Modelling hydrogen redistribution and deep trapping, and considerations on a new method for hydrogen reduction

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Abstract

Hydrogen trapping is considered to play an important role in the embrittlement of some high performance alloys. A correct understanding of hydrogen redistribution from the onset of the manufacturing process could allow to predict and prevent severe material degradation.

Traps are generaly 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 disolved hydrogen accumulates at the later sites in large concentration it transforms into molecular hydrogen (gas) and pressure builds up. If pressure becomes sufficiently high to exceed the yield strength of the material at that temperature, irreversible macroscopic damage results.

A physical model of interstitial element diffusion is used to study the fluxes of hydrogen during solidification and cooling of ferrous alloys. The model incorporates physical description of thermal agitation and atom mobility, the influence of temperature gradients, solubility and saturation of hydrogen as function of temperature and matrix phases. In particular, the present model assumes 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 occurs to reduce the concentration gradient, as is usually considered in a system at constant matrix composition and temperature. Consequently, diffusion may occur even up-hill the composition gradient as long it still leads to a reduction of Gibbs energy in the system (Darken, 1949, 1954). Finally, the model used incorporates the possibility of degassing to the atmosphere at high temperature, or the formation of hydrogen gas within microscopic defects when the metal matrix becomes supersaturated.

The results of this model describe how hydrogen localises in some regions of the component to a degree that depends on manufacturing conditions and that it may locally reach concentrations several times the initial average concentration in the metal and beyond the solubility limit. By assuming that the excess hydrogen accumulates in irreversible traps as molecular hydrogen, it is possible to estimate the stresses generated due to the pressure build up.

Finally, the viability of a method for the reduction of hydrogen developed during this work, which is based on the imposition of severe temperature gradients to the component during cooling, is evaluated.

A Model on Hydrogen Redistribution

Characteristics of the Model:

- Thermal history including large T gradients (T evolution model)
- Incorporate phase transition (*i.e.* from FCC to BCC on cooling)
- Interstitial solubility as function of temperature and matrix phase
- Atomic thermal agitation and diffusion
- Interstitial site saturation
- At free surfaces: local equilibrium across the surface (Sievert's law)
- (H trapping and detrapping are not included *per se* in the model, but trapping severity is estimated from supersaturation)

Operation of the Model

- Starting distribution C_i of interstitial elements determined by initial conditions. Then, for each cell and time interval...

1. Temperature T_i evaluated
2. Phase transitions accounted as function of T_i
3. Saturation composition $C^0(T_i)$ and partial saturation $C_i/C^0(T_i)$ determined
4. Displacement of interstitial atoms via **random walk**, with a mean walk distance $\Delta x = \sqrt{\Delta t \cdot D}$
5. Atomic flux distribution relative to the partial saturation in adjacent cells
6. Diffusion described as thermaly activated process via Arrhenius-type expression, $D = D_0 \exp\left(-\frac{\Delta H}{R \cdot T}\right)$
7. Local equilibrium between dissolved and molecular hydrogen, following Sievert's law, describes the flux of atoms across the surface

- Iterate...

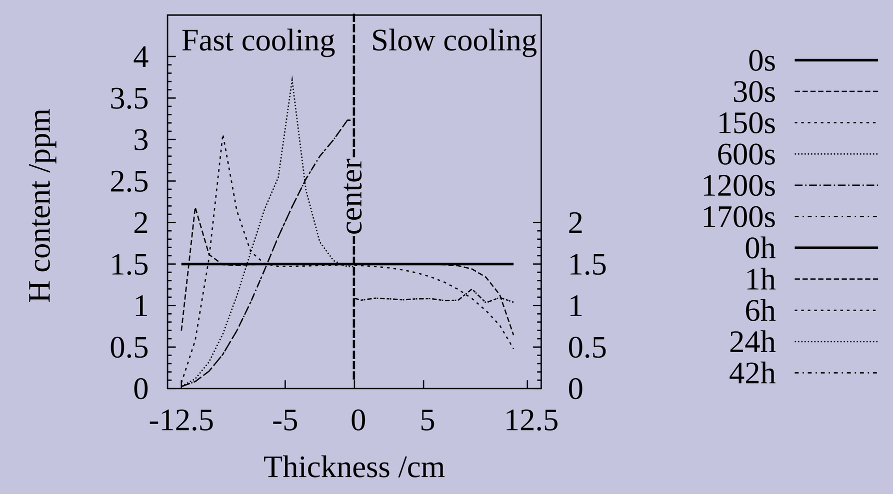
Description of the Model:

