ON THE EFFECTIVENESS OF BAKING AS HYDROGEN EMBRITTLEMENT REDUCTION TREATMENT

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Abstract

Several methods are used in industry to deal with the excess of dissolved hydrogen in metal aloys. Strict control on disolved hydrogen is necessary to reduce the risk of metal embrittlement and severe property loss. Composition and microstructure selection, vacuum casting, imposed thermal gradient diffusion and baking are some of the possible methods to reduce the risk of embrittlement.

Each of these methods have its advantages and disavantages. One of hydrogen embrittlement mitigation methods most widely used in the steel industry consists in storing the metal parts in heated ovens for a long period of time, in a process known as baking, intended to promote the diffusion of hydrogen out of solution and into the atmosphere.

By modelling the fluxes of hydrogen and its redistribution into various microstructure features 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, which in turn influence where in the microstructure hydrogen is stored at the time of the treatment.

Keywords: hydrogen, steel, baking, microstructure, physical model

1.   INTRODUCTION

The severe degradation caused by hydrogen on some high strength alloys has long been acknowledged [1,2], and due to their technological and economic relevance, it is a phenomenon that has attracted intense research for decades[1-6].

A common method used to minimise the detrimental effect of this element on the mechanical properties of metal components is *baking*. Typically, a *baking* treatment, consists in storing the metal component at *low* temperature (*i.e.* 190°C) for a long period of time (typically 12 to 48 hours) [7].

During this treatment, a fraction of the hydrogen in the lattice diffuses to the surface of the component and is exuded to the atmosphere. However, a quantity of hydrogen is also be stored in microstructure defects, or *traps*. The release of hydrogen atoms from such *traps* is conditional to the overcoming of a detrapping energy barrier characteristic to the type of trapping site.

The effectiveness of a treatment like baking is therefore influenced by the distribution of hydrogen among different types of sites, either in the lattice or into various types of trap site. Thermal desorption spectroscopy (TDS) studies make evident the different rates of hydrogen release from different types of trap sites and how that process is influenced by thermal activation, as is illustrated in **Fig. 1** [8-10].

Although many different embrittlement mechanisms have been characterised, often they share a local supersaturation in hydrogen as a start. By considering the fluxes between phases and trap types and their respective saturation limits, it is possible to determine the risk of hydrogen supersaturation, and therefore, estimate and minimise the risk of embrittlement.
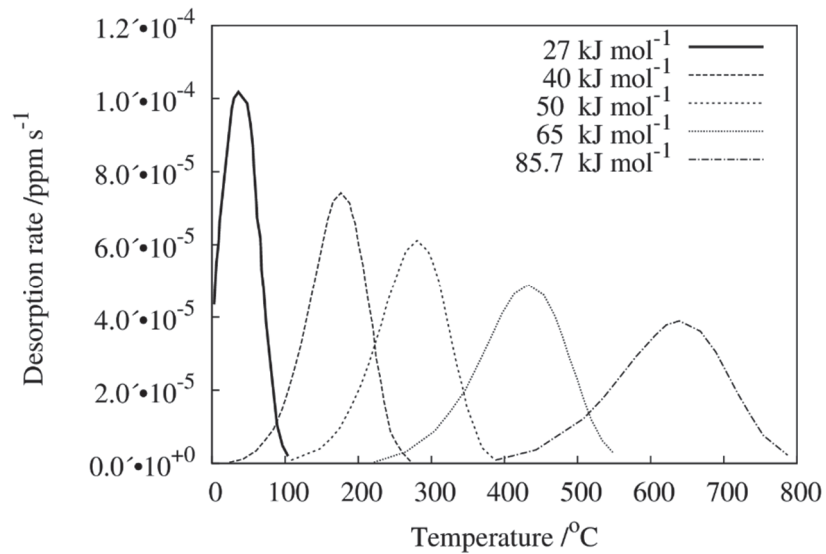
Fig. 1 Hydrogen desorption curves as function of detrapping energy barrier (reproduced from [10], **Fig. 5**).

