JOURNAL OF MATERIALS SCIENCE 27 (1992) 6583–6589

Model of hydrogen behaviour in enamelling grade steels

Part II *Application*

R. VALENTINI, A. SOLINA, L. PAGANINI
Università di Pisa, Dipartimento di Ingegneria Chimica, Chimica Industriale e Scienza dei Materiali, Via Diotisalvi 2, 56100 Pisa, Italy

P. DeGREGORIO
Centro Sviluppo Materiali SpA, CP 10747 Roma-EUR, 00100 Roma, Italy

A check has been made of a new model of hydrogen behaviour in enamelling-grade steels in relation to the fishscale surface defect. The quantity C_L of free hydrogen which remains in the enamelled product is determined as a function of its solubility and diffusivity in the steel. The seriousness of the defect or the resistance to the defect, resulting from various metallurgical treatment conditions, can be correlated with the hydrogen parameters. It is shown that the parameter C_L can be adopted in quality control as a new criterion for fishscaling prediction and in planning thermomechanical cycles for enamelling-grade steels in order to prevent the defect.

1. Introduction

Fishscaling, the delayed surface defect of enamelled products, is due to the presence of hydrogen in the metal. The susceptibility to the defect is currently controlled by the first-passage permeation time after Strölein or ATEL [1]. These methods give an indication of the susceptibility of the tested material to the defect, but they are far from being accurate. A practical direct test is the enamel test [1]. Neither of these methods explains the reason for the failure or resistance to it.

In our previous study [2] a model was developed which takes into account the characteristics of hydrogen solubility, diffusivity and trapping in the steel; these parameters together determine the quantity of free hydrogen C_L which remains in the metal after enamelling:

$$C_L = \frac{(C_C - N_I)}{(D_L/D_2)} \quad (1)$$

where C_C is the hydrogen concentration attained in the steel during enamelling, N_I is the concentration of irreversible traps, D_2 is the coefficient of second diffusion and D_L the diffusion coefficient in pure ferrite (7.2×10^{-9} m^2 s^{-1} [3]).

The formula leads to a criterion for measuring the resistance of enamelled products to fishscaling by comparing the calculated free hydrogen with its critical quantity:

$$C_L \geq C_{CR} \quad (2)$$

This paper reports experimental tests made for quantitative determination of the parameters involved in the model and for verifying its applicability in industrial practice.

2. Experimental procedure

2.1. Materials

Table I gives the chemical compositions of the continuous-casting low-carbon steels that have been used. In order to have materials with different trapping characteristics both hot-rolled (HR) and cold-rolled (CR) strips were tested; furthermore cold-rolled strips were also subjected to diverse thermomechanical treatments (coiling temperature, degree of cold reduction, batch annealing temperature and position on the strip, i.e. H on the head and T on the tail of the coil) as reported in Table II. Samples of hot-rolled steels came from cycles with an end-rolling temperature of 900 °C and a coiling temperature of 700 °C.

2.2. Hydrogen permeation tests

Hydrogen diffusion and trapping characteristics were determined by means of electrochemical permeation tests according to Devanathan *et al.* [4]. Specimens (30 mm × 30 mm) from samples of strips were cleaned mechanically using 500 SiC paper, pickled in a 50% aqueous solution of H_2O_2, washed in distilled water at 25 °C and degreased in acetone. Each specimen was then mounted as a working electrode with a useful area of 5 cm^2, between the two halves of a glass cell; the anode side was clad with Pd to eliminate surface impedance to hydrogen flow [5]. A solution of 0.1 N NaOH was used for both half-cells, with the addition of 10 mg l^{-1} of As_2O_3 in the cathode compartment as a hydrogen recombination poison [6]. Both half-cells were de-aerated with a stream of N_2 to lessen the background current due to reduction of the oxygen. The anode compartment was held at + 200 mV SCE

0022–2461

TABLE I Chemical composition of steels used

Material	C(%)	Si(%)	Mn(%)	S(%)	P(%)	Al(%)	Cu(%)	Ti(%)	B(p.p.m.)	N(p.p.m.)	O(p.p.m.)
A(CR)	0.050	0.020	0.22	0.020	0.020	0.050	0.010	—	—	52	39
B(HR)	0.005	0.023	0.20	0.010	0.022	0.032	0.019	0.13	—	39	47
C(HR)	0.006	0.018	0.25	0.007	0.022	0.050	0.016	—	31	27	41
D(HR)	0.006	0.011	0.22	0.010	0.018	0.043	0.014	—	—	56	50

