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Model of hydrogen behaviour in enamelling grade steels

Part I *Theory*

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A model has been developed of the behaviour of hydrogen in enamelling-grade steels in relation to the delayed defect of blow-off of enamelled surface (fishscaling). The model is based on current theories concerning reversible and irreversible trapping of hydrogen in metallic materials. It leads to the establishment of a "free hydrogen" parameter C_L which can be used to assess the susceptibility of a steel to fishscaling following the usual enamelling processess. The model can also be used to study the effect of both thermomechanical steelmaking cycles and enamelling processes on resistance to the defect.

Nomenclature

E_{aD}	Activation energy of hydrogen diffusion through normal lattice
E_s	Saddle-point energy
E_B	Trap binding energy
E_{aT}	Trap activation energy $= E_s + E_B$
A	Trapping site
B	Normal lattice site
ν_0	Vibration frequency of hydrogen at a normal lattice site
ν_1	Vibration frequency of hydrogen at a trapping site
N_L	Density of normal lattice sites for hydrogen
N_T	Density of trapping sites for hydrogen
C_L	Concentration of hydrogen on lattice sites
C_T	Concentration of hydrogen captured on traps
k	Probability of trapping $= \nu_0 \exp(-E_s/RT)$
p	Probability of detrapping $= \nu_1 N_L \exp(-E_{aT}/RT)$
n	Fraction of trapping sites occupied with hydrogen atoms among the total trapping sites $= C_T/N_T$
t	Time
T	Temperature
R	Gas constant

1. Introduction

Fishscaling is one of the worst defects in the production of enamelled steel products [1]. It is caused by an excess of hydrogen which dissolves into the steel during the enamelling process, especially during enamel firing at a temperature of 800–850 °C. Since its solubility steeply decreases during subsequent cooling, hydrogen moves towards the steel–enamel interface in quantities that can cause fishscaling even after a lapse of time.

The problem arises of creating an adequate system for fixing hydrogen in the steel (trapping). However, the reduction of hydrogen to an acceptable concentration does not depend solely on the number and binding energy of the existing traps, but also on the amount of hydrogen absorbed by the steel during the enamelling process. Therefore any objective control criterion must evaluate not only the quantity of hydrogen that can be stably trapped, but also that which may remain free and dangerous to the surface enamel layer.

A model of hydrogen behaviour in enamelling-grade steels has been developed on the basis of an analytical treatment of hydrogen trapping, together with the relative electrochemical permeation measurement method proposed by Devanathan *et al.* [2]. The model evidences the parameter C_L (free hydrogen) as a function of the amount of soluble hydrogen in the steel, of the diffusion parameters and of the critical concentration for the appearance of the defect.

Whatever hydrogen trapping system is involved, this parameter provides a criterion for evaluating the resistance of the steel to the deleterious influence of hydrogen, also as a function of enamelling conditions. It also leads to the calibration of a new enamel test [3], less ambiguous than those presently adopted (measurement of first-passage t_0 permeation times with industrial-type apparatus), the validity of which is now in doubt, especially for new types of steel [3].

2. Background of hydrogen entrapment

At $T < 200\,^{\circ}\mathrm{C}$ the diffusivity of hydrogen in steels differs markedly from the behaviour expected by extrapolating data from higher temperatures [4]. This is attributed to the fact that its atoms remain fixed in certain sites (traps) activated at temperatures below 200 °C.

The traps consist typically of lattice defects such as dislocations, microvoids and grain boundaries. Other traps that have been identified involve the atoms of some dissolved elements such as Ti and the interfaces between the matrix and precipitates and non-metallic inclusions (carbides, nitrides, sulphides, oxides, etc.) [5, 6].

