Understanding hydrogen redistribution during steel casting, and its effective extraction by thermally induced up-hill diffusion

GAUDE-FUGAROLAS, Daniel

Independent Research and Consultancy in Physical Metallurgy and Engineering
c/.Alcalde Joan Batalla, 4, 08340 Vilassar de Mar (Spain)
dgaude@cantab.net

Abstract: The severe loss of ductility caused by hydrogen in high strength steels has been the object of intense research during decades. Because of the high mobility of hydrogen once has entered the metal, even in comparison with other interstitial atoms like carbon and nitrogen, a rigorous description of hydrogen fluxes during manufacturing of steel components is considered to be essential.

A physical model of interstitial element diffusion is used to study the fluxes of hydrogen during solidification and cooling of cast 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. Usually, it is only considered the case in which diffusion occurs to reduce the concentration gradient of an element at constant matrix composition and temperature. However, in a more general view, and as was proven by Darken (1949), diffusion may occur even up-hill the composition gradient as long it still leads to a reduction of Gibbs energy in the system. When diffusion occurs due to a temperature gradient, it has been referred to as thermal diffusion or Ludwig-Soret effect.

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.

The application of this model shows how hydrogen localizes in some regions of the component to a degree that depends on manufacturing conditions and where it may reach concentrations well beyond the initial average concentration in the metal. The model describes as well how the FCC to BCC phase transformation may drive hydrogen concentration beyond supersaturation, due to the disparate capability of these phases to dissolve hydrogen. On the other hand, this study has also enabled the development of a method for the reduction of hydrogen based on the imposition of severe but controlled temperature gradients to the component during cooling.

Keywords: hydrogen, diffusion, embrittlement, extraction

The severe degradation caused by hydrogen on some high strength alloys has long been acknowledged [1], and due to their technological and economic relevance, it is a phenomenon that has attracted intense research for decades [2-4].

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. A more precise description of hydrogen fluxes during manufacturing can only lead to better understanding of the phenomenon and to better methods to reduce the occurrence of hydrogen embrittlement.

This work presents a physical model on interstitial diffusion which has been used to study hydrogen redistribution patterns during metallurgical processes. Finally, the same model has been used to study the effect of directional heat extraction in the final hydrogen distribution and content in the component.

1. Description of the model

A physical model describing the diffusion of interstitial atoms has been built on and applied to the redistribution of hydrogen [5]. This model incorporates previously developed models of temperature evolution and phase transformations in steel [6-7].

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 [8]). 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 ($h = 6$ $Wm^{-2}K^{-1}$) to forced cooling using water spray cooling ($h = 22 \cdot 10^3$ $Wm^{-2}K^{-1}$) [7-8]. Phase transformation during cooling is modelled using thermodynamic criteria and classic nucleation and growth kinetics as described in previous work [6-7].

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_i as well as the relative saturation C_i/C^0_i are determined as function of temperature and matrix phase according to [9], 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, Δx,* in a time interval Δt, is related to the thermal agitation, via the diffusion coefficient D, using the random walk expression [10]:

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

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 [2-3,11]. 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 [4,8-9].

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

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 [2-3,8]. 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, $\left(0.0 \leq S \leq 1.0 \right)$.

2. Results and discussion

2.1. Effect of cooling rate

The model described has been used to study the influence of manufacturing and material 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 2ppm of hydrogen. During a long slow cooling ($h = 6$ Wm^{-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 ($h = 22 \cdot 10^3$ Wm^{-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 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 join at the centre of the piece.
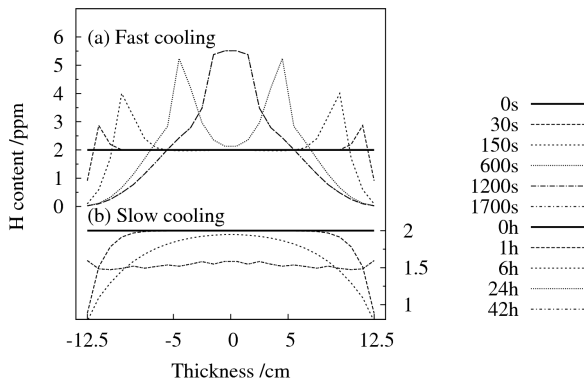

Fig.1 Hydrogen redistribution during fast and slow cooling of a 25cm thick plate with 2ppm start H content.

