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Understanding hydrogen redistribution and designing a new hydrogen extraction method

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Abstract

Hydrogen redistribution and trapping plays an important role in the embrittlement of some high performance alloys. A correct understanding of hydrogen redistribution would allow the prediction and prevention of this severe type of material degradation.

A physical model of interstitial element diffusion is used to study the fluxes of hydrogen during manufacturing of metallic alloys. In particular, the present model contemplates diffusion in its most comprehensive description, i.e., atom diffusion is driven by a reduction of the Gibbs energy of the system (and not only related to composition gradients). The model presented incorporates physical description of thermal agitation and atom mobility of interstitial elements, the influence of temperature gradients, solubility and saturation of the interstitial elements as function of temperature and matrix phases, as well as the kinetics of degassing at high temperature. Finally, it incorporates the role of traps as potential energy pits presenting a characteristic energy barrier to the release of hydrogen atoms.

Such a model permits the study of the effect of different microstructure characteristics on the trapping, de-trapping and general redistribution of hydrogen, taking into account the thermal cycle and the separate contribution of microstructure, deformation level, dislocation distribution, grain size, carbide presence and distribution, et c. and their interaction, to finally obtain the degree of saturation at the lattice and each trapping site type during and after a heat treatment.

Two industry-relevant applications have been analysed: First, the study of hydrogen redistribution during casting and cooling; and second, a study on the effectiveness of baking.

The first study has provided insight on redistribution patterns that lead to supersaturation related to processing parameters, and once that is understood, to the design of a new treatment to reduce hydrogen content in cast components, which has obtained several patents.

The second, by studying the effect of storing a metal part in a heated oven for a long period of time, in a process known as baking, it is possible to explain why this standard method presents varying degrees of success. This variability is related to the alloy microstructure and cooling process prior to baking, which in turn influence where in the microstructure hydrogen is stored at the time of the treatment.

Keywords: Hydrogen, Diffusion, Model, Reduction method, Embrittlement, Baking, Casting

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1. Introduction

The severe degradation caused by hydrogen on some high strength alloys has long been acknowledged[1-3], and due to their technological and economic relevance, it is a phenomenon that has attracted intense research for decades [4-6].

Although several satisfactory methods already exist that are able to limit hydrogen content on ferrous alloys it is still sensible to improve our understanding of hydrogen behaviour during processing.

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This work presents a physical model on interstitial diffusion which has been used to study hydrogen redistribution patterns during metallurgical processes and that has allowed to develop a new method for the effective extraction of hydrogen from metal alloys[7-9].

2 Description of the model

2.1 Hydrogen diffusion

A physical model describing the diffusion of interstitial atoms has been built on and applied to the redistribution of hydrogen[7, 10]. Phase transformation during treatment is modelled using thermodynamic criteria and classic nucleation and growth kinetics as described in previous work[11-12].

The driving force for diffusion, using its more rigorous definition, is related to the gradient of chemical activity (and not just to the composition gradient, as often seen in simplified models)[13]. In the present work, 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[4-5, 14]. 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 other possibilities, like 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[7].

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, Δx, in a time interval Δt, is related to the thermal agitation, via the diffusion coefficient D, using the random walk expression[15]:

$$\Delta \mathrm{x} = \sqrt{\Delta \mathrm{t} \cdot D} \qquad (1)$$

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, $P = 1/6 \cdot (\Delta x/l_c)$ where l_c is the calculation cell length in one of the 6 main directions of displacement. These probabilities are modified in the model to account for the gradient in partial 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, 16-18].

2.2 Supersaturation, trapping and equivalent gas pressure

The metal's microstructure is able to store a certain amount of hydrogen distributed either in the lattice or in various typologies of lattice defects. In some cases, these defects consist in subtle distortions of the lattice itself, like the distortion around a dislocation, or on the surface of a coherent precipitate. In other cases, these defects represent a severe rupture of the lattice structure, like for instance voids, microcracks or the surfaces of specific incoherent precipitates.

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[4].

In the case of microcracks, 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.)[4, 19].

