribution around the diffusing element [8].

The inclusion of microstructure evolution in the model allows it to be used to describe real industrial processes [8, 9].

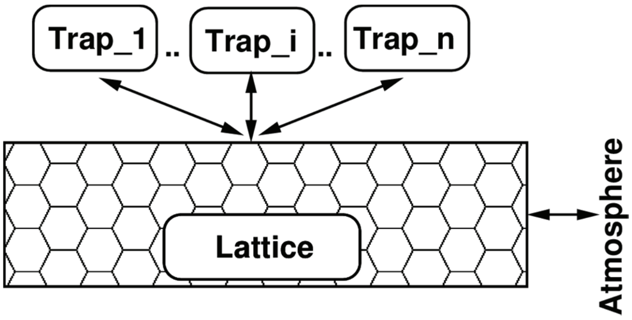

Figure 1 Hydrogen redistribution fluxes between the atmosphere, the lattice and *n* trap site types

Hydrogen trapping sites are described as a potential wells, with a negligible trapping energy barrier and a characteristic release energy barrier, for each type of trap - see **Figure 1** and **Table 1**. Diffusion in and out of a trap is also driven by the difference in partial saturation between lattice sites and trap sites. In many respects, this description makes the analogy with diffusion between two lattice sites and between a lattice site and a trap site [9].

Table 1 Examples of the characteristic release energy for each trap site type considered in this work, as well as lattice diffusion activation energy for comparison [4, 8]

Trap type	**E_t kJ mol^{-1}**
Dislocation distortion	20.6
Grain boundary	58.6
Precipitate surface	84.0
Diffusion in ferrite	13.4

Hydrogen desorption is estimated assuming local equilibrium at the surface, and therefore that the relationship between hydrogen dissolved in the metal at the surface and the partial pressure of hydrogen gas in the atmosphere follows Sievert's law [4, 8]. Additionally, the flux of hydrogen atoms across the surface is restricted by the atom mobility conditions as described earlier and limited by site saturation (*i.e.* partial saturation).

When supersaturation occurs, atomic hydrogen unable to remain in solution neither in the lattice nor within the trap distribution, would eventually either distort the lattice structure or find its way into micro-cavities in the lattice and form molecular hydrogen (*i.e.* hydrogen gas) at high pressure. Several criteria have been developed during the advancement of the present project to estimate the risk of damage nucleation and embrittlement, for each of the different sites where hydrogen could concentrate [9].

3. RESULTS AND DISCUSSION

3.1. Modelling a Thermal Desorption Analysis (TDA) test

In a TDA test, a small sample loaded with hydrogen is heated slowly and the flux of hydrogen expelled is measured. Different release energies for different trapping sites will produce peaks at different temperatures. Unfortunately, the different peaks are superposed with each other and de-convoluting the different curves from the experimental data is never a simple task. Besides, hydrogen released from some trapping site does not pour directly into the atmosphere, but diffuse into the lattice, with the possibility of becoming trapped and de-trapped repeatedly before it reached the surface, where it is finally able to flow out and be measured. Some previous attempts to model desorption during TDA tests sometimes ignore that complexity, or account for it in models with numerous fitting parameters. Additionally, many previous TDA models choose to ignore the prior redistribution of hydrogen (after specimen charging but before the start of the experiment), by assuming a starting homogeneous distribution of hydrogen [6, 10-11]. There is no need for that sort of simplification with the present model. By using the present model, some of that complexity is taken into account invoking only physical parameters like the distribution and partial saturation of the different sites [9].

The use of the model opens the possibility to compare model descriptions with experimental data from literature and experiment. Because of its detailed description of de-trapping from different trap sites and eventual desorption, this model allows a better understanding of the de-trapping, diffusion and desorption process.

3.1.1. Simulations used

As an example of the use of the model to analyse TDA tests, let's consider desorption in a steel sample 1 mm thick, with a microstructure containing three types of traps, those related to dislocation distortion, grain boundaries and precipitate surfaces. The start hydrogen content is 1 ppm, in a distribution that is not artificially homogeneous, but that reflects the redistribution that would have occurred while cooling down after being hydrogen charged at high temperature.

