

## APPLICATION OF A PHYSICAL MODEL ON INTERSTITIAL DIFFUSION TO THE ISSUE OF HYDROGEN DAMAGE DURING CASTING AND FORMING OF FERROUS ALLOYS.

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### Abstract

Hydrogen trapping is considered to play an important role in many of the mechanisms explaining embrittlement in high performance alloys. Traps are generally categorised in two wide groups: shallow or reversible traps and deep or irreversible traps. The later include microstructure defects like voids, microcracks and the surfaces of specific incoherent precipitates. When dissolved hydrogen accumulate at these sites in large concentration it transforms into molecular hydrogen (gas) and pressure builds up.

A set of physically-based models describing heat transfer and phase transformation in ferrous alloys has been combined with a model of interstitial element diffusion which incorporates thermally driven diffusion to account for interstitial redistribution across thermal gradients, considering phase transformation and varying interstitial solubility and diffusivity as well as limited desorption at free surfaces.

As is well known, atom diffusion is driven by a reduction of the Gibbs energy of the system. In the most usual case diffusion reduces concentration gradients at constant matrix composition and temperature. However, as shown by Darken (1949), under a temperature gradient diffusion could occur up-hill the composition gradient as long as that still leads to a reduction of Gibbs energy in the system. This effect is also known as thermal diffusion or Ludwig-Soret effect.

This set of models is used to study in detail the phenomenon of concentration of hydrogen gas in microstructural defects in steel and assess its severity related to microstructure, phase transformation temperature, defect distribution and manufacturing conditions, like initial hydrogen content, component size and thermal history. The results of the calculations are related to the occurrence of macroscopical damage resulting from the build up of high pressure hydrogen gas in microstructure defects.

**Keywords:** Hydrogen damage, irreversible trapping, modelling, gas pressure.

### 1. INTRODUCTION

The solution of small amounts of hydrogen in steel during manufacturing is in some cases responsible for severe degradation of the metal's mechanical properties. As this phenomenon is specially relevant in high performance alloys, much effort has historically been applied to understand and avoid such problem, and such effort still continues nowadays <sup>[1-6]</sup>.

Hydrogen content in the molten metal is reduced during refining or using vacuum technologies, while hydrogen pick-up is minimised all thorough the process. These operations enable bringing the overall hydrogen content in the metal down to 1.5ppm with standard refining practices (like AOD) and to 0.5ppm by using vacuum technology. Any remaining hydrogen stays either in solution up to the matrix phase's solubility limit or becomes distributed (*trapped*) into various types of lattice defects.

The nature of trapping sites ranges from the distortion field surrounding dislocations to the surfaces of certain precipitates and microcracks in the material, but they can all be modelled as a potential well, with a

characteristic activation energy necessary for the release of an hydrogen atom contained in them<sup>[3-4]</sup>. Using this description, it is usual to classify trap sites into two broad categories, shallow or reversible trap sites and deep or irreversible ones. Reversible traps (*i.e.* dislocations, alloying elements and some precipitates) are also referred to as finite traps, as they can only accommodate a small amount of hydrogen<sup>[3-4]</sup>. Apparently, reversible trapping need not be detrimental and several methods have been proposed that involve using a distribution of reversible traps to minimise the effect of residual hydrogen in mechanical properties by avoiding the build up of large concentrations of hydrogen in a small region<sup>[4-5]</sup>.

Irreversible traps, on the other hand (like for instance voids, microcracks or the surfaces of specific incoherent precipitates) are usually able to accommodate a larger amount of hydrogen. In their case, hydrogen trapped in large concentration may transform into its molecular form (gas), and produce an increase in pressure inside the defect, potentially leading to irreversible damage in the form of cracking and plastic deformation (fisheyes, flaking, etc)<sup>[2-3]</sup>.

Keeping in mind that a distribution of reversible trap sites can only hold a limited amount of hydrogen and that it may not necessarily be detrimental to the mechanical properties of the metal, this work applies the conservative assumption that all hydrogen beyond the solubility limit concentrate on irreversible trap sites. Particularly, as the main types of irreversible traps are -or may be assimilated to- microcracks, it is to be expected that at large concentrations, the hydrogen atoms trapped at such sites combine into their more stable form of molecular hydrogen (gas).