- GAUDE-FUGAROLAS, D. *Understanding hydrogen redistribution during steel casting, and its effective extraction by thermally induced up-hill diffusion.* HSLA Steels 2011 (High Strength Low Alloy Steels International Conference). (Beijing, China. 31 May-2 June 2011).
- GAUDE-FUGAROLAS, D. Journal of Iron and Steel Research International. vol.18 supl.1.1 pp.159-163 (Beijing, China. 2011)
- GAUDE-FUGAROLAS, D. *Application of a physical model on interstitial diffusion to the issue of hydrogen damage during casting and forming of ferrous alloys.* METAL2011. (Brno, Czech Republic. 18-20 May 2011)

H Redistribution during Standard Process

Effect of Cooling Rate on Concentration

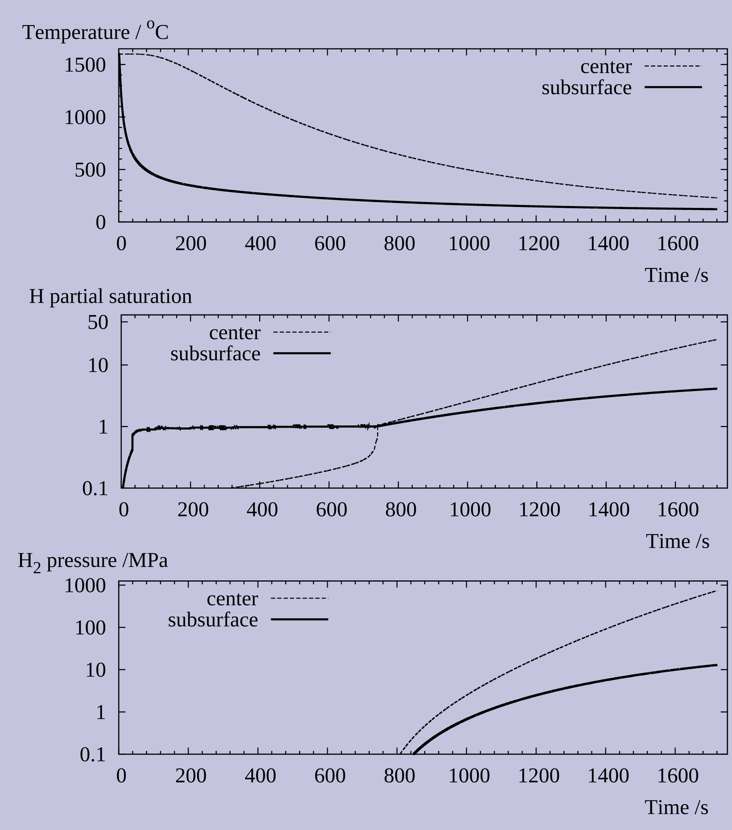
Steel piece 25cm thick **Initial [H] = 1.5ppm**



Fast cooling [H] peak ≈ 4ppm!!