During the simulated experiment, a heating rate: (*i.e.* ≈ 200 C) is applied to the specimen and we obtain the desorption curves shown in **Figure 2**.

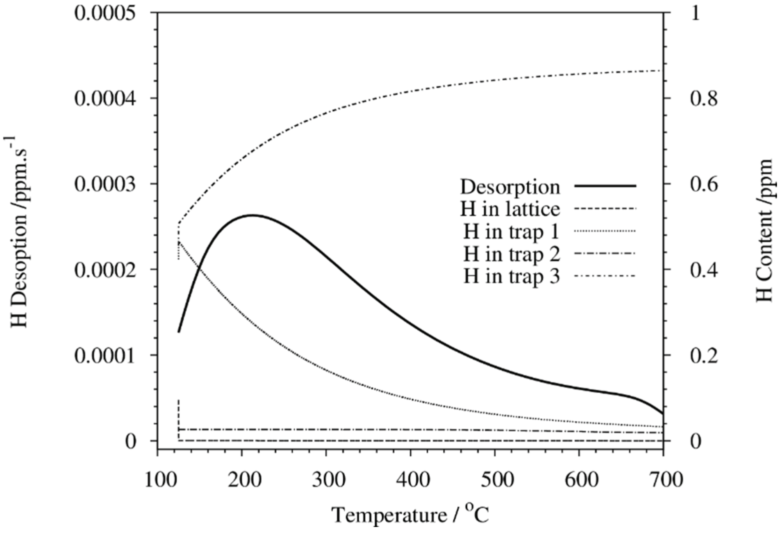

Figure 2 Evolution of hydrogen content at various sites and desorption flux during a simulated TDA test. Start Hydrogen content: 1 ppm. Heating rate: (*i.e.* ≈ 200 C)

In this example, we observe how, as the specimen starts heating, the hydrogen content in lattice sites drop rapidly. Hydrogen content in dislocation and grain boundary sites is reduced progressively as the test progresses and the temperature increases. At the same time, and due to the larger de-trapping energy barrier, hydrogen content at precipitate trapping sites increases.

The flux of hydrogen leaving the specimen increases initially, but peaks as soon as much of the hydrogen leaving the traps within the dislocation distribution has been shed and diffused, across the lattice, to the surface of the specimen.

3.2. Modelling a permeation across a wall

Another possible use of this model is also of great interest for several industries. The description of hydrogen transport through a metal wall separating two volumes, one volume with high hydrogen pressure and temperature and another volume with low hydrogen pressure and temperature was studied. By varying temperature and pressure conditions, and geometrical and microstructural parameters this simulation could be applied, among others, to hydrogen storage and distribution, to petrochemical processes or for some designs of nuclear power generation.

3.2.1. Used simulations

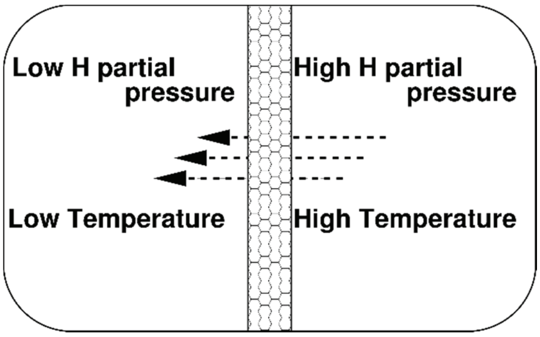

Figure 3 The diagram describes the system analysed in this section. A thin metal wall separates two volumes, one with high partial pressure of hydrogen and high temperature and another volume with lower partial pressure of hydrogen and lower temperature.

The diagram in **Figure 3** represents the system analysed in this section. Two volumes at different temperatures and with different hydrogen partial pressures are separated by a metal wall. The focus of the simulation is to study the transport of hydrogen through such wall, analysing the transient flux rate, the accumulation of hydrogen at different trapping sites and in different regions across the wall and obtaining insight on the possible saturation level of the microstructure.