To determine the distribution of hydrogen in a metal component during manufacturing, a model on the diffusion of of interstitial atoms has been used, which includes the effect of phase transformation and a physical description of the fluxes of hydrogen across a free surface (external or internal). The model allows therefore the estimation of hydrogen supersaturation during different manufacturing conditions and the pressure that could be potentially reached in microstructure defects acting like irreversible trap sites. The information inferred from this work is expected to contribute to avoid manufacturing practices that lead to severe material degradation.

## 2. DESCRIPTION OF THE MODEL

A physical model describing the diffusion of interstitial atoms has been built on and applied to the redistribution of hydrogen<sup>[6-7]</sup>. This model incorporates previously developed models of temperature evolution and phase transformations in steel<sup>[6-8]</sup>.

Temperature evolution during cooling of a metal component has been modelled by integrating the heat equation numerically, using a finite difference implicit scheme (Crank-Nicholson<sup>[8]</sup>). This model incorporates the effects of natural and forced convection as well as radiation as heat extraction mechanisms. To describe a number of situations, the value of  $h$ , the heat transfer coefficient, could be adjusted to describe from air convection ( $h = 6 \text{ Wm}^{-2}\text{K}^{-1}$ ) to forced cooling using water spray cooling ( $h = 22 \cdot 10^3 \text{ Wm}^{-2}\text{K}^{-1}$ )<sup>[6-8]</sup>. Phase transformation during cooling is modelled using thermodynamic criteria and classic nucleation and growth kinetics as described in previous work<sup>[6-8]</sup>.

The integration of these models with the hydrogen diffusion model runs the following scheme. The starting distribution of interstitial composition in each calculation cell,  $C_i$ , is taken from initial conditions. From the temperature evolution model mentioned above, the temperature for each calculation cell is determined for the current time interval, and the saturation composition  $C^0$ , as well as the relative saturation  $C/C^0$ , are determined as function of temperature and matrix phase according to<sup>[9]</sup>, vol.1, Eqs. 7.4.2-5. Subsequently, these values are recalculated for all the thermal history of the process.

The evolution of hydrogen distribution is determined as a function of thermal agitation and atom mobility by relating it to a random walk process. The expression of the final distance covered by each atom, the *mean random walk distance*,  $\Delta x$ , in a time interval  $\Delta t$ , is related to the thermal agitation, via the diffusion coefficient  $D$ , using the random walk expression<sup>[10]</sup>:

$$\Delta x = \sqrt{\Delta t \cdot D}$$

If the jump is totally random, the probability  $P$  of an atom ending its random walk in the adjoining cell in direction  $j$  is given by,

$$P = \frac{1}{6} \frac{\Delta x}{l_c}$$

where  $l_c$  is the calculation cell length in one of the 6 main directions of displacement.

In the present model, it has been considered that for dilute solutions the gradient in chemical activity of an interstitial atom may be related to the gradient in partial saturation at the matrix phase in which it lies [6-7]. With that assumption, the actual flux of atoms is function of the relative saturation, that is, interstitial atoms will tend to flow from regions with high levels of saturation to regions with lower levels of saturation (*i.e.* down-hill the partial saturation gradient). In a situation of uniform temperature this would be equivalent of considering that atoms flow from regions with high concentration to regions with low concentration, but in an scenario with large temperature (and therefore solubility) gradients, or with phases with distinct solubilities, it allows the possibility of diffusion happening up-hill the composition gradient. The difference in partial saturation in adjoining regions is used to determine the probability of an atom to diffuse there. In this way, by using partial saturation it is possible to deal simultaneously with interstitial site saturation.