An analytical description of trapping phenomena can be provided on the basis of energy levels of the hydrogen within any given trap (Fig. 1) [7]. According to McNabb and Foster [4], the rate of occupation of traps in time $n(t)$ varies according to

$$\frac{\mathrm{d}n}{\mathrm{d}t} = (1 - n)kC_\mathrm{L} - np \qquad (1)$$

and under stationary conditions ($\mathrm{d}n/\mathrm{d}t = 0$)

$$n = \frac{kC_\mathrm{L}}{p + kC_\mathrm{L}} = \frac{kC_\mathrm{L}}{p} \Bigg/ \left(1 + \frac{kC_\mathrm{L}}{p}\right) \qquad (2)$$

On the hypothesis that $\upsilon_0 = \upsilon_1$ and substituting the expressions for k and p in Equation 2

$$n = \left[\frac{C_\mathrm{L}}{N_\mathrm{L}} \exp\left(\frac{E_\mathrm{B}}{RT}\right)\right] \Bigg/ \left[1 + \frac{C_\mathrm{L}}{N_\mathrm{L}} \exp\left(\frac{E_\mathrm{B}}{RT}\right)\right] \qquad (3)$$

Each trap has its own hydrogen binding energy, but a classification is generally made on the basis of the probability of hydrogen release by the traps themselves, at room temperature. If this probability is negligible [8] the trap is referred to as irreversible (TiC, MnS, etc.); otherwise it is known as reversible (dislocations, microvoids, solute atoms such as Ti, etc.).

The trend of $n(T)$ for two cases (reversible traps with $E_\mathrm{B} = 27\,\mathrm{kJ\,mol^{-1}}$ and irreversible traps with $E_\mathrm{B} = 65\,\mathrm{kJ\,mol^{-1}}$ [5]) is reported in Fig. 2, assuming a hydrogen concentration of $17.7\,\mathrm{mol\,m^{-3}}$ [9]. At low temperature, in the case of irreversible traps, n tends towards unity as can be obtained immediately from Equation 2 by putting $p = 0$ according to the definition of an irreversible trap.

3. Theoretical model of hydrogen behaviour in enamelling grade steels

During the enamelling process, especially during the firing, hydrogen dissolves into the steel (Fig. 3) until a concentration C_C is reached. A part C_T of this hydrogen is directly trapped at the enamel-firing temperature. At this temperature there is thus an excess of hydrogen:

$$C_\mathrm{exc} = C_\mathrm{C} - C_\mathrm{T} \qquad (4)$$

C_T can be calculated from the relation

$$C_\mathrm{T} = nN_\mathrm{T} \qquad (5)$$

Considering for C_C the value of $17.7\,\mathrm{mol\,H\,m^{-3}}$ [9], and assuming that the steel contains a quantity of reversible traps $N_\mathrm{R} = 25.3\,\mathrm{mol\ H\,m^{-3}}$ at average energy $E_\mathrm{BR} = 27\,\mathrm{kJ\,mol^{-1}}$ and a quantity of irreversible traps $N_\mathrm{I} = 2.5\,\mathrm{mol\ H\,m^{-3}}$ with $E_\mathrm{BI} = 65\,\mathrm{kJ\,mol^{-1}}$ [5], then C_T at the enamel-firing temperature T ($\simeq 830\,°\mathrm{C}$), is respectively

$$C_\mathrm{T} = 0.01\,\mathrm{mol\ H\,m^{-3}} \qquad (0.05\%\ \text{of the total}\ C_\mathrm{C})$$

$$C_\mathrm{T} = 0.18\,\mathrm{mol\ H\,m^{-3}} \qquad (1\%\ \text{of the total}\ C_\mathrm{C})$$

It ensues that C_T is negligible compared with C_C and Equation 4 becomes

$$C_\mathrm{exc} = C_\mathrm{C} \qquad (6)$$

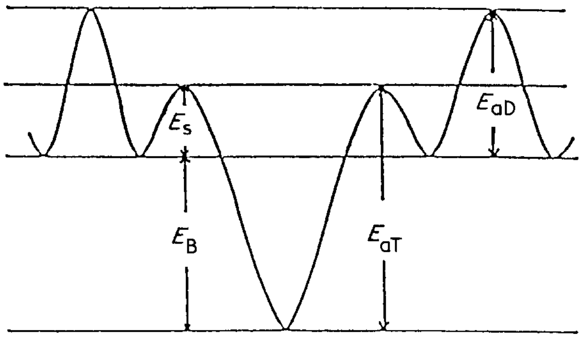

Figure 1 Model for trapping sites (after Lee and Lee [7]).