Two pairs of examples are shown below. In all cases the volume at the hot side of the wall stays at 290C, while the colder side stays either at 200C or 50C. In one set of examples the high pressure (hydrogen partial pressure) is 1.5MPa, and in the other 0.5MPa, while the low pressure side has atmospheric conditions. The thickness of the wall is 5mm. The alloy has fine microstructure and contains no hydrogen at the start of the simulation.

3.2.2. Intermediate H partial pressure (0.5 MPa)

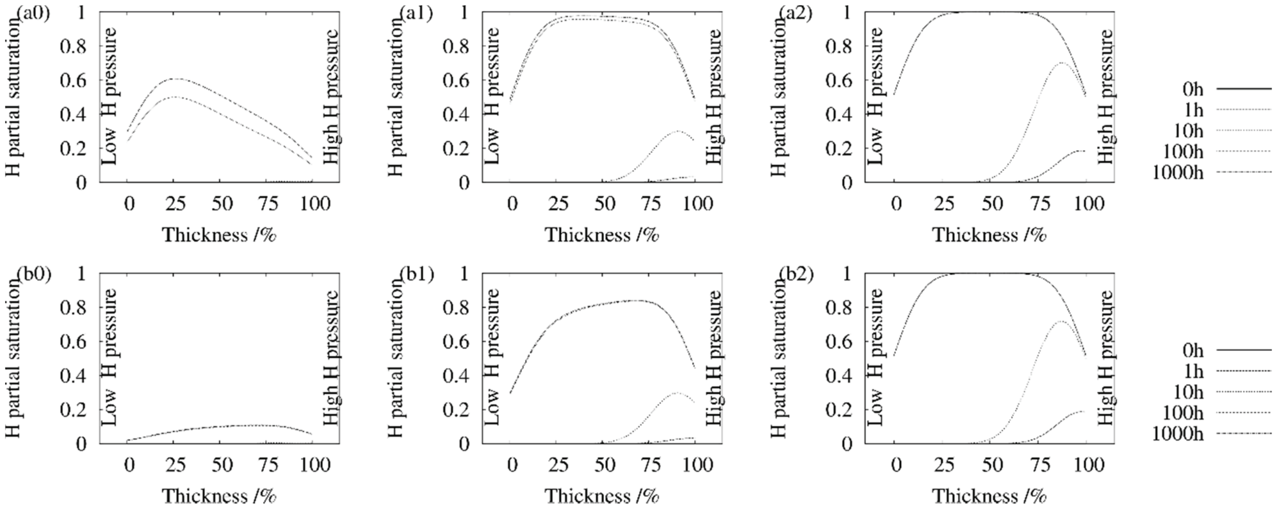

Figure 4 Hydrogen redistribution curves during permeation of a 5 mm steel wall between two volumes with different temperature and hydrogen partial pressure. High hydrogen partial pressure is 0.5 MPa. Low hydrogen partial pressure is equivalent to atmospheric conditions. Top plots (a*x*) present results for system with 50/290C bounding temperatures and bottom plots (b*x*) for 200/290C. Indexes **0** to **2** refer to lattice, dislocation and grain boundary trapping sites respectively.

In both these examples, there is a trend towards saturating the structure of trapping sites before reaching some sort of adsorption-desorption steady state. In both these cases that occurs shortly before 200 hours. Grain boundaries close to the high pressure boundary saturate first, saturation that then extends to the thickness of the specimen. Similarly for the dislocation distribution it was studied (see **Figure 4**). For the lattice, it only becomes partially saturated in the case with larger temperature gradient.

3.2.3. High H partial pressure (1.5 MPa)

In the present example, the specimen bounded by a larger temperature gradient experiences a rapid supersaturation at the grain boundary level, while the rest of the structure grow richer in hydrogen till reaching a sort of adsorption-desorption steady state shortly after 100 hours. Afterwards, this supersaturation declines till the hydrogen content become close to saturation (**Figure 5**). Using the level of maximum supersaturation at this site type, it would be possible to predict the risk of embrittlement, by using criteria described previously [9].