The equivalent gas pressure in a microcavity due to supersaturation is an illustrative parameter to estimate the risk of hydrogen embrittlement. Moreover, even though the physical meaning of the equivalent gas pressure becomes less clear for trapping sites other than microcavities, it has been considered that it is still a good indicator of the embrittlement risk that superaturation implies. Therefore, it is calculated for both the lattice and all trapping sites considered, not necessarily as a physical prediction of actual pressure, but as an estimate of the potential embrittlement risk, as described elsewhere[20].

2.3 Trapping

The effect of various types of trap to the redistribution of hydrogen is incorporated into the model by providing that hydrogen contained in the metal either stays in solution up to the lattice phase's solubility limit or is expelled from the lattice and becomes trapped into various types of lattice defects available[17-18, 21].

The nature of trapping sites vary, but they can all be modelled as a potential well. In many respects, this description makes the analogy between the energy barrier for the release of an atom from a lattice site at each diffusion jump and the release from a trap site[21].

This process is suitably described by a characteristic activation energy. Each trap type is then characterised by the speciffic activation energy needed for the release of an hydrogen atom contained in them[4, 21].

2.4 Hydrogen desorption

Finally, 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[4-5, 16]. 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)[7, 20].

3. Results and discussion

The model described has been used to study the influence of manufacturing parameters and material conditions on the redistribution of hydrogen in steel. First, a description of the hydrogen redistribution occurring during cooling is presented. Then a detailed study of *baking*, a commonly used method for the reduction of hydrogen embrittlement, is also presented. Finally, the improved understanding of hydrogen redistribution is used to design a novel method for the reduction of hydrogen content in metallic alloys, with the aim to reduce the risk of hydrogen embrittlement.

3.1. Description of casting

The model described above has been applied to a cooling process, in order to better understand the effect of various parameters to the redistribution of hydrogen[7].

An important aspect that sometimes is not well understood is the effect of cooling rate after solidification. Fig.1 shows the difference in hydrogen distribution obtained between fast and slow cooling of a steel plate 25cm thick containing 2ppm of hydrogen. In these calculations is possible to see how during a long slow cooling ($h=6\ \mathrm{W\ m^{-2}\ K^{-1}}$), 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 1.53ppm.

On the other hand, during fast cooling ($h=22 \cdot 10^{3}\ \mathrm{W\ m^{-2}\ K^{-1}}$), 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 further to the flux towards the core region.

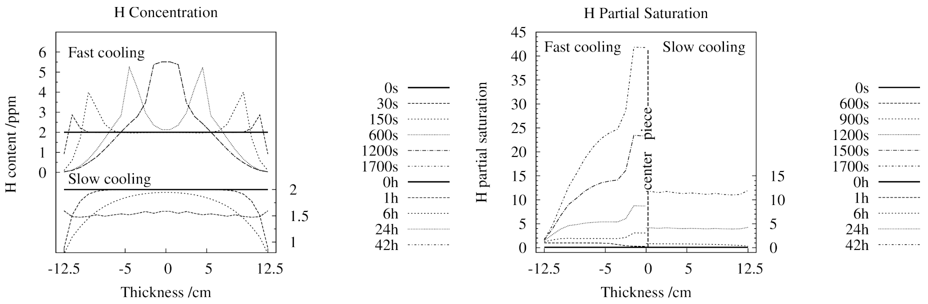

Figure 1: Hydrogen redistribution during fast and slow cooling of a 25cm thick plate with 2ppm start H content. Concentration and partial saturation (or supersaturation if above 1.0).

During slow cooling, 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. In the present example, the fast cooled component with a starting hydrogen content of 2.0ppm reaches in its core region supersaturation over 40 times the solubility limit of the BCC matrix.

This effect is intensified with increasing component size (as a larger volume implies larger absolute hydrogen content for the same average content), as well as being function of the FCC to BCC transformation temperature, as shown in Fig. 2[7].