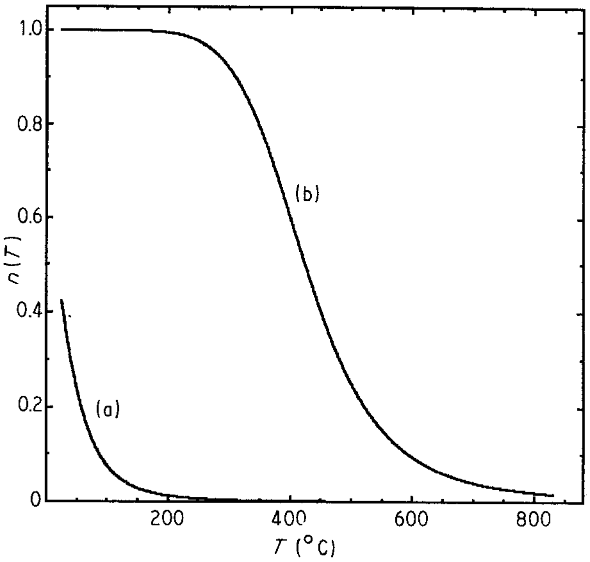

Figure 2 Trap occupancy fraction $n(T)$ for E_B = (a) 27 and (b) $65\,\mathrm{kJ\,mol^{-1}}$.

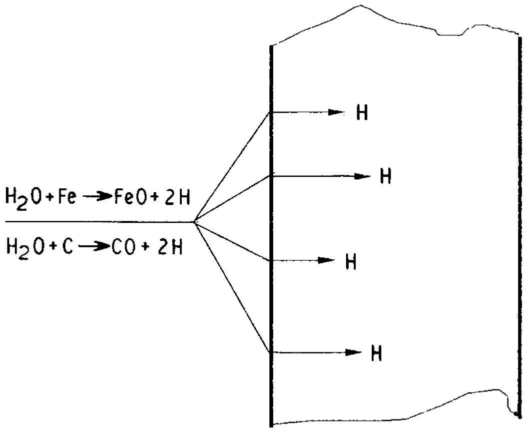

Figure 3 Schematic representation of possible hydrogen adsorption into the steel during enamel firing.

Consequently all the hydrogen dissolved can be considered in excess of the normal solubility value.

During the subsequent cooling, assuming the complete impermeability of vitrified enamel to the hydrogen, part of the hydrogen goes to occupy the traps in the steel, while part of it remains mobile in the matrix (Fig. 4):

$$C_C = C_I(T) + C_R(T) + C_L(T) \tag{7}$$

where C_I is the hydrogen concentration in the irreversible traps and C_R is that in the reversible traps. C_L is the mobile hydrogen that tries to escape to the outside, grouping itself at the steel–enamel interface and threatening the integrity of the enamel itself. In order to get C_L explicit, Equation 7 can be expressed as

$$C_C = n_I(T)N_I + n_R(T)N_R + C_L(T) \tag{8}$$

and in stationary conditions

$$C_C = \left[\frac{C_L(T)N_I}{N_L}\exp\left(\frac{E_{BI}}{RT}\right)\right] \Big/ \left[1+\frac{C_L(T)}{N_L}\exp\left(\frac{E_{BI}}{RT}\right)\right] + \left[\frac{C_L(T)\,N_R}{N_L}\exp\left(\frac{E_{BR}}{RT}\right)\right] \Big/ \left[1+\frac{C_L(T)}{N_L}\exp\left(\frac{E_{BR}}{RT}\right)\right] + C_L(T) \tag{9}$$

The low occupation rate of the reversible traps at temperatures between 25 and 850 °C allows the following simplification [10]:

$$\frac{C_L(T)}{N_L}\exp\left(\frac{E_{BR}}{RT}\right) \ll 1 \tag{10}$$

and Equation 9 becomes

$$C_C = \left[\frac{C_L(T)N_I}{N_L}\exp\left(\frac{E_{BI}}{RT}\right)\right] \Big/ \left[1+\frac{C_L(T)}{N_L}\exp\left(\frac{E_{BI}}{RT}\right)\right] + \frac{C_L(T)\,N_R}{N_L}\exp\left(\frac{E_{BR}}{RT}\right) + C_L(T) \tag{11}$$

Practical use of Equation 11 is dependent on knowledge of the parameters which define the number and binding energy of the traps present in the steel. Such knowledge is not easy to acquire experimentally, but practical observations on the appearance of fishscaling show that it occurs essentially at room temperature. The model can therefore be limited to knowledge of C_L at room temperature, thus permitting considerable simplification.