H Redistribution during Fast Cooling

Steel piece 25cm thick **Initial [H] = 1.5ppm**



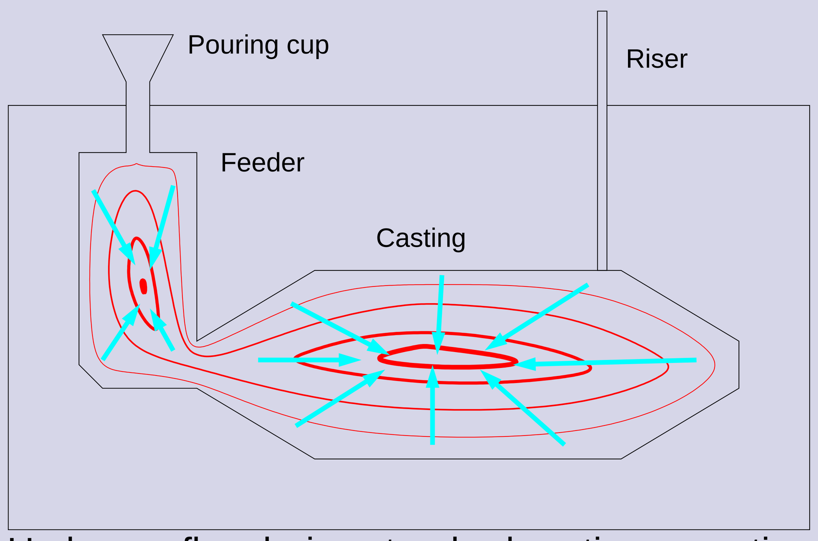
Fast cooling produces ≈25 times supersaturation!!

Supersaturation leads to high pressure!

A New Method: Redirection of Interstitial Element Flux

Standard Cooling Process

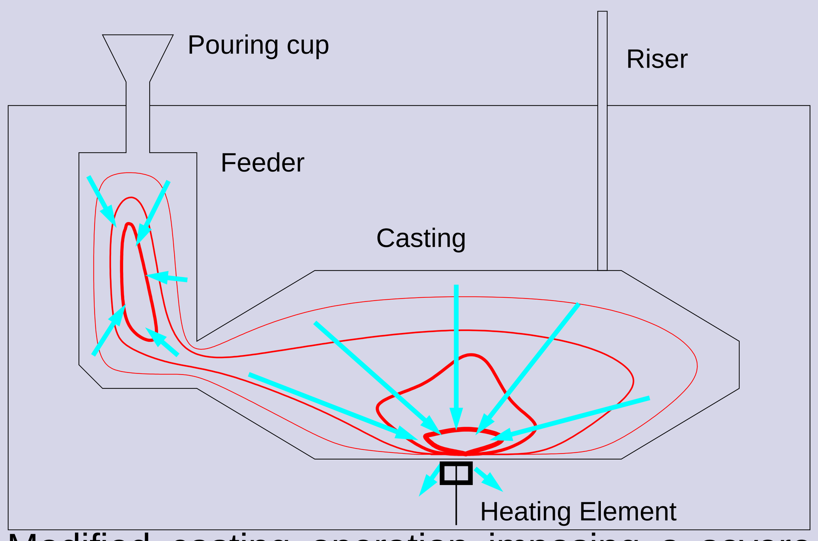
During a fast cooling in the standard process a severe temperature gradient forces hydrogen to flow towards the core region of a component, where it can reach severe supersaturation.



Hydrogen flux during standard casting operation

Directional Cooling Process

Actually, hydrogen flows towards higher temperature regions!! Then, why don't we try and redirect the hydrogen flux towards the surface? (and then get rid of it)