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 but unchanged. 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 2ppm to 1.53ppm), although at the cost of a lengthy cooling process (42 hours).

2.2 Effect of size and transformation temperature

The effect of the size of the component in the redistribution of hydrogen has two components. On one hand, the thermal mass of the component will define the thermal gradients during cooling. Additionally, a larger volume implies larger absolute hydrogen content for the same average content. Larger hydrogen content that, when forced towards the core of the component during fast cooling, will result in a larger concentration peak with increasing component size, as shown in Fig.2.

Fig.2 represents as well the effect of the FCC to BCC transformation temperature on the severity of the concentration peak formed during fast cooling. The transformation temperature for Steel A is 700°C (*i.e.* Fe0.4C, and forming allotriomorphic ferrite) while Steel B transforms at 450°C (*i.e.* Fe04C3.0Ni0.5Cr, forming bainitic ferrite) [6-7].

In both cases, during fast cooling hydrogen flows towards regions more able to dissolve it, either because they still present FCC structure or

because they are still at higher temperature. In the case of Steel A, transformation occurs earlier during cooling and at higher temperature with respect to Steel B. Hydrogen solubility in BCC is considerably lower than in FCC in both cases, but when the transformation occurs at higher temperature, diffusion velocity is larger, allowing larger redistribution fluxes to occur, leading to a higher final concentration peak and, therefore, severe supersaturation on transformation to BCC of the enriched core region.
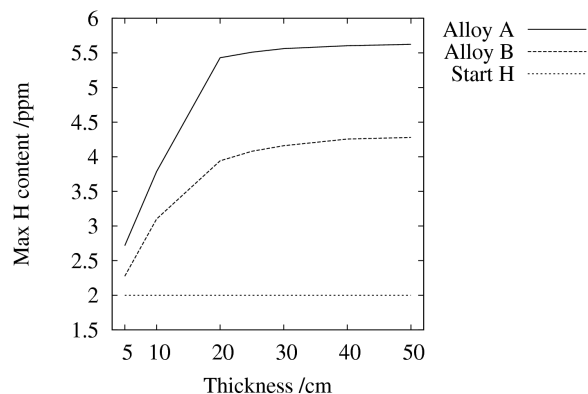

Fig.2 Effect of component size and FCC/BCC phase transformation temperature on hydrogen concentration peak after fast cooling. Steel A transforms at 700°C and Steel B at 450°C.

2.3 Removal of hydrogen by the application of a severe temperature gradient

In the previous sections has been shown that at temperatures where atom mobility is sufficient and in the presence of a temperature gradient, interstitial atoms like hydrogen tend to flow towards the regions at higher temperature, as a consequence of the higher mobility and higher relative solubility encountered there, occurring even up-hill the composition gradient. This phenomenon can be related to the Ludwic-Soret effect in gases and solutions and was already identified in metals by Darken [12-13].

In many standard industrial practices, during cooling of a component the flux of hydrogen occurs towards the hot core of the metal component, as heat is extracted from all of its surface. However, if a small region of the surface of that component were to be kept at high temperature during the cooling process, hydrogen would not accumulate in the core region but it would be directed to the heated surface and effectively extracted from the metal [14].

Fig.3 shows the evolution of hydrogen distribution during such an operation. A plate of

the same dimensions (25cm thick) as in the calculation in Fig.1 is cooled from 1600ºC to just above room temperature. The only difference with the calculation shown in Fig.1(a) is that while one face of the plate is cooled ($h = 22 \cdot 10^3$ $Wm^{-2}K^{-1}$) the one opposite is kept at 1500ºC for 7200s. (2 hour), the time needed to reduce the overall hydrogen content to below half the starting content (*i.e.* from 2ppm to 0.99ppm).
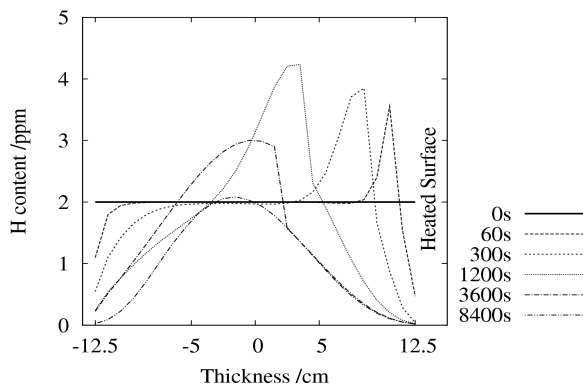