TABLE II Thermomechanical parameters of cold-rolled sheets

Specimen	Coiling temperature (°C)	Cold reduction (%)	Batch annealing temperature (°C)
A BH	560	55.2	650
A BH	560	55.2	800
A CT	700	67.7	650
A CT	700	67.7	700
A CT	700	67.7	750
A CT	700	67.7	800
A FH	700	50.8	700
A FH	700	50.8	750
A AH	700	53.1	650
A AH	700	53.1	800
A AT	700	67.5	650
A AT	700	67.5	800
A GH	700	67.3	No annealing
A GH	700	67.3	650
A GH	700	67.3	800

*H: Head, T: Tail; position of the sample on the coils B, C, F, A, G from casting A.

with a potentiostat. All the permeation tests were run by imposing a current of $-10\ A\ m^{-2}$ on the cathode side, using a galvanostat; this current was low enough to avoid damage to the membrane.

The time-lag method [7] was used to calculate the first diffusion coefficient D_1 from the current–time curve, applying the relation $D = L^2/6t_L$ (t_L is the time needed for the appearance of hydrogen on the opposite surface [8] and L the thickness of the specimen). The cathodic current was subsequently interrupted, permitting the discharge of the mobile hydrogen.

In the same conditions as in the first phase, a second charging phase followed which permitted determination of the second diffusion coefficient D_2. The concentration of irreversibly trapped hydrogen (C_I) could then be estimated by measuring the area between the first and second permeation curves [8].

To compare samples of different thicknesses, the curves were normalized as a function of $\tau = D_L t/L^2$ where D_L is the coefficient of diffusion of hydrogen in pure ferrite, t is the time in seconds and L the thickness of the specimen in metres. The flow of hydrogen was also normalized (J_{norm}) with respect to the stationary case. As a matter of comparison, the conventional first-passage permeation time was also measured using the ATEL Hyperm method [6].

2.3. Hydrogen solubility during the enamelling process

The quantity C_C of hydrogen absorbed by the steel during the enamelling process was determined by means of a commercial Ströhlein instrument. The specimens were enamelled on both sides so as to seal the entire surface, using the following procedure:

(i) *Pretreatment of test pieces.* Place the test-pieces in a hot (90–95 °C) alkaline degreasing solution for 25 min. Rinse well in running water at 30 °C and then in distilled water; after rinsing the film of water on the test-pieces must be continuous. Dry in oven at 100–105 °C for 10 min. Spray the enamel (e.g. Ferro RW50W) on both sides of the test piece; spray so as to obtain a 0.1 mm thick uniform layer of enamel after firing. Dry in oven at 105 °C for 10 min.

(ii) *Firing.* The test-pieces are placed in the firing chamber and are fired at 830 °C ± 10 °C for 3 min 10 s to 4 min 40 s (for thickness of samples 0.6 to 3 mm).

(iii) *Results.* 24 h after firing see whether appreciable fishscales are visible to the naked eye.

This procedure has been proposed as a standard for determination of the susceptibility of a steel to the fishscaling (preliminary classification: UNI E14.07.994).

After the firing of enamel, the specimens were placed in the furnace of the instrument and held at 150 °C until all the hydrogen had been desorbed. Measurements were also made on the same specimens in the as-supplied state and after the pickling before enamelling.

2.4. Electrochemical fishscaling tests

The critical quantity of hydrogen for blow-off of the defect was determined by electrochemically-forced fishscaling tests run on one-side enamelled samples. The cell already described and the same enamelling procedure (see above) were used.

The breakaway of the first piece of enamel on the measuring side causes a current peak, whose position on the time axis corresponds to the time t' of first fishscaling [9]. The critical rupture concentration of hydrogen is derived by the relationship [10]

$$C_{CR} = \frac{i_\infty L}{F D_2}\left[1 - \frac{4}{\pi}\exp\left(-\frac{D_2 t}{4L^2}\right)\right] \quad (3)$$

where i_∞ is the stationary permeation current deduced from the permeation tests, L the membrane thickness, F the Faraday constant, D_2 the coefficient of second diffusion of the hydrogen and t the time of first fishscale.

2.5. Controlled enamel test

A direct check on the susceptibility of the steel to fishscaling was carried out by the enamel test. Since it

is well known that humidity has a marked influence on the results, the test was performed with the aid of an apparatus which controls the humidity of the air entering the oven, the dew point (d.p.) being regulated at 25 °C and 30 °C ± 0.1 °C [1]. The test procedure is given in section 2.3 above.