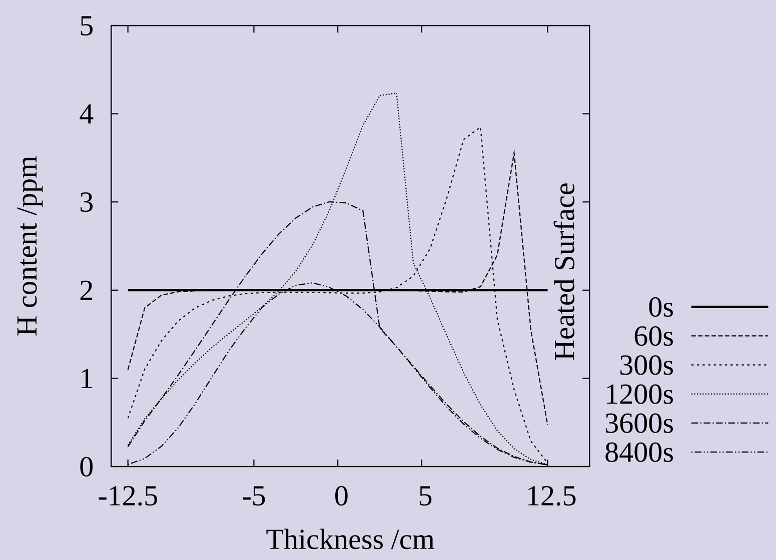


Modified casting operation imposing a severe thermal gradient towards the surface

Effect on Concentration

Steel piece 25cm thick **Initial [H] = 2ppm**

Surface I: **Fast cooling** Surface II: **Kept 2h at 1500°C**

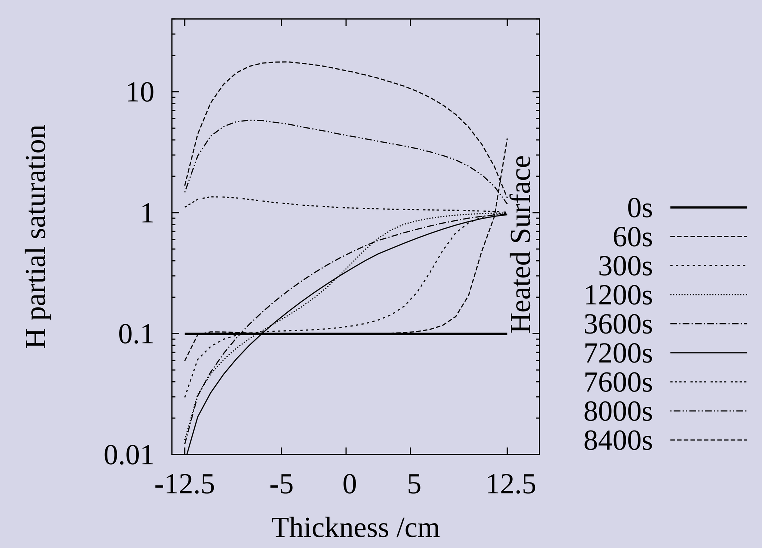


Final H content 0.99ppm !!

Effect on Partial Saturation

Steel piece 25cm thick **Initial [H] = 2ppm**

Surface I: **Fast cooling** Surface II: **Kept 2h at 1500°C**



Partial Saturation during treatment below 1.0 !!

Summary and Conclusions:

Comparison of the Effect of Process Conditions on H Redistribution

Cooling a 25cm thick plate with 2ppm H:

Slow cool	Some H reduction (≈ 25%) No concentration peaks Low supersaturation Long time: 42 hours
Fast cool	No H reduction (≈ 1%) Severe concentration peaks Severe supersaturation Short time: 1.5 hours
Directional cool	Large H reduction (≈ 50%)* Some concentration peaks* Low supersaturation* Short time: 2.5 hours*

* Possible to be improved by modifying cooling severity and treatment time

Final Conclusions

A novel physical model had been used to improve our understanding of hydrogen redistribution during manufacturing processes.

The model shows that hydrogen content usually considered harmless could still lead to severe supersaturation.

Excess hydrogen stored (*trapped*) in microcavities may transform to gas. The potential gas pressure has been used as an indicator of potential material degradation.

The large pressures predicted are consistent with mechanisms leading to the formation of typical macroscopical hydrogen damage.

Hydrogen may be reduced without incurring in large supersaturation by imposing a temperature gradient onto the solid metal.
(*International PCT patent, in process*).