Fig.3 Hydrogen redistribution during directional cooling of a 25cm thick steel plate, where one of its surfaces is kept at 1500ºC for 7200s.

During the suggested treatment, a severe concentration peak still occurs, but of smaller magnitude, and occurring while the material is at high temperature and it is still able to dissolve the large interstitial content. As the treatment proceeds and hydrogen escapes 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 to 0.99ppm, lower than the 1.53ppm obtained during slow cooling, and taking only 8400s (2 hours and 20 minutes) instead of 42 hours.

In the same way, and taking into account the geometry of the component and the hydrogen content requirements it is possible to design tailored heat treatments optimising the final hydrogen content, and limiting the concentration peak by adjusting the temperature of treatment and severity of cooling.

3. Conclusions

(1) A novel physical model had been presented that allows a correct description of hydrogen redistribution during manufacturing processes.

(2) The model predicts that on fast cooling, hydrogen content redistributes forming concentration peaks that may reach several times the average concentration value.

(3) Phase transformation and the temperature at which it occurs greatly influence the redistribution of hydrogen.

(4) Finally, a method has been presented which enables to reduce hydrogen content from the metal via the use of imposed temperature gradients.

References:
[1] Clayton, C. Y., Foley, F. B, Laney, F. B. *Flaky and woody fractures in nickel-steel gun forgings.* Transactions of the Metallurgical Society of AIME. 1919, 62: 211-245.
[2] Hirth, J. P. *Effects of hydrogen on the properties of iron and steel.* Metallurgical Transactions A. 1980, 11A: 861-890.
[3] Krom, A. H. M. Bakker, A. *Hydrogen trapping models in steel.* Metallurgical and Materials Transactions B. 2000, 31B: 1475-1482.
[4] Olden, V. Thaulow, C. Johnsen, R. *Modelling of hydrogen diffusion and hydrogen induced cracking in supermartensitic and duplex stainless steels.* Materials and Design. 2008, 29: 1934-1948.
[5] Gaude-Fugarolas, D. *Hydrogen reduction during steel casting by thermally induced up-hill diffusion..* METAL2010, Roznov pod Radhostem, (Czech Republic), 2010
[6] Gaude-Fugarolas, D. *Modelling phase transformations on steel during induction hardening.* Mathematical Modelling and Information Technologies in Welding and Related Processes. Crimea (Ukraine), 2002.

[7] Gaude-Fugarolas, D. *Modelling Induction Hardening.* Saarbrüchen (Germany): VDM Verlag Dr. Muller, 2008
[8] Poirier, D. R. Geiger, G. H. *Transport phenomena in materials processing.* Warrendale (US): The Minerals, Metals & Materials Society, 1994.
[9] Fast, J. D. *Interaction of Metals and Gases.* Vol.1&2. London: Macmillan, 1965 & 1971.
[10] Ågren, J. *Numerical treatment of diffusional reactions in multicomponent alloys.* Journal of Physics and Chemistry of Solids. 1982, 43: 385-391.
[11] Bockris, J. O'M. Beck, W. Genshaw, M. A. Subramanyan, P. K. Williams, F. S. *The effect of stress on the chemical potential of hydrogen in iron and steel.* Acta Metallurgica, 1971, 19: 1209-1218.
[12] Chipman, J. *The Soret effect.* Journal of the American Chemical Society, 1926, 48: 2577-2589.
[13] Darken, L. S. Oriani, R. A. *Thermal diffusion in solid alloys.* Acta Metallurgica, 1954, 2: 841-847.
[14] Gaude-Fugarolas, D. *Method for the reduction of interstitial elements in cast alloys and system for performing said method.* PCT Patent Application (pending).