3. Results

3.1. Electrochemical permeation

Figs 1 to 3 provide examples of first and second permeation curves. The results obtained are summarized in the first three columns of Table III for the cold-rolled samples and of Table IV for the hot-rolled ones.

The data of the Table III reveal variations in D_1, D_2 and C_I, up to almost two orders of magnitude. This confirms the reports made by other workers [11–13] that even limited variations in the thermomechanical parameters (degree of cold-rolling, annealing temperature, etc.) may cause large variations in the solubility and diffusivity of hydrogen in low-carbon steels. There is much less variation in the case of the hot-rolled specimens (Table IV), because the hot thermomechanical cycle is more homogeneous and generally causes fewer lattice defects [11].

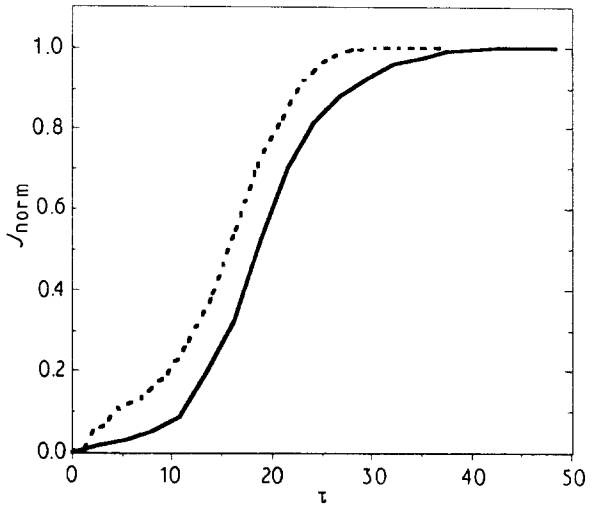

Figure 1 Hydrogen permeation curves for sample A CT 750: (—) first permeation, (. . .) second permeation.

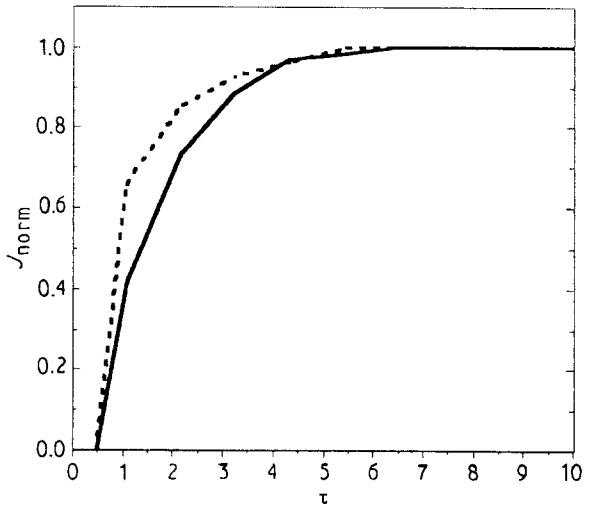

Figure 2 Hydrogen permeation curves for sample A BH 800: (—) first permeation, (. . .) second permeation.

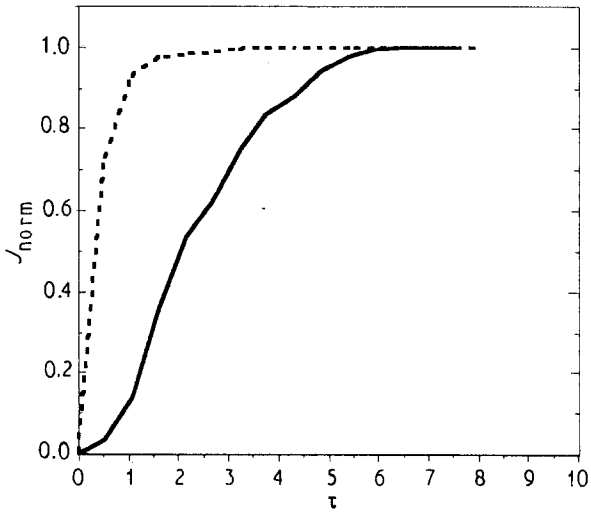

Figure 3 Hydrogen permeation curves for sample C: (—) first permeation, (. . .) second permeation.

3.2. Hydrogen absorbed during enamelling

On specimens of "as-is" steel the average desorption measured was 0.08 mol H m^{-3}; after pickling, the figure rose to 1.6 mol H m^{-3}. After the enamel firing at 830 °C under two humidity conditions (d.p. of 25 and 30 °C), the desorbed hydrogen rose to 7.9 and 13.8 mol H m^{-3}, respectively.