The influence of thermal activation is captured by using an Arrhenius-type description of diffusion. The diffusion pre-exponential and activation energy coefficients obtained from literature [6-9].

$$D = D_0 \exp\left(\frac{-\Delta H}{RT}\right)$$

Special considerations need to be taken when studying the effect of the free surface on the behaviour of interstitial atoms, specially those as mobile as hydrogen. Hydrogen desorption is estimated assuming local equilibrium at the surface, and 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 [3,7]. Additionally, the flux of hydrogen atoms across the surface is still restricted by the atom mobility conditions as described earlier and limited by site saturation (*i.e.* partial saturation). Finally, the influence of the surface condition is introduced using an empirical coefficient  $S$ , ( $0.0 \leq S \leq 1.0$ ).

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of cooling rate on concentration distribution

The model described has been used to study the influence of material and manufacturing conditions on the redistribution of hydrogen in steel. Fig.1 shows the difference in hydrogen distribution obtained between fast and slow cooling of a steel plate 25cm thick containing 1.5ppm of hydrogen. During a long slow cooling ( $h = 6 \text{ Wm}^{-2}\text{K}^{-1}$ ), and while the surface is still at high temperature, some hydrogen diffuses from the subsurface region out of the metal, and as the temperature gradients within decrease the hydrogen concentration homogenises to an average content of 1.08ppm. On the

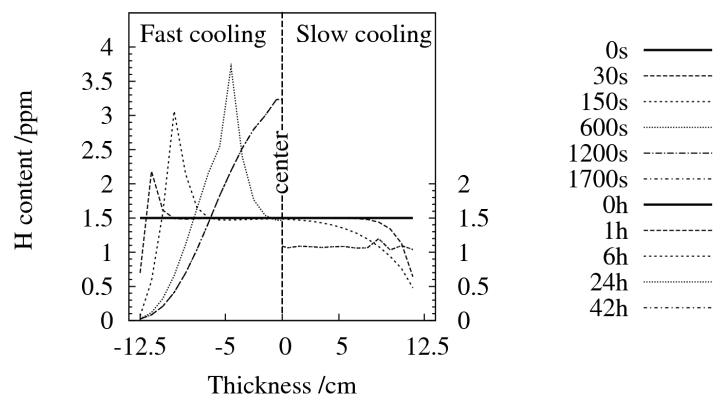


Fig 1: Hydrogen redistribution during fast and slow cooling of a 25cm thick plate with 1.5ppm start H content, in steel with FCC to BCC phase transition occurring at 700°C.

other hand, during fast cooling ( $h = 22 \cdot 10^3 \text{ Wm}^{-2}\text{K}^{-1}$ ), the severe temperature gradient between the surface and the core of the plate favour the hydrogen flux towards the core region. At the same time, as the surface temperature decreases rapidly, diffusion out of the metal is reduced. Phase transformation from FCC to BCC as the metal cools, with the later phase being less able to dissolve hydrogen, contribute to the flux towards the core region. The lower saturation threshold of BCC also impedes diffusion in the subsurface region and therefore, loss of hydrogen towards the atmosphere. In summary, and as shown in Fig.1(a), during fast cooling hydrogen in the subsurface region becomes pushed towards the core region, forming two concentration peaks that grow as they move towards the high temperature core until they eventually join at the centre of the piece.

Fast cooling of a thick component produces a substantial enrichment in hydrogen of the core region, reaching several times the starting overall concentration, while the total content remains barely unchanged (1.49ppm). Then, on transformation to BCC the core region becomes severely supersaturated. Slow cooling of the same component produces an uniform hydrogen distribution, and a certain reduction of the overall content (in this example, from 1.5ppm to 1.08ppm), although at the cost of a lengthy cooling process (42 hours). An alternative method has also been proposed elsewhere aiming for the reduction of hydrogen content during cooling, which avoids the core concentration of hydrogen content [6,7-11].

### 3.2. Hydrogen supersaturation

As described in the previous section, some manufacturing operations may force the hydrogen content in a metal component to redistribute causing the formation of high concentration regions, where the hydrogen content could achieve concentrations several times larger than the overall starting concentration in the component. Furthermore, hydrogen solubility decreases with decreasing temperature, and suffers a sudden additional reduction on the transformation from FCC to BCC structure.

