

PREDICTION OF HYDROGEN DAMAGE IN STEELS

GAUDE-FUGAROLAS Daniel

Prime Innovation SLU, Vilassar de Mar, Spain, EU dgaude@cantab.net

Abstract

Hydrogen may cause severe degradation on some high strength alloys, and although research efforts have intensified in recent years, our understanding of such phenomena still has room for improvement.

For the metallurgical industry it would be useful to have applicable criteria able to predict the risk of hydrogen embrittlement and therefore be able to prevent embrittlement damage to industrial products.

Several complex and competing mechanisms are ultimately responsible for hydrogen embrittlement (HAC, HIE, AIDE, HELP, HEDE, etc.), although it should be obvious that many embrittlement episodes originate from a localised excess in hydrogen concentration. A physical model of hydrogen diffusion that has been hitherto applied to study the manufacturing of metallic alloys is used in this work to develop and illustrate some useful criteria of embrittlement risk associated to industrial practices.

By estimating the degree of supersaturation at specific regions in the component, and considering microstructure features or mechanical properties, it is possible to anticipate defect formation and embrittlement risk, opening the possibility to prevent it.

Keywords: Hydrogen, steel, damage prediction, microstructure, physical model

1. INTRODUCTION

The fact that some high strength alloys suffer from hydrogen embrittlement has been known for almost a century and a half [1]. Because of its economic, technological, and safety implications it is a phenomenon that has attracted intense research for decades [1-8]. Unfortunately, hydrogen embrittlement is a complex phenomenon involving multiple and often competing mechanisms, ranging from [9-10]

- HIE : Hydride-induced embrittlement, due to the formation of a brittle second phase. This mechanism is not of much relevance in steels.
- AIDE: Adsorption-induced dislocation-emission,
- HELP: Hydrogen enhanced localised plasticity, where hydrogen atmospheres surrounding dislocations influencing the effectiveness of that deformation mechanism, and
- HEDE: Hydrogen enhanced decohesion mechanism, leading to brittle fracture, either intra or intergranular. And of course, all those and any others combining into various typologies of hydrogen-assisted cracking (HAC), like
- macroscopic structural and surface damage, like microcracking, flaking, surface defects, porosity, *et c.*

Nevertheless, developing criteria able to predict the onset of permanent damage in real structural components and during industrial practices would perform an invaluable service in component and process design and supervision.

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 [11-12].

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, and therefore implies 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, produced by the thermal activation and atom mobility of such elements and governed by the differences in partial saturation distribution around the diffusing element [11].

As the model also incorporates thermodynamic description of microstructure evolution it can be used to describe real heat treatments [11].

Trap sites are modelled as a potential well, with negligible trapping energy barrier and a characteristic release energy barrier, E_t , for each type of trap. 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 [12].

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 [4,13]

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 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, 11]. 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). As in the case of desorption, the hydrogen transfer between a saturated lattice and micro-voids occur under local equilibrium following Sievert's Rule. Using this method it is possible to estimate a potential (or equivalent) gas pressure from the degree of supersaturation. Even though the accumulation of molecular hydrogen at high pressure is not the only mechanism by which the metal degradation may occur, this *equivalent hydrogen gas pressure* has been considered in the past to provide a good estimate of the severity of the potential damage occurring to the alloy [13]. In this work additional criteria, related to physical properties of the alloy, are used as more accurate predictors of damage nucleation.

2.2. Simulations used

The simulations performed to obtain the results presented in this work consist on the calculation of hydrogen redistribution in a 1.5m thick component during solidification and constant cooling to room temperature (with $h = 2000\text{Wm}^{-2}\text{K}^{-1}$). Two different alloys have been considered: *Steel A* with FCC to BCC transformation at 725 °C producing ferrite characterised by larger grain size (100 μm) and moderate dislocation density (10^{12}m^{-2}), and *Steel B* with FCC to BCC transformation at 450 °C producing ferrite characterised by smaller grain size (10 μm) and higher dislocation density (10^{14}m^{-2}). Only two starting hydrogen content levels have been considered: 1.0 and 3.5 ppm.