Taking into account also the concentration of irreversibly trapped hydrogen C_I, the total C_C values are 11.8 and 17.7 mol H m^{-3}, respectively (1.5 and 2 p.p.m.). These values agree with that of 14.2 mol H m^{-3} already reported [14], and show that the larger increase of hydrogen in the steel occurs during the last phase of enamelling (firing).

3.3. The free hydrogen parameter

The values of free hydrogen were derived from the Equation 1 of our model, using the data of D_2 and C_I reported in Tables III and IV and those of C_C estimated at two level of relative humidity (d.p. 25 and 30 °C). Results are reported in the fourth and fifth columns of the same Tables III and IV, where the specimens have been arranged in lowering order of C_L.

3.4. Electrochemical fishscaling

The following results were obtained by application of Equation 3:

A AH 650: $C_{CR} = 0.68$ mol H m^{-3} (0.087 p.p.m.) (4)

A AT 650: $C_{CR} = 0.78$ mol H m^{-3} (0.099 p.p.m.) (5)

Bearing in mind the approximations due to the application of Equation 3, these results may be considered consistent and independent of the differences in diffusivity of the samples.

TABLE III Cold-rolled samples: results of permeation and enamel tests

Specimen	D_1 (10^{-10} m^2 s^{-1})	D_2 (10^{-10} m^2 s^{-1})	C_I (mol H m^{-3})	C_L (mol H m^{-3}) d.p. = 25 °C	C_L (mol H m^{-3}) d.p. = 30 °C	Enamel test d.p. = 30 °C	Hyperm t_0 (min, s)
A BH 800	12.00	15.00	0.55	2.34	3.57	Heavy	49″
A AH 800	10.90	11.40	0.16	1.84	2.78	Heavy	1′ 27″
A FH 750	3.74	5.19	3.22	0.62	1.04	Medium	2′ 16″
A BH 650	3.45	5.55	4.48	0.56	1.02	Light	4′ 26″
A FH 700	2.67	3.33	2.99	0.41	0.68	None	2′ 11″
A AH 650	1.81	2.61	4.56	0.26	0.48	None	3′ 27″
A CT 700	1.84	2.32	4.09	0.25	0.44	None	1′ 30″
A CT 650	1.61	2.07	4.56	0.21	0.38	None	5′ 26″
A AT 800	1.20	1.33	3.54	0.15	0.26	None	8′ 20″
A GH 800	0.71	0.86	6.84	0.06	0.13	None	33′ 09″
A CT 800	0.71	0.86	7.86	0.05	0.12	None	4′ 52″
A GH 650	0.67	0.75	7.23	0.05	0.11	None	10′ 09″
A AT 650	0.55	0.66	6.68	0.05	0.10	None	12′ 45″
A GH n.a	0.29	0.32	12.03	0.00	0.03	None	122′ 30″
A CT 750	0.43	0.60	20.91	0.00	0.00	None	4′ 47″

TABLE IV Hot-rolled samples: results of permeation and enamel test

Specimen	D_1 (10^{-10} m^2 s^{-1})	D_2 (10^{-10} m^2 s^{-1})	C_I (mol H m^{-3})	C_L (mol H m^{-3} d.p. = 25 °C	C_L (mol H m^{-3}) d.p. = 30 °C	Enamel test d.p. = 25 °C	Enamel test d.p. = 30 °C
C	6.49	30.31	2.12	4.05	6.56	Heavy	Heavy
B2	3.67	7.35	4.01	0.80	1.40	Heavy	Heavy
D	4.56	5.97	2.99	0.73	1.22	Medium	Heavy
B1	2.22	4.17	3.93	0.46	0.80	None	None