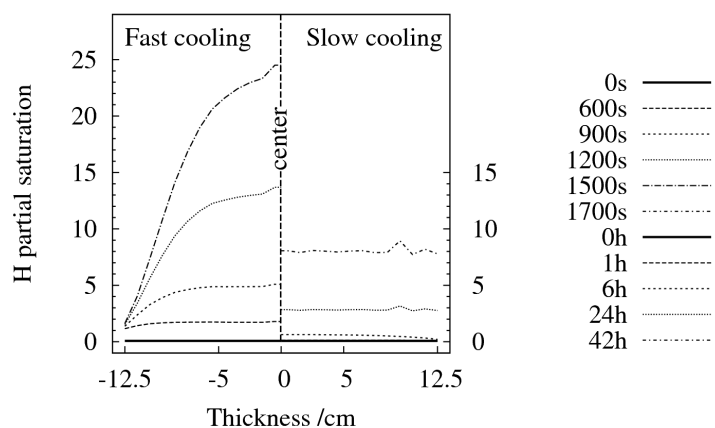


Fig.2 shows the same operations as shown in Fig.1, but in terms of partial saturation. Partial saturation is defined as the hydrogen content divided by the solubility limit as function of matrix phase and temperature ( $C_i / C^o(T_i)$ ). Above unity, the content is *beyond* the solubility capability of the matrix and such supersaturation needs to be redistributed among various trapping sites. During slow cooling (Fig.2, right), hydrogen content remains homogeneously distributed, and although hydrogen content reaches supersaturation and increases to several times the solubility of the BCC matrix, the supersaturation is still less severe than in the core region of a fast cooled component (Fig.2, left). In the present example, the fast cooled component with a starting hydrogen content of 1.5ppm reaches in its core region supersaturation over 24 times the solubility limit of the BCC matrix.

Fig 2: Hydrogen partial saturation (or supersaturation if above 1.0) due to redistribution during fast and slow cooling of a 25mm thick plate with 1.5ppm start H content, in steel with FCC to BCC phase transition occurring at 700°C.

### 3.3. Equivalent gas pressure in irreversible traps

As discussed before, an excess in hydrogen content, that is, beyond the solubility limit of the metallic matrix, distributes among trapping sites of various typologies. The resulting effect on the mechanical properties of the alloy depends directly on the type of trapping site and the amount of hydrogen that contains,

As several types of trapping sites coexist, various embrittlement mechanisms might be at work<sup>[3]</sup>. Reversible trapping sites are able to accommodate a limited amount of hydrogen, and their effect on mechanical behaviour is ambiguous<sup>[3-5]</sup>. Irreversible traps are able to hold a larger amount of hydrogen and affect the alloy detrimentally<sup>[3-5]</sup>.

The distribution and number density of sites of each type it is characteristic of each alloy and the thermal history it has sustained and therefore it is not possible to offer a general estimate of the effect of excess hydrogen on the mechanical properties of ferrous alloys. However, by assuming that in a general situation, the fraction of hydrogen trapped in reversible traps (and its effect on the mechanical behaviour of the alloy) is small compared to that trapped in irreversible traps, it is possible to offer a conservative estimate of the potential severity of the resulting degradation. To that end, it has been assumed that in most cases any type of irreversible traps could be assimilated to voids or microcracks.

Fig.3 compares the temperature and partial saturation evolution for the core and subsurface regions during the fast cooling of the component in Fig.1 and Fig.2. In this case, molecular hydrogen unable to remain in solution in the surrounding matrix would diffuse into the trap distribution and form molecular hydrogen (*i.e.* hydrogen gas). The hydrogen transfer between matrix and void has been considered to occur under local equilibrium and therefore to follow Sievert's Rule. Fig.3 plots as well the potential gas pressure in irreversible traps equivalent to the matrix supersaturation. As supersaturation increases during cooling with hydrogen diffusion towards the component core, more gas accumulates and pressure in the microcavities builds up. Even though the accumulation of hydrogen gas at high pressure is not the only mechanism by which the metal degradation may occur, hydrogen gas pressure is considered to provide a good estimate of the severity of the potential damage occurring to the alloy.