At room temperature n_I is unity so that the first term in Equation 11 is reduced to N_I. Further, the second term in Equation 11 can be calculated knowing the diffusion coefficient D_2 relative to the contribution made by the reversible traps. In fact, again assuming a low rate of occupation of the traps, it is

$$\frac{N_R}{N_L}\exp\left(\frac{E_{BR}}{RT}\right) = \frac{D_L}{D_2} - 1 \tag{12}$$

substituting in equation 11,

$$C_C = N_I + \left(\frac{D_L}{D_2} - 1\right)C_L + C_L \tag{13}$$

and rearranging, at last

$$C_L = \frac{C_C - N_I}{(D_L/D_2)} \tag{14}$$

This equation shows that the mobile hydrogen concentration C_L is a function of the hydrogen concentration absorbed in enamelling and of the steel trapping system. The relation has a physical significance only when $C_C - N_I > 0$; otherwise all the hydrogen absorbed is, of course, locked in the irreversible traps.

Let C_{CR} be the critical hydrogen concentration that primes the fishscaling at room temperature. The conditions under which the defect can appear or not is indicated by the relation between C_L and C_{CR}:

$$C_L = \frac{C_C - N_I}{D_L/D_2}\begin{cases} > C_{CR} & \text{(defect)} \\ = C_{CR} & \text{(critical)} \\ < C_{CR} & \text{(no defect)} \end{cases} \tag{15}$$

5. Method of applying model

Substituting D_L/D_2 by h in Equation 15, then

$$h\,C_{CR} + N_I - C_C = 0 \tag{16}$$

At given values of C_C and C_{CR} Equation 16 is represented by a straight line in the $\{h, N_I\}$ plane. This line separates the defective materials from the resistant ones in relation to N_I and D_2 (Fig. 5).

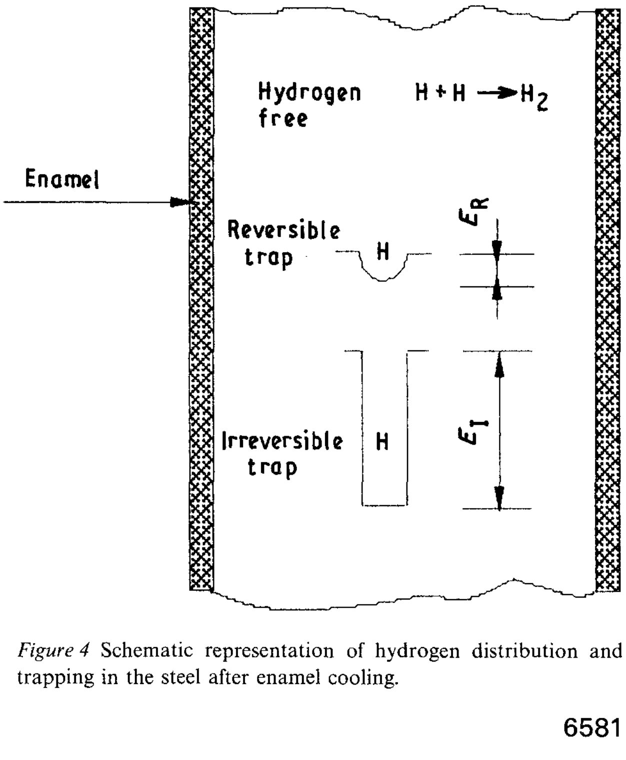

Figure 4 Schematic representation of hydrogen distribution and trapping in the steel after enamel cooling.