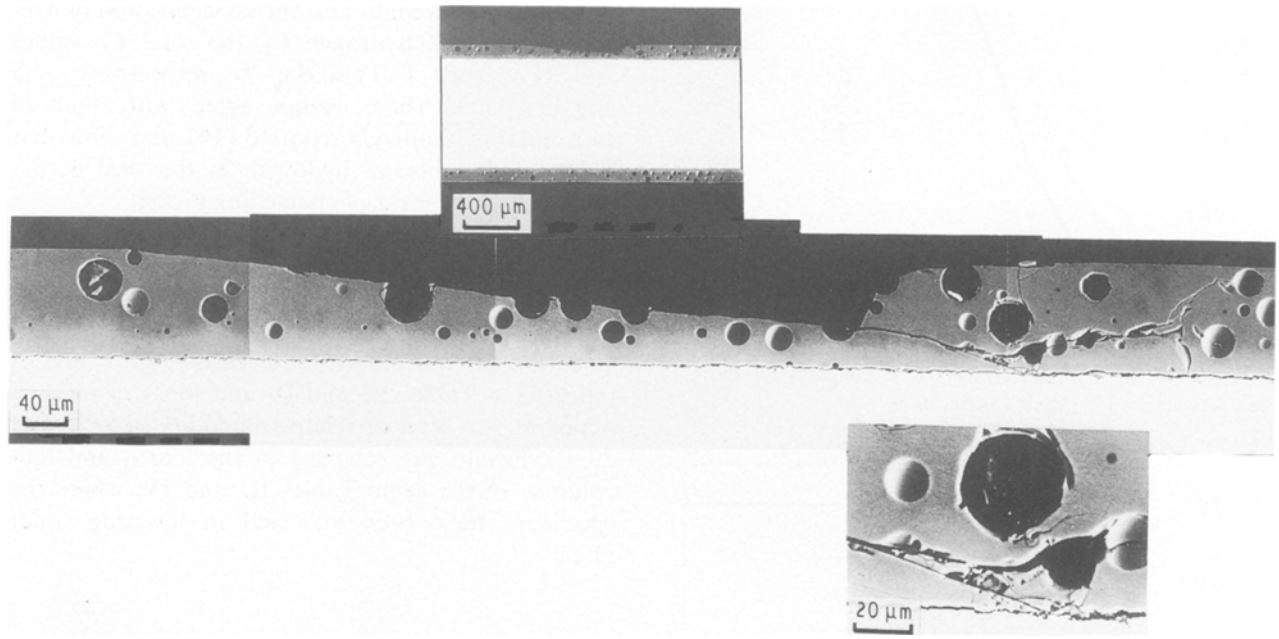

Figure 4 SEM morphology of a typical fishscale (section).

3.5. Enamel test

The results of the enamel test are also reported in Tables III and IV, where the following rough classification of fishscaling is suggested: none (no fishscale), light (small, sporadic fishscales), medium (small but widespread fishscales), and heavy (extensive fishscales with breakaway of large pieces of enamel). As an example Fig. 4 illustrates the morphology of a typical fishscale, seen in section.

4. Discussion

4.1. Comparison of permeation results with enamel test results

Considering the two series of values of C_L reported in Table III for cold-rolled samples, the larger and most dangerous quantity of free hydrogen present in the second case (d.p. 30 °C) obviously depends on the higher humidity present during the enamel firing. Variations within the same column, instead, depend