3. RESULTS AND DISCUSSION

Industrial alloys are usually polycrystalline and often multiphase. As metallographic orientation varies from grain to grain, and with it the availability of deformation mechanisms that could become active to reduce an applied stress, any internal stress distribution will also vary to a certain extent within the metal component. Any criteria on the onset of permanent damage in the metal necessarily can only be approximate, and a margin of safety needs to be considered. Nevertheless, developing criteria able to predict the onset of permanent damage in structural components serves an invaluable role in component production and process design and supervision.

3.1. Lattice hydrogen supersaturation and microplasticity damage

Permanent damage in a ductile material occurs when the capacity of elastic (*i.e.* reversible) deformation is exceeded and plastic (*i.e.* irreversible) deformation takes place. Brittle fracture, on the other hand, occurs when the energy required to create fresh fracture surfaces is lower than the energy to activate any of the available deformation mechanisms that could reduce the stress distribution by yielding under the stress [9-10]. In the first case, and for commercial ferrous alloys, the onset of plastic deformation occurs around the point where shear stress τ reach $10^{-3} \cdot G$, where G is the Shear Modulus of the metal for that alloy composition, phase and temperature [14]. In engineering terms it is usually expressed as 0.1% of shear deformation ($\gamma = \tau / G = 0.001$) [10].

As described in a previous work, hydrogen supersaturation could produce a stress distribution akin to an equivalent internal pressure on the lattice structure, as well as a real pressure within existing micro-defects in the metal, like micro-cracks, voids and incoherent interfaces [13]. It is the proposition of this work that by determining the equivalent pressure in the lattice and by applying the criterion described above, it is possible to estimate the risk of irreversible deformation and therefore, the onset of permanent damage in the metal component.

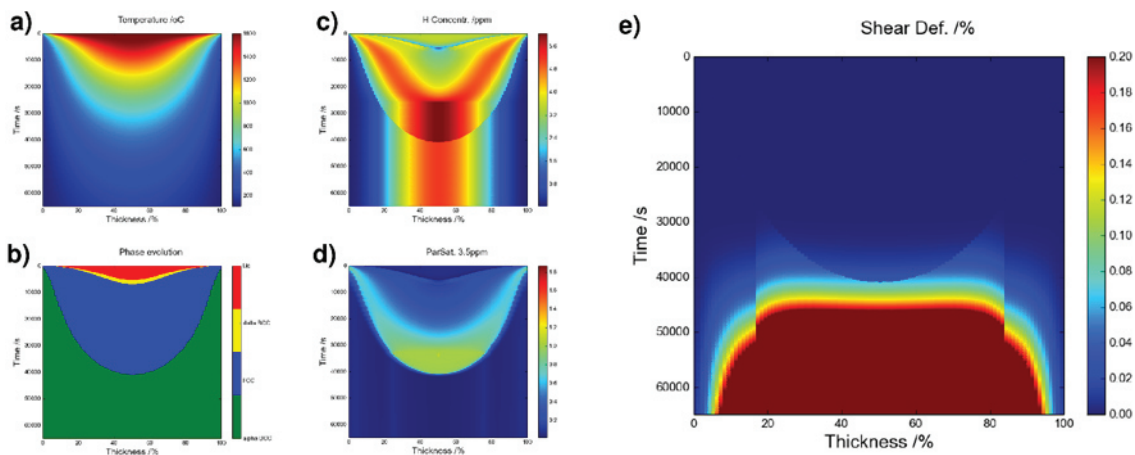


Fig. 1 Plots presenting the evolution of a) temperature, b) phase, c) hydrogen concentration, d) hydrogen partial saturation in the metal lattice and e) shear deformation (as criteria for microdamage risk) during solidification and cooling of a 1.5 m thick steel component with a homogeneous starting hydrogen concentration of 3.5 ppm. FCC to BCC phase transformation occurring at 450°C