2. BRIEF DESCRIPTION OF THE MODEL

The physical model used to study hydrogen behaviour during the baking process has already been extensively described at this conference and elsewhere and therefore, only a brief overview is presented at this time [11-13].

A simple but physically robust model is used to describe the redistribution of hydrogen in steel. As this model incorporates a thermodynamic description of microstructure evolution it can be used to study a simple heat treatment.

Diffusion, in its more general description, is driven by a reduction of the Gibb's energy of the system. The evolution of hydrogen distribution is therefore determined as a function of thermal agitation and atom mobility by relating it to a random walk process, taking into account diffusivity and partial saturation of hydrogen through each of the different metallic phases [11-12].

The effect of various trap types 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.
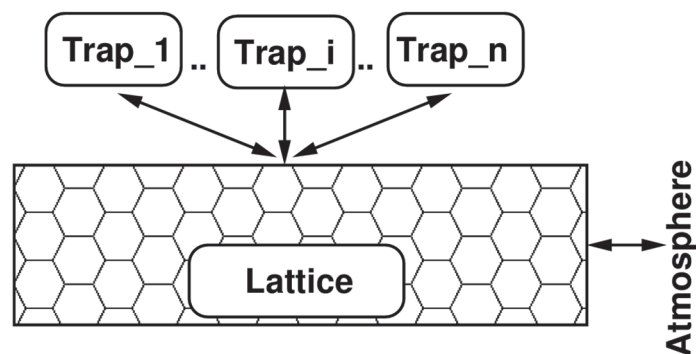

Fig. 2 Hydrogen redistribution fluxes between the atmosphere, the lattice and *n* trap site types.

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 difusion jump and the release from a trap site[13].

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

Table 1 Characteristic release energy for each trap site type considered in this work, as well as lattice diffusion activation energy for comparison [4,14].

Trap type	$E_t \left[kJ \cdot mol^{-1} \right]$
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, 12]. 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).

3. RESULTS AND DISCUSSION

3.1 Modelling results

The purpose of this study is to understand the physical processes occuring during a baking treatment, in particular those aspects regarding the redistribution and effective extraction of hydrogen from a metallic alloy.

To that purpose, 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 with a similar carbide distribution. 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 [13].

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 1600°C to room temperature. The baking treatment starts immediately after that. For that treatment two baking temperatures have been modelled (190 °C and 300 °C), with treatment durations of 2 and 12 h.

From a range of starting hydrogen content from 1 ppm to 3 ppm and higher, the calculations corresponding to 1 ppm has been chosen as better illustrating the process itself and the influence of the process parameters. Similarly, only the 2 hour treatment results are shown as they already convey most of the conclusions of the study.

Table 2 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 → BCC:	725°C	450°C
BCC Microstructure:	Allotriomorphic Ferrite	Bainite & Martensite
Grain size:	Large 0.1 mm	Small 10μm
Dislocation site density:	Low $4 \cdot 10^{22} site/m^3$	High $4 \cdot 10^{24} site/m^3$
Ppt. trap site density:	$2 \cdot 10^{22} site/m^3$	$2 \cdot 10^{22} site/m^3$

3.2   Discussion

A first observation is that for a given hydrogen content, trap nature and distribution will greatly influence the distribution of hydrogen and therefore local partial saturation (or supersaturation). In that sense, the microstructure phases, and their grain size and dislocation distribution, as well as any precipitate distribution or any other defect distribution are paramount to the final outcome of any treatment.

In order for hydrogen to be able to diffuse in the microstructure and also to be able to be extracted from the metal, the lattice of the alloy must not be saturated. Only when the lattice partial saturation is below unity can hydrogen circulate and arrive to the surface and be extracted.

The rate of hydrogen extraction is roughly inversely dependent on the degree of saturation of the lattice. The lower the partial saturation, the faster the desorption to the atmosphere will occur.