In practice, the excess hydrogen would distribute among various types of traps, so not all of it would contribute to the increase in pressure. However, the excess hydrogen estimated by modelling is high enough that even if a fraction of it is accommodated in other types of trap site the resulting pressure in microcavities would still be matter of concern. Moreover, as pressurised gas starts to accumulate in microcavities while at high temperature, it would be necessary to consider not only the static yield strength of the matrix at each temperature, but also the dynamic yield strength, as rigorously this issue would sit on the boundary between static deformation and creep. Excessive pressure may open microcrack interfaces apart and induce the nucleation of new cracks around cavities, leading to the formation of macrostructural damage, like *hairlines*, *flaking* and *fisheyes*, all of them typical of macroscopic hydrogen damage<sup>[2-3]</sup>.

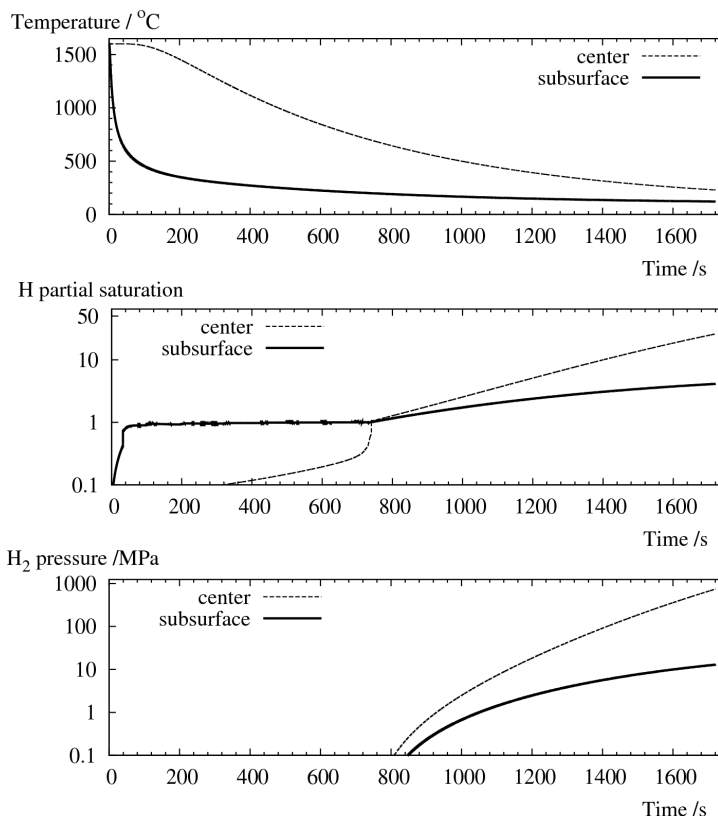


Fig 3: Evolution of temperature, partial saturation (or supersaturation if above 1.0) and potential hydrogen gas pressure in microcavities for the core and subsurface regions of a 25mm thick plate under fast cooling, with 1.5ppm start H content.

#### 4. CONCLUSIONS

A physical model on hydrogen redistribution has been used to estimate the degree of hydrogen degradation during manufacturing processes. The model predicts that on fast cooling, hydrogen content redistributes forming concentration peaks that may reach several times the starting average concentration value. Acute concentration, together with diminishing hydrogen solubility with decreasing temperature leads to the metal matrix becoming severely supersaturated in hydrogen.

Excess hydrogen becomes stored in microstructural defects (traps), of which irreversible traps (assimilable to microcracks) to store a larger proportion. As hydrogen in microcavities easily becomes molecular hydrogen (gas), the potential gas pressure in these trapping sites has been taken as indicator of potential material degradation.

The large pressures that could potentially develop in microcavities in a supersaturated metal, are consistent with mechanisms leading to the formation of macroscopical defects, typical of hydrogen damage. These defects would occur by plastic deformation at high temperature and crack nucleation.

Finally, this work shows that hydrogen content usually considered harmless could still become detrimental when misguided manufacturing or heat treating practices are used.

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