Fig. 1 shows an example on the application of this criterion. A component made with alloy *Steel B* and containing 3.5 ppm of hydrogen solidifies and is actively cooled to room temperature. The evolution of temperature as well as the phase evolution during cooling and at any position within the thickness of the component are shown in **Fig. 1a)** and **b)**. During the cooling process hydrogen redistributes, and different regions in the steel (ferritic) lattice attain diverse levels of hydrogen partial saturation or even supersaturation.

By determining the equivalent hydrogen gas pressure related to those regions where supersaturation occurs, and then applying the criterion of $0.1\%G$, (with G the Shear Modulus of the metal) it is possible to estimate the risk of permanent damage to the component due to microplasticity. $\tau=10^{-3}G$ is equivalent to shear deformation $\gamma=0.1\%$ [10].

In this example we observe the apparition, just before 30 ks, of two regions at 20% and 80% of the thickness of the component where the shear strain starts to build up towards the yield shear strain limit defined above. As the process progresses, at around 45 ks, these two regions converge into a larger region comprising the whole core of the component. Within this region levels of strain considered to be unsustainable are reached.

3.2. Hydrogen saturation in dislocation distribution

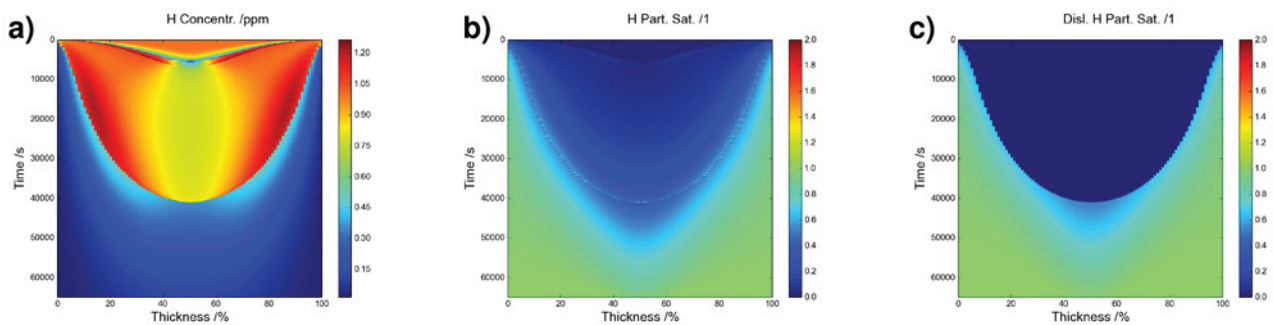


Fig. 2 Plots presenting a) the evolution of hydrogen concentration in metal lattice, b) hydrogen partial saturation in lattice and c) hydrogen partial saturation in dislocation distribution, during solidification and cooling of a 1.5 m thick steel component with a homogeneous starting hydrogen concentration of 1.0 ppm. Temperature and phase evolution identical to those shown in **Fig. 1a) and b)**. FCC to BCC phase transformation occurring at 450°C

Another criterion proposed here to estimate the risk of embrittlement of an alloy under the influence of hydrogen consists in observing the degree of partial saturation of the dislocation distribution. Dislocations presenting a large partial saturations in hydrogen are expected behave differently than dislocations free of hydrogen presence [6, 10].

Fig. 2 shows the calculations for a component of the same alloy and geometry as in the example above (section 3.1.) but containing only 1.0 ppm of hydrogen. The evolution of temperature as well as the phase evolution during cooling are identical as shown in **Fig. 1a) and b)**.