For each of the trap types present, the flux between trap sites and the surrounding lattice will occur related to the relative partial saturation of trap and lattice. Hydrogen will flow from higher partial saturation to lower partial saturation. However, the release of hydrogen from a trap will be conditional to overcoming the energy barrier characteristic of that trap type.

When the trap site is less saturated than the lattice, the flux of hydrogen will occur from lattice to trap site till they become equally saturated.

Traps with a higher detrapping energy barrier might not be able to release any hydrogen, even when the surrounding lattice is less saturated. This is observed clearly for *deep traps* like precipitates, at both temperatures studied, 190°C and 300°C and for grain boundaries at 190°C.

On the other hand, if the lattice is less saturated than one of the trap type sites, it could increase its hydrogen content by absorbing hydrogen from the traps at the same time as hydrogen is extracted from the lattice into the atmosphere. Once the partial saturation of lattice and traps become equally saturated the lattice content will start reducing as the flux of hydrogen form the lattice to the atmosphere is larger than from the traps to the lattice.

When a trap type with large detrapping energy (a *deep* trap) starts the treatment with a partial saturation lower than the surrounding lattice, and irrespectively to the flux of hydrogen from the lattice to the atmosphere, the deep trap would keep absorbing hydrogen, and increasing its total content. If the temperature is not high enough for the hydrogen to escape from such *deep* trap, that trap distribution could end the treatment with higher hydrogen content that it started, despite the lattice becoming less saturated during the treatment.
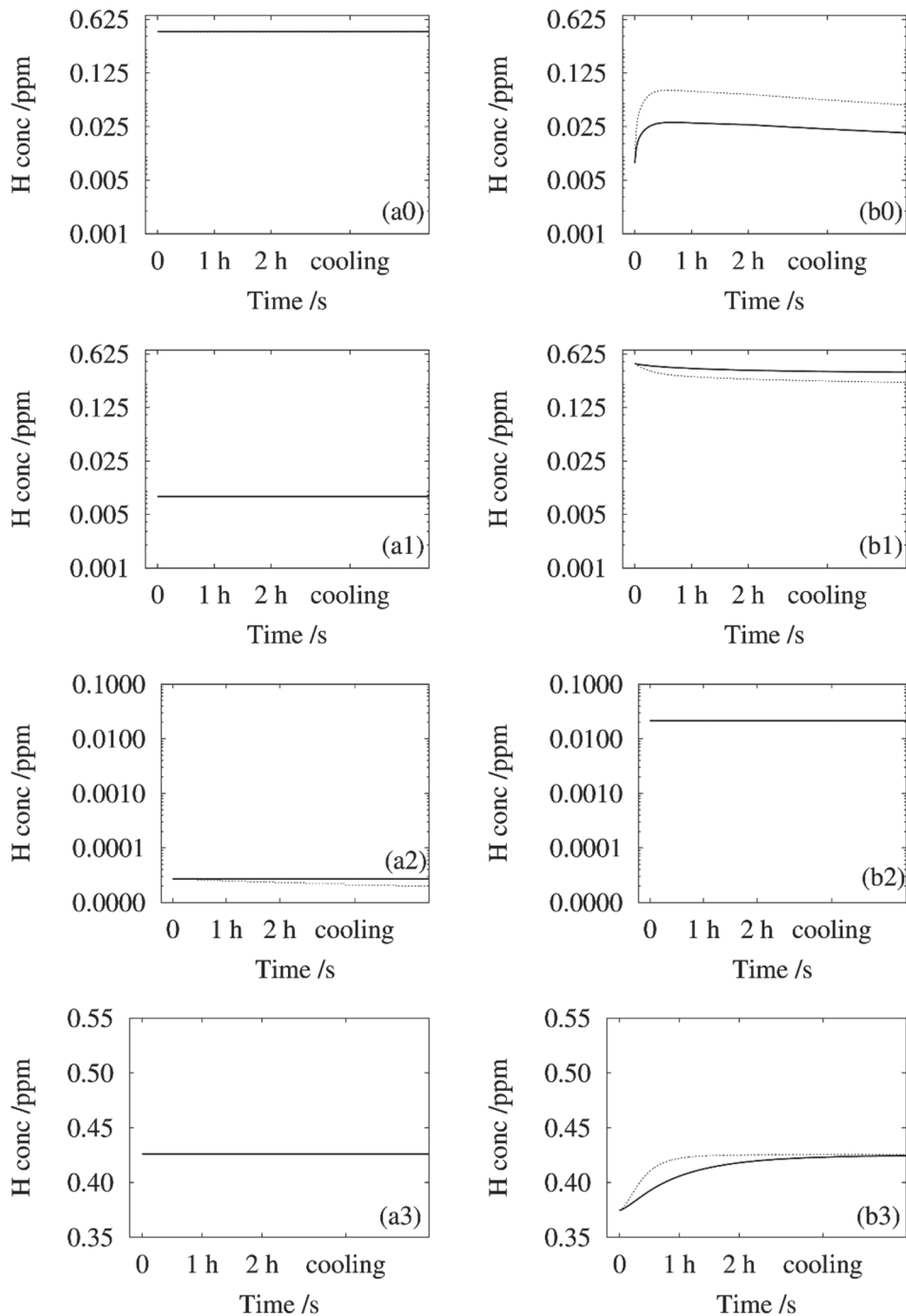
Fig. 3 Hydrogen desorption curves during baking for two microstructures and two baking temperatures, detailing the hydrogern content evolution for lattice and each type of trap sites. **ax)** and **bx)** refer to Steels A and B, indexes **0** to **3** to lattice, dislocation, grain boundary and precipitate trapping sites. Solid line correspond to baking temperature of 190 °C and dotted line to 300 °C