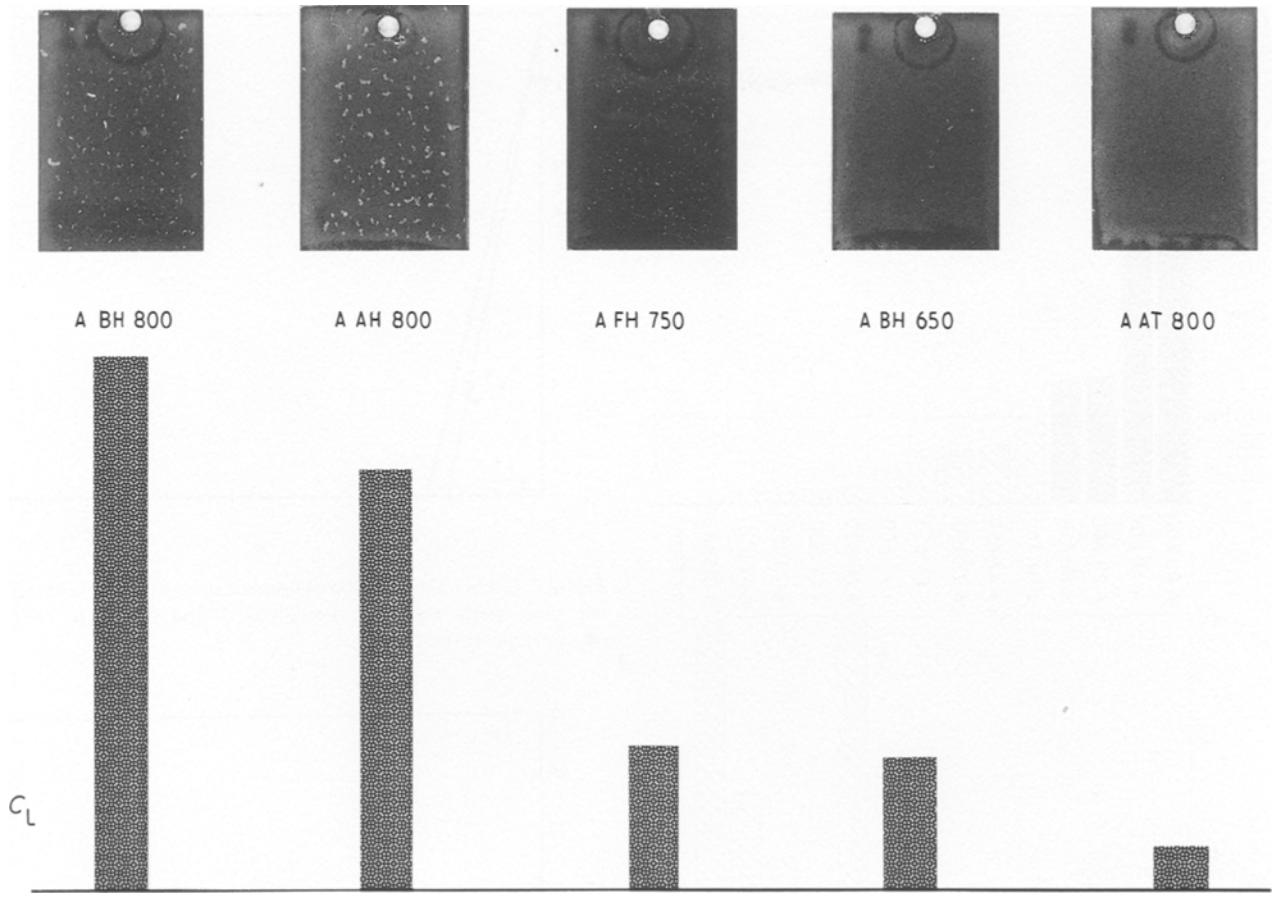

Figure 5 Comparison of magnitude of free hydrogen C_L with the enamel test results.

on the entrapment parameters (C_I and D_2) of each specimen.

If the average value of $C_{CR} = 0.73\ \text{mol H m}^{-3}$ is adopted for the critical concentration of free hydrogen, and the values of C_L are compared with the results of the enamel test, it can be seen that values of $C_L \simeq C_{CR}$ effectively separate the safe specimens from the defective ones. In Fig. 5 the values of parameter C_L are compared directly with the photos of fishscaled specimens; the variation of C_L is congruent with that exhibited by the images.

In Fig. 6 the values of C_L are graphically compared with those of the conventional first-passage permeation time. It can be seen that the Hyperm times may give indications in opposition to the real fishscaling resistance of the steel.

Hence the parameter C_L appears to be more reliable for predicting whether the enamelled product will remain sound; furthermore, it becomes possible to establish a quantitative scale of the susceptibility or resistance to the defect and the relative degree of uncertainty.

4.2. Application of diagnostic model

On the basis of the model previously described [2], graphs have been plotted to determine the boundary between safe and defective samples, with reference to the enamel test. Combining Equations 1 and 2:

$$h C_{CR} + N_I - C_C = 0 \qquad (6)$$

where $h = D_L/D_2$. Substituting in Equation 6 $C_C = 17.7\ \text{mol H m}^{-3}$ (d.p. 30 °C) and C_{CR} from Equations 4 and 5, two straight lines are obtained.

$$N_I = 17.7 - 0.68\,h \qquad (7)$$

$$N_I = 17.7 - 0.78\,h \qquad (8)$$

which block out a band on the (h, N_I) plane separating the defective materials from the others, as can be seen in Fig. 7. The graph reports all the samples which reflect the condition $C_C - N_I > 0$ (the others, of course, cannot be and in fact are not defective).

Applying the same procedure with $C_C = 11.8\ \text{mol H m}^{-3}$ (d.p. 25 °C), two other straight lines are obtained:

$$N_I = 11.8 - 0.68\,h \qquad (9)$$

$$N_I = 11.8 - 0.78\,h \qquad (10)$$

In this case too, the correlation with the results of the enamel test (Fig. 8) appears satisfactory.

Figs 7 and 8 show that the highly defective specimens lie close to the origin of the axes, while the samples with lighter defects are closer to the boundary zone. Thus, not only does application of the model bear out the diversity in susceptibility to fishscaling, it also indicates the margin of resistance of the sound samples, as a function of the distance from the boundary zone.