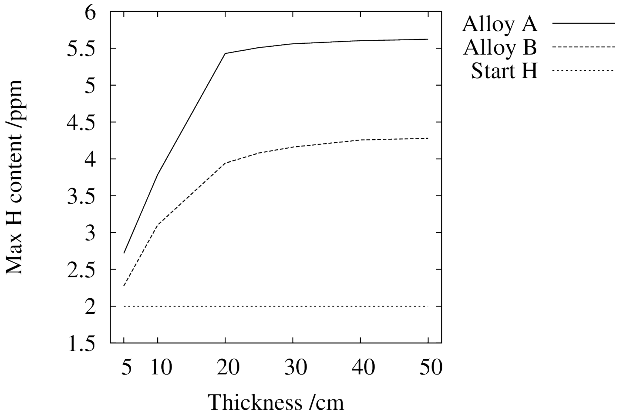

Figure 2: Effect of component size and FCC/BCC phase transformation temperature on hydrogen concentration after fast cooling. Steel A transfroms at 700ºC and Steel B at 450ºC.

3.2. Description of baking

A common method used to minimise the detrimental effect of hydrogen on the mechanical properties of metal components is baking. Typically, a baking treatment, consists in storing the metal component at low temperature (*i.e.* 150 to 230ºC) for a long period of time (typically 12 to 48 hours)[22].

During this treatment, a fraction of the hydrogen atoms in the lattice diffuses to the surface of the component where it leaks to the atmosphere. However, a quantity of hydrogen is also stored in microstructure defects, or traps. The release of hydrogen atoms from such traps is conditional to overcoming the detrapping energy barrier characteristic to the type of site[8, 23-25].

With the purpose of analysing what parameters affect the effectiveness of baking, two steel microstructures have been considered, defined by the temperature of transition from FCC to BCC during cooling and their characteristic microstructures. The microstructures are described in terms of characteristic dislocation density and grain size but presenting a similar carbide distribution (Table 1). These parameters are used to define the trap density and distribution. Each of the trap types is defined by its characteristic energy barrier for the release of an hydrogen atom[8, 21].

The temperature cycle prior to the baking treatment defines the starting hydrogen distribution in the metal. In this case it consists in continuous cooling from 1600ºC to room temperature. A 12 hour baking treatment starts immediately after that. For that treatment two baking temperatures have been modelled (190ºC and 300ºC).

Table 1. Austenite transformation temperature and final microstructure obtained from its decomposition, and trapping site distribution for Steel A and Steel B.

	Steel A	Steel B
FCC to BCC	725 ºC	450 ºC
BCC structure	Allotriomorphic	Acicular
Grain size	Large ~ 0.1mm	Small ~ 10μm
Dislocation density	Low 4e22 site/m3	High 4e24 site/m3
Ppt trap density	2e22 site/m3	2e22 site/m3

Fig.3 shows how the overall hydrogen content, microstructure and trap distribution interact in a complex way during any thermal treatment, as in this case in a baking treatment [8].

The capability of hydrogen to diffuse is roughly inversely dependent on the degree of saturation of the lattice. Therefore, a microstructure better suited to absorb large concentrations of hydrogen without becoming supersaturated will reduce its hydrogen content more effectively during a baking treatment than one that is already saturated at the start of the treatment.

Table 2 shows the hydrogen reduction obtained for both microstructures and baking temperatures. Smaller grain size, larger dislocation densities and more extensive precipitate or inclusion distributions allow for a larger capacity of the microstructure to absorb hydrogen before becoming saturated. Therefore, an acicular or bainitic ferrite microstructure, with its large dislocation network combined with a fine precipitate distribution will fare better at dissolving hydrogen and shedding it during a baking treatment than another microstructure with large grained allotriomorphic ferrite, low dislocation density and few carbide surface area.

Table 2. Reduction in hydrogen content during baking for 12 h at 190ºC and 300ºC for Steel A and Steel B.

Baking T	Steel A	Steel B
190ºC	0.005%	9.2%
300ºC	0.6%	19.6%

The role played by different types of traps is a function of their partial saturation related to the lattice and of their characteristic energy barrier to the release of hydrogen. As long as the lattice presents lower partial saturation and the temperature allows the release of hydrogen from the trap distribution, the flux of hydrogen will occur towards the lattice (and then to the atmosphere). However, for some deep traps it may occur that they keep absorbing hydrogen while the rest of the microstructure releases hydrogen to the atmosphere[8].