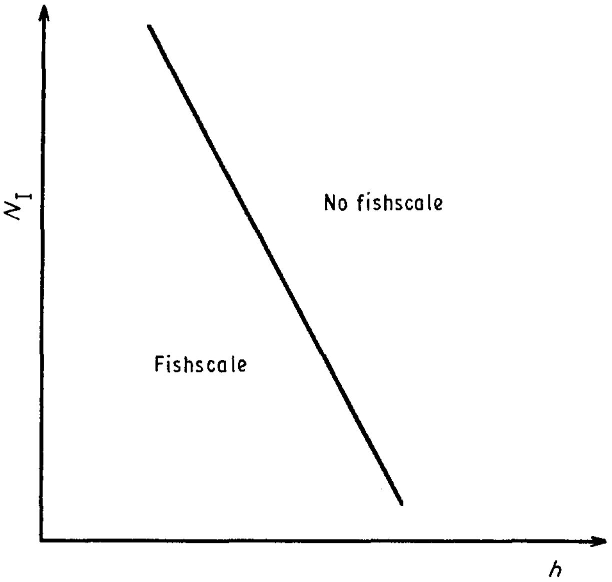

Figure 5 Plot of Equation 16. The straight line separates the defective materials from the resistant ones in relation to N_I and D_2 at given values of C_C and C_{CR}.

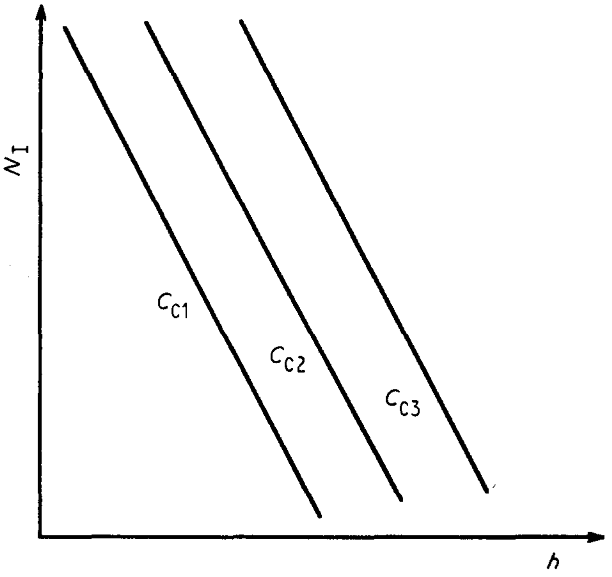

Figure 6 Effect of the variation of C_C: $C_{C3} > C_{C2} > C_{C1}$. An increase of C_C shifts the critical line towards the right side, provoking a greater risk of fishscaling.

Fig. 6 shows the effect of the variation of C_C. An increase of C_C causes a parallel shift of the critical line towards the right side of the $\{h, N_I\}$ plane, resulting in a greater risk of fishscaling. Moreover, it can be observed that the difference $C_L - C_{CR}$ (namely with hydrogen in excess of the minimum needed for appearance of the defect) can also give an indication of the extent and seriousness of the possible defect.

These parameters can be deduced from a series of experimental tests. C_C can be measured on enamelled samples by means of commercial hydrogen analysers. The value of C_{CR} can instead be taken to be the same as the maximum values of C_L of the samples that do not fishscale during intensive experimentation, or it can be evaluated by electrochemical fishscaling tests. N_I and D_2 can be derived from electrochemical permeation tests.

From a purely analytical evaluation of Equation 16 it might seem that a hypothetical sample without irreversible traps ($N_I = 0$) and with a sufficiently high h should not be defective. However, account must be taken of the fact that in this case the percentage occupation of the reversible traps would tend to increase greatly to a point where the simplification made in the model (low rate of occupation of reversible traps) would have to be reconsidered; in practice it may well be that near the h axis ($N_I \geq 0$) Equation 16 may no longer be linear.

However, the existence of a commercial steel with similar characteristics is highly improbable; in fact, the traps often have a mixture of reversible – irreversible characteristics.

6. Conclusions

A new criterion, based on the evaluation of the quantity C_L of mobile hydrogen remaining in the steel after enamelling, leads to an objective estimation of the resistance of the enamelled product to fishscaling. This parameter also allows a margin of safety to be fixed as regards the occurrence of fishscaling.

A practical method of control may be developed through comparing the calculated values of C_L with the results of the enamel test. In order to calibrate the test at a hydrogen content compatible both with steelmaking processes and industrial enamelling processes, it would appear essential to correlate a considerable number of enamel tests with information deriving from diffusivity measurements.

A better knowledge of the influence of reversible and irreversible traps can lead to substantial improvements in steelmaking (chemical composition and thermomechanical processing) in order to obtain a product with guaranteed fishscaling resistance. Furthermore, evaluation of the influence of enamelling process parameters will permit a better utilization of the steel.

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