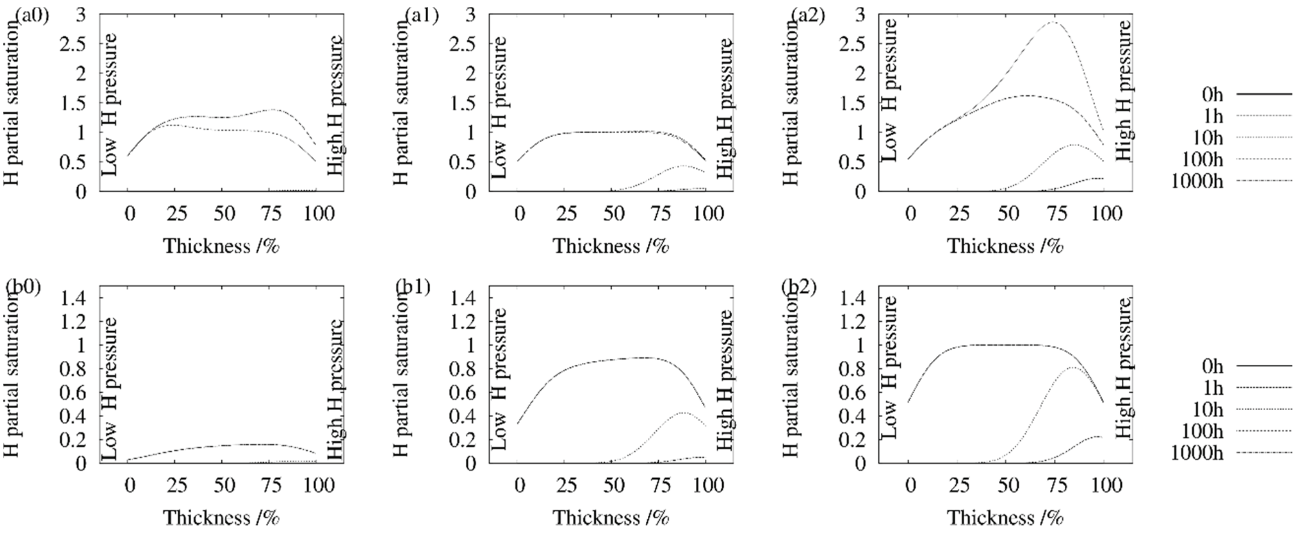

Figure 5 Hydrogen redistribution curves during permeation of a 5 mm steel wall between two volumes with different temperature and hydrogen partial pressure. High hydrogen partial pressure is 1.5 MPa. Low hydrogen partial pressure is equivalent to atmospheric conditions. Top plots (a*x*) present results for system with 50/290C bounding temperatures and bottom plots (b*x*) for 200/290C. Indexes **0** to **2** refer to lattice, dislocation and grain boundary trapping sites respectively.

For the case of a smaller temperature gradient, and as happened in the previous example with lower partial hydrogen pressure, the lattice never experiences large partial saturation, while both trapping distributions reach towards saturation, starting from the boundary at higher temperature and pressure, and then growing to the whole thickness.

4. CONCLUSION

A physical model on hydrogen redistribution has been applied to simulate two experimental situations of interest both in academia and industry, Thermal Desorption Analysis (TDA) and hydrogen permeation through a metal wall, driven by a gradient in partial pressure and against a temperature gradient.

By using this type of model it becomes possible to obtain a better understanding of the fluxes of hydrogen within the metal and among different lattice and trapping sites present in the microstructure. By using previously presented criteria it would be possible to predict embrittlement risk.

Similar simulations could be applied to various industries, including hydrogen storage and distribution, in petrochemical processes or in some designs of nuclear power generation, simply by varying temperature and pressure conditions, and geometrical and microstructural parameters to suit each application.

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