In the present case, lattice partial saturation stays close to saturation but never reaching severe supersaturation, and therefore (by applying the microplasticity criterion above) without expected risk of embrittlement due to that mechanism. On the other hand, at the same time it is possible to observe that the dislocation distribution in the ferrite phase also becomes close to saturation. It is at this moment that needs to be pondered what could be the effect of a hydrogen saturated dislocation distribution. If dislocations become blocked due to hydrogen then the metal would be expected to develop hardening and decreased ductility, eventually producing embrittlement of the material. The severity of this effect is nevertheless also related to the ability of the alloy to create new dislocations [7].

3.3. Hydrogen saturation at grain boundaries

The last criterion proposed here to estimate the risk of embrittlement of an alloy under the influence of hydrogen consists in observing the degree of partial saturation at grain boundaries (and the same could be applied to precipitate interfaces). Grain boundaries presenting hydrogen supersaturation could become embrittled due to various mechanisms, ranging from the obstruction of deformation mechanisms characteristic of grain

boundaries, to the apparition of microplasticity damage similar to what is described in section 3.1. for the metal lattice [9].

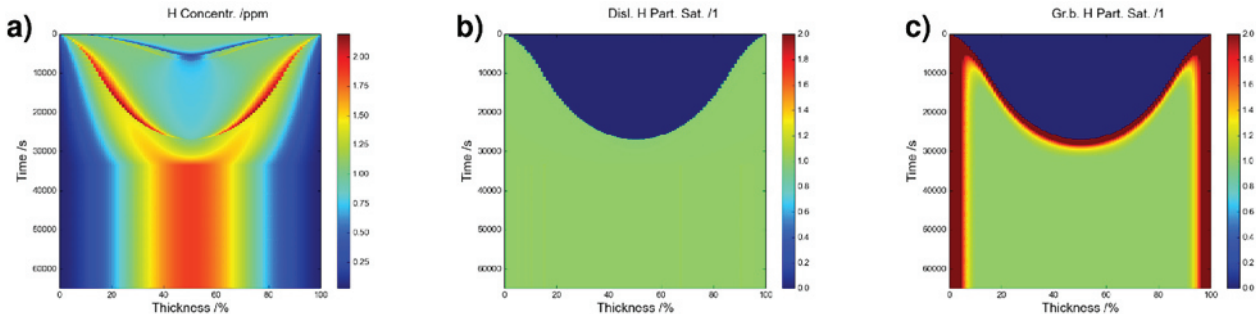


Fig. 3 Plots presenting a) the evolution of hydrogen concentration in metal lattice, b) hydrogen partial saturation in dislocation distribution, and c) hydrogen partial saturation at grain boundaries during solidification and cooling of a 1.5 m thick steel component with a homogeneous starting hydrogen concentration of 1.0 ppm. Temperature evolution identical to that shown in **Fig. 1a**). FCC to BCC transformation occurring instead at 725°C

Fig. 3 shows the calculations for a component of the same geometry as in the examples above (section 3.1.), but in a different alloy, *Steel A*. In *Steel A* austenite transforms to ferrite at higher temperature than in *Steel B* and with different characteristics (larger grain, lower dislocation density). For this calculation, containing only 1.0 ppm of hydrogen. The evolution of temperature is identical as for other examples in this work, and shown in **Fig. 1a**).

The microstructure of the alloy in this example is less able to dissolve hydrogen in its trap site distribution than *Steel B* of sections 3.1. and 3.2. In this case, the hydrogen dissolved in the lattice tends to concentrate at the core of the component, while the dislocation distribution become immediately saturated on transformation from austenite to ferrite. The interesting aspect though is the distribution of hydrogen in the grain boundary trapping sites. Effectively, grain boundaries become severely supersaturated on transformation to ferrite. As the process proceeds, hydrogen in grain boundaries at the core of the component redistribute reducing their hydrogen supersaturation to levels close to full saturation. Grain boundaries close to the surface, where the temperature does not allow redistribution of the hydrogen, remain supersaturated till the end of the process (**Fig. 3c**). In both cases, the degree of supersaturation would suggest a risk of embrittlement. In particular, in the surface grain boundaries, could be a mechanism to explain intergranular brittle fracture and crack formation in the surface and immediate subsurface regions.