3.3. Design of hydrogen extraction method

The model discussed above has allowed to obtain better understanding of the fluxes of hydrogen during heat treating. With this better understanding it has been possible to design a novel method to eliminate hydrogen from metallic alloys.

As discussed earlier, during the cooling of a component the flux of hydrogen occurs towards the core of the metal component, because it stays at higher temperature as heat is extracted from all the surface of the component. However, lets consider the case in which a small region of the surface of that component were to be kept at high temperature during the cooling process. In that scenario, hydrogen would still flow towards the hot regions of the component, with the difference that in this case, it would not accumulate in the core region but it would be directed to the heated surface and effectively extracted from the metal[7, 9].

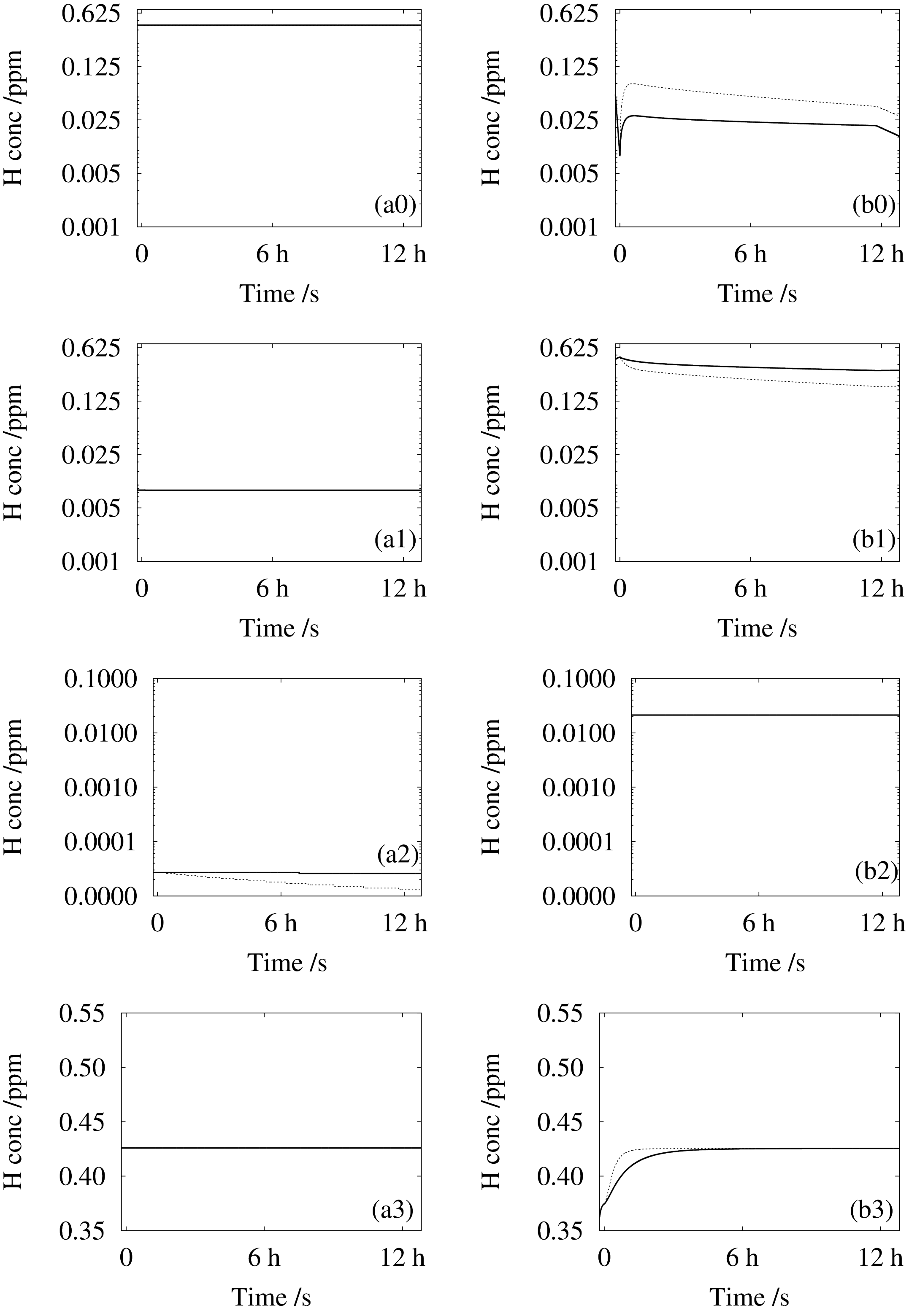

Figure 3: Hydrogen redistribution curves during baking for two microstructures and two baking temperatures, detailing the hydrogern content evolution for lattice and each type of trap sites. **ax)** and **bx)** refer to Steels A and B, indexes **0** to **3** to lattice, dislocation, grain boundary and precipitate trapping sites respectively. Solid line correspond to baking temperature of 190ºC and dotted line to 300ºC.

Fig.4 shows the evolution of hydrogen distribution during such an operation. A plate of dimensions (25cm thick) as in the calculation in Section 3.1 is cooled from 1600ºC to just above room temperature. The only difference with the calculation shown in Fig.1 is that while one face of the plate is cooled ($h=22 \cdot 10^{3}$ W m^{-2} K^{-1}) the one opposite is kept at 1500ºC for 7200s. (2 hour). During this time the overall hydrogen content becomes reduced to below half the starting content (*i.e.* from 2ppm to 0.99ppm).

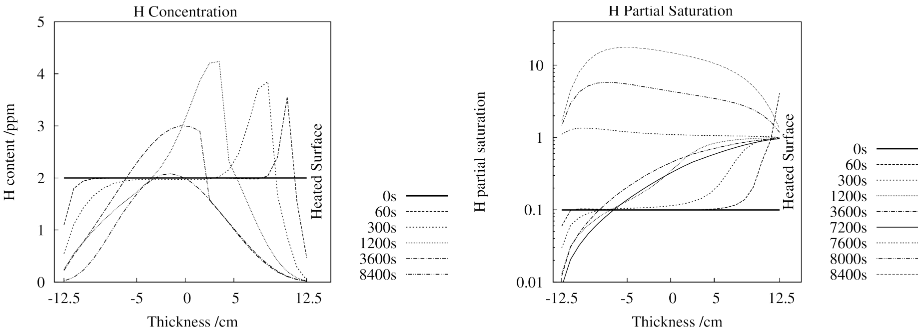