It can be observed that, in practice, an assessment of fishscaling susceptibility may be made solely with the

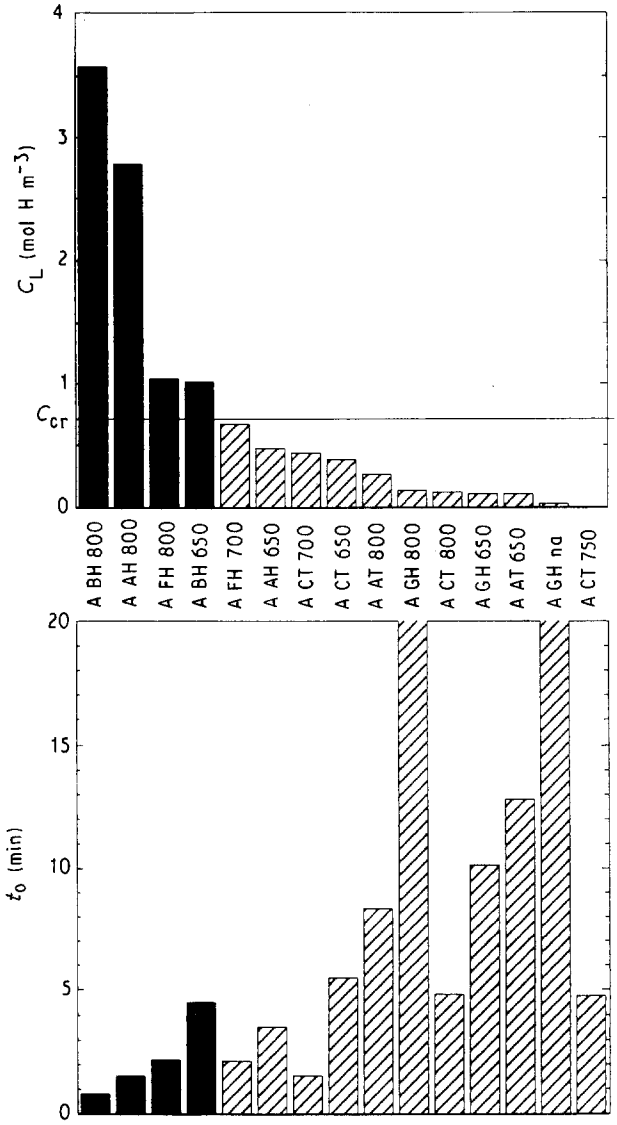

Figure 6 Graphical comparison between C_L (calculated values) and t_0 (measured first-passage Hyperm permeation times): ■ fish-scale, (□) no fishscale.

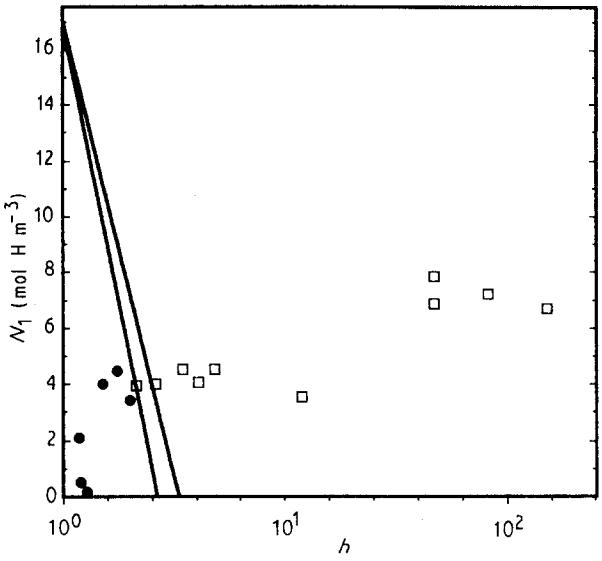

Figure 7 Graphical evaluation of fishscale susceptibility of enamelling sheet steels based on Equations 7 and 8 at d.p. 30 °C: (●) fishscale, (□) no fishscale.