4. CONCLUSION

A model on hydrogen diffusion has been applied to predict the risk of hydrogen damage. This approach is based on the idea that severe supersaturation of either lattice or any defect structures in the metal is involved in damage formation and embrittlement. Three criteria have been suggested in order to try and predict different embrittlement mechanisms:

- A microplasticity threshold related to *Shear Modulus* as predictor to lattice microcracking.
- Dislocation supersaturation as a possible origin for ductility loss.
- Grain boundary supersaturation as a possible origin for intergranular decohesion, as well as of subsurface defects like *flaking*.

The next step is to start applying these criteria, for real, and in actual industrial processes, and to prevent hydrogen embrittlement.

REFERENCES

- [1] W. H. Johnson. On some remarkable change produced in iron and steel by the action of hydrogen and acids. *Proceedings Royal Society London*, 23:168-179, 1874.
- [2] H. S. Rawdon. Microstructural features of flaky steel. *Transactions of the Metallurgical Society of AIME*, 62:246-286, 1919.
- [3] C. A. Zappfe and C. E. Sims. Hydrogen embrittlement, internal stress and defects in steel. *Transactions of the Metallurgical Society of AIME*, 145:225-271, 1941.
- [4] J. P. Hirth. Effects of hydrogen on the properties of iron and steel. *Metallurgical Transactions A*, 11A:861-890, 1980.
- [5] A. H. M. Krom and A. Bakker. Hydrogen trapping models in steel. *Metallurgical and Materials Transactions B*, 31B:1475-1482, 2000.
- [6] T. Hickel, E. J. McEniry, R. Nazarov, G. Leyson, and J. Grabowski, B. and Neugebauer. Ab initio based understanding of the segregation and diffusion mechanisms of hydrogen in steels. In *Proceedings of SteelyHydrogen 2014, Ghent, Belgium, 5-7 May 2014*, pages 214-225, 2014.
- [7] L. Moli-Sanchez, Z. Zermout, L. Duprez, and Malet L. Hydrogen Embrittlement of 4 martensitic steels with strength levels above 1000 MPa. In *Proceedings of SteelyHydrogen 2014, Ghent, Belgium, 5-7 May 2014*, pages 70-84, 2014.
- [8] H. K. D. H. Bhadeshia. Eliminating the hydrogen problem in steel. In *Proceedings of 3rd UK-China Steel Research Forum, Rutherford Appleton Laboratory (UK), 10-11 July 2014, published in Materials Today: Proceedings*, 2015.
- [9] R. W. Hertzberg. *Deformation and fracture mechanics of engineering materials*. John Wiley & sons, inc., New York, 1996.
- [10] A. Cottrell. *An introduction to metallurgy*. The Institute of Materials, London, 1995.
- [11] D. Gaude-Fugarolas. Understanding hydrogen redistribution during steel casting, and its effective extraction by thermally induced up-hill diffusion. *Journal of Iron and Steel Research International*, 18 suppl.1.1:159-163, 2011.
- [12] D. Gaude-Fugarolas. Effect of microstructure and trap typology on hydrogen redistribution in steel. In *Proceedings of METAL2013, Brno, Czech Republic, 15-17 May 2013*, 2013.
- [13] D. Gaude-Fugarolas. Application of a physical model on interstitial diffusion to the issue of hydrogen damage during casting and forming of ferrous alloys. In *Proceedings of METAL2011, 18-20 May, Brno, Czech Republic*. Tanger Ltd., 2011.
- [14] H. J. Frost and M. F. Ashby. *Deformation-Mechanism Maps: The Plasticity and Creep of Metals and Ceramics*. Pergamon Press, US, 1982.