Figure 4: Hydrogen redistribution during directional cooling of a 25cm thick steel plate, where one of its surfaces is kept at 1500ºC for 7200s. Concentration and partial saturation (or supersaturation if above 1.0).

During the suggested treatment, a severe concentration peak still occurs (Fig 4), but on this case it occurs while the material is at high temperature and it is still able to dissolve the large interstitial content. Fig 4 shows as well how the partial saturation remains below saturation during all the treatment, and only increases slightly during the final cooling to room temperature. Even then, the final supersaturation is similar to the one obtained during an extremely slow cooling, as described earlier.

As the treatment proceeds and hydrogen discharges to the atmosphere at the heated surface, the overall content and the magnitude of the concentration peak both diminish. At the end of the treatment the overall hydrogen content has been reduced more that in a slow cooling or baking, to reach 0.99ppm This is sensibly lower than the 1.53ppm obtained during extremely slow cooling, and taking only 8400s (2 hours and 20 minutes) instead of 42 hours by slow cooling. It is also an improvement with respect to a baking treatment.

4. Conclusions

A physical model had been presented that allows an accurate description of hydrogen redistribution during manufacturing processes.

This model is able to describe and predict the behaviour of hydrogen during standard industrial practices, and it has been used to explain the effect of component size, cooling rate, microstructure, and phase transformation temperature on hydrogen redistribution and also to anticipate embrittlement risk.

By using this model, a method has been developed which enables to reduce hydrogen content from the metal via the use of imposed temperature gradients. This method has recently obtained several patents[9].

Similarly, it permits to explain whether and to what extent a baking treatment would be effective and when it would not, and relate it to hydrogen content, steel microstructure and treatment parameters.

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