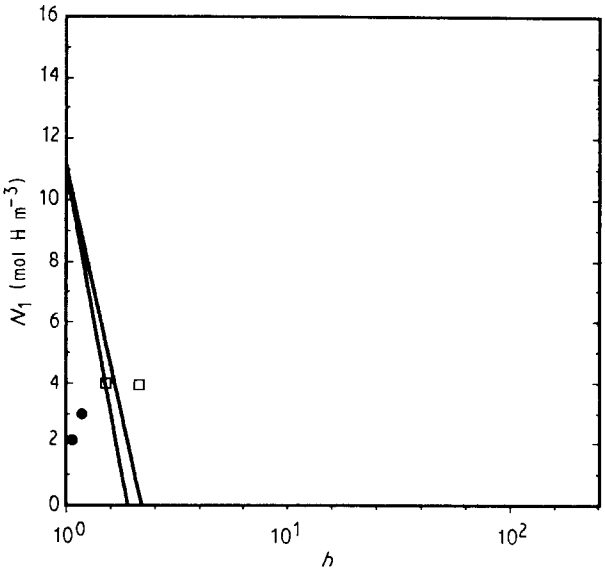

Figure 8 Graphical evaluation of fishscale susceptibility of enamelling sheet steels based on Equations 9 and 10 at d.p. 25 °C: (●) fishscale, (□) no fishscale.

coefficient of first diffusion [15]. However, this coefficient does not distinguish between reversible and irreversible traps, it only evaluates the total effect of the traps with diverse hydrogen entrapment efficiency [16].

For this reason our criterion permits a more thorough evaluation to be made of the real defect resistance of the steel and the relative safety margins. Furthermore, correlation between free hydrogen C_L and parameters of the steel treatment cycle indicates how these variables can be correlated with the real hydrogen entrapment mechanisms [13].

5. Conclusions

Application of this model to the behaviour of hydrogen in enamelling steels provides a more objective evaluation of the fishscaling behaviour of steels than do the tests currently adopted. From the point of view of the user of enamelling-grade steels, instead, the model permits classification of the steels on the basis of their safety threshold *vis-à-vis* the defect; it ensures more careful checks on enamelling process parameters, especially the humidity of the oven atmosphere, in the case of materials at greater risk.

Another suggested use of the criterion presented is the study of the effect of thermomechanical cycles best suited for the production of enamelling-grade steels, since the effect of the various treatment parameters can be correlated directly with the hydrogen entrapment mechanisms.

Further studies are now being pursued to arrive at a more precise evaluation of some of the parameters involved in the model and to furnish criteria for the reliable classification of steels in relation to their fishscaling susceptibility.

References

1. G. BASSANO, P. DeGREGORIO, G. FIERRO, F. GASTALDO and P. ZAMPRONI, in Proceedings, "XV International Enameller's Congress", Praha, June 1989 (Kolektiv, DT 3971) p. 171.

2. R. VALENTINI, A. SOLINA, L. PAGANINI and P. DeGREGORIO, *J. Mater. Sci.* **22** (1992) pp. 6579–6582.
3. K. KIUCHI and R. McLELLAN, *Acta Metall.* **31** (1983) 961.
4. M. A. V. DEVANATHAN and Z. STACHURSKI, *Proc. R. Soc.* **270** (1962) 90.
5. G. M. PRESSOUYRE and I. M. BERNSTEIN, *Corros. Sci.* **18** (1978) 1819.
6. T. ZAKROCZYMSKI, in "Hydrogen Degradation of Ferrous Alloys" (Noyes, Park Ridge, 1985) p. 215.
7. A. McNABB and P. K. FOSTER, *Trans. TMS-AIME* **227** (1963) 618.
8. G. M. PRESSOUYRE and I. M. BERNSTEIN, *Met. Trans.* **9A** (1978) 1571.
9. B. WALKER, *Vitreous Enameller* **20** (1969) 22.
10. J. CRANCK, "The Mathematics of Diffusion" (Clarendon, Oxford, 1975) p. 71.
11. G. M. EVANS and E. C. ROLLASON, *JISI* **207** (1969) 1591.
12. S. X. XIE and J. P. HIRT, *Corrosion* (1982) 486.
13. P. DeGREGORIO, R. VALENTINI, A. SOLINA and F. GASTALDO, *Metallurgia Italiana*, **83** (6) (1991) 520.
14. E. LUNARSKA, in "Hydrogen Degradation of Ferrous Alloys", (Noyes, Park Ridge, 1985) p. 712.
15. G. PAPP, D. GEYER, G. GIEDENBACKER and G. OBERHAUSER, *Mitteilunges d. Vereins Deutcher Emailfachleute* **38** (10) (1990) 129.
16. M. IINO, *Met. Trans.* **16A** (1985) 401.

Received 1 August 1991
and accepted 18 March 1992