CONCLUSION

The overall hydrogen content, microstructure and trap distribution interact in a complex way during any thermal treatment aiming to modify the hydrogen distribution or to reduce its content, as it is the case in a baking treatment.

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.

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 releasing it during a baking treatment than another microstructure with allotriomorphic ferrite, low dislocation density and few carbide surface area.

Finally, while *shallow* trap sites are able reduce their hydrogen content during a low temperature baking treatment, *deep* trap sites could remain unaffected or even increase their hydrogen content during such treatment.

REFERENCES

[1]   C. Y. Clayton, F. B. Foley, and F. B. Laney. Flaky and woody fractures in nickel-steel gun forgings. *Transactions of the Metallurgical Society of AIME*, 62:211-245, 1919.

[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]   V. Olden, C. Thaulow, and R. Johnsen. Modelling of hydrogen diffusion and hydrogen induced cracking in supermartensitic and duplex stainless steels. *Materials and Design*, 29:1934-1948, 2008.

[7]   S. D. Cramer and B. S. Jr. Covino. *ASM Metals Handbook 13A - Corrosion Fundamentals, Testing and Protection*. ASM, US, 2003.

[8]   A. Turnbull, R.B. Hutchings, and D.H. Ferriss. Modelling of thermal desorption of hydrogen from metals. *Materials Science and Engineering A*, A238:317 â" 328, 1997.

[9]   K. Takai, Y. Chiba, K. Noguchi, and A. Nozue. Visualization of the hydrogen desorption process from ferrite, pearlite, and graphite by secondary ion mass spectrometry. *Metallurgical and Materials Transactions A*, 33A:2659-2665, 2002.

[10] M. Iino. Evaluation of Hydrogen-Trap Binding Enthalpy I. *Metallurgical Transactions A*, 18A:1559-1564, 1987.

[11] D. Gaude-Fugarolas. Hydrogen reduction during steel casting by thermally induced up-hill diffusion. In *Proceedings of METAL2010, Roznov pod Radhostem, Czech Republic*. Tanger Ltd., 2010.

[12] 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 supl.1.1:159-163, 2011.

[13] D. Gaude-Fugarolas. Effect of microstructure and trap typology on hydrogen redistribution in steel. In *Proceedings of METAL2013, Bnro, Czech Republic, 15-17 May 2013*, 2013.

[14] 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.