Evaluating the susceptibility of steels to hydrogen embrittlement using statistical analyses

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Delayed failure tests of hydrogen-charged specimens result in a large scatter of failure times and failure stresses, analogous to the brittle behaviour exhibited by ceramics. Because of the considerable variation in results, a large number of specimens have to be tested in order to gain an indication of the performance of a particular material; when two materials of similar susceptibility to hydrogen embrittlement are tested, interpretation of the results is often difficult. In the present investigation, seven similar steels were tested in the delayed failure mode to determine their relative susceptibilities to hydrogen embrittlement. These steels were of similar composition and microstructure and showed a low susceptibility to hydrogen embrittlement. The results were analysed using established statistical analysis methods, and by a modified statistical analysis which was developed to describe the failure behaviour. The results of the delayed failure tests and the statistical analyses are presented.

1. Introduction

Hydrogen embrittlement is a long established phenomenon which can severely affect the mechanical properties of a wide range of steels under many different environmental conditions [1, 2]. It has been the main cause, or a contributing factor, of many catastropic failures [3]. One damaging effect of hydrogen is to cause delayed failure to occur in steels which under normal operating conditions would not otherwise fail. This has been the most common type of failure encountered in service applications of steels containing hydrogen or steels exposed to hydrogen environments. As a result, a great deal of research has centered on the hydrogen-induced delayed failure behaviour of several steels [4, 5].

In delayed failure, fractures initiate in regions of highly localized stress where hydrogen is concentrated, due to the diffusion of hydrogen into triaxially stressed sites [4]. Because of its importance, the delayed failure behaviour of steels was extensively investigated by early workers in laboratory studies using static loading of precharged specimens. Fractographic studies have shown that there are often variable amounts of cleavage or quasi-cleavage modes of failure on the fracture surfaces of materials subject to delayed failure. Troiano *et al.* [6] consider that delayed failure in precharged notched steel specimens occurs as a series of events; these are incubation, crack initiation, crack propagation and final failure.

In notched specimens the region of maximum triaxial stress is just ahead of the notch. The first cracks will be initiated as such regions after critical hydrogen concentrations have accumulated there. The crack initiation process is thus dependent upon the temperature and stress gradient, as they both affect the diffusion of hydrogen in the steel. To demonstrate the effect of microstructural state on susceptibilities of hydrogen embrittlement, Cain and Troiano [7] performed sustained-load delayed failure measurements of notched plain carbon-manganese steel specimens which were cathodically charged, cadmium plated, then homogenized to obtain a uniform hydrogen distribution. At a normal strength level of 690 MPa, a mixed ferrite and pearlite structure was more susceptible to fracture than either tempered bainite or martensite. At higher strength levels for the same steel, tempered martensite was superior to tempered bainite. In all the above cases tests were performed at or above the nominal yield strength of the material.

On unnotched specimens, delayed failure tests show a large scatter in times to failure and failure stresses thus indicating the need to test a large number of specimens to obtain any qualitative information for comparing the susceptibility of different types of steel to hydrogen embrittlement [8]. The present investigation examines methods of analysing these data in a qualitative manner.

2. Procedure

Two pipeline steels were used in the investigation; one a micro-alloyed steel and the other a plain carbon-manganese steel, designated American Petroleum Institute (API) grades X65 and X52, respectively.

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TABLE I Composition of X65 and X52 steels

	C	Mn	V	Nb	Si	Cu	S
X65 steel	0.05	1.40	0.06	0.04	0.20	0.32	0.006
X52 steel	0.15	1.26	0.004	0.03	0.34	0.03	0.03

These were supplied as rolled plate, and their compositions are given in Table I. In order to obtain the desired mechanical and metallurgical properties, controlled rolling tests were performed on slabs of the X65 and X52 steels. These resulted in a series of five X65 steels and two X52 steels with the same average grain size but varying yield strengths, as shown in Table II. These seven rolled steels then formed the basis of a detailed examination of the effect of yield strength and microstructure on hydrogen embrittlement.

The specimens used for the hydrogen embrittlement studies were flat strip tensile specimens made to BS18 specification [9]. They were machined from the rolled slabs with their longitudinal axis transverse to the rolling direction of the slabs. The specimens were machine ground, hand polished and finally electropolished in a solution of 8% perchloric acid in 92% glacial acetic acid at an open circuit potential of 40 V d.c. Prior to testing in the delayed failure mode, the specimens were cathodically charged in a solution of 1 N sulphuric acid poisoned with $0.4\,\mathrm{g\,l^{-1}}$ arsenious trioxide at a current density of $10\,\mathrm{A\,m^{-2}}$. All specimens were tested exactly 4 min after the completion of charging on an axial testing machine with a ramp generator and constant load holding facility. The ramp generator was set to reach the required load in 2 sec at a constant loading rate, then maintain the load until the specimen failed. The output from the axial machine was connected to a microcomputer which was used to record the load and time [10].

3. Statistical analyses

The delayed failure results were analysed on the basis of the Yokobori [11] analysis used previously [5, 8] and also using a modification of this analysis developed during the present study [10].

3.1. Yokobori analysis

Yokobori analysed the results of delayed failure tests of glass specimens. He proposed that the probability of cracks being produced of sufficient size to cause failure in the time interval, dt, is given by

$$P_s x \, dt = -dP_s \quad (1)$$

where P_s is the probability of survival at time t, and x is the probability per unit time of a crack occurring of sufficient size to cause failure. Rearranging

$$\frac{dP_s}{P_s} = -x \, dt \quad (2)$$

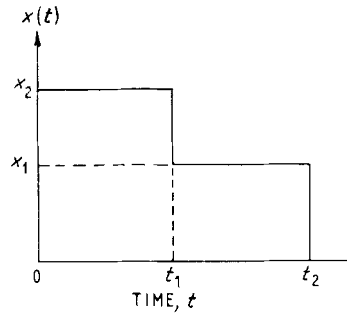

Figure 1 Proposed dependence of x upon t.

Integrating

$$\ln (P_s) = -xt + c \quad (3)$$

where c is a constant. At $t = 0$, $P_s = 1$, thus $c = 0$. Therefore

$$\ln (P_s) = -xt \quad (4)$$

For delayed failure tests, this equation is generally expressed as

$$\ln (P_s) = -Kt_f \quad (5)$$

The value of K can be determined by plotting a graph of P_s against t_f on a logarithmic scale, and calculating the gradient.

3.2. Proposed analysis

For hydrogen embrittlement tests, however, the probability per unit time of a crack occurring of sufficient size to cause failure (x in Equation 2), may not be constant and may thus be dependent upon time. The proposed modification is a time-step function which is shown diagrammatically later in Fig. 4.

(i) Assume $x = f(t)$, as shown in Fig. 1. Equation 3 now becomes

$$\ln (P_s) = -x_1 t + c_1 \quad \text{for } 0 \leqslant t \leqslant t_1 \quad (6)$$

$$\ln (P_s) = -x_2 t + c_2 \quad \text{for } t_1 \leqslant t < t_2 \quad (7)$$

$$\ln (P_s) = 0 \quad \text{for } t_2 < t \quad (8)$$

where x_1, x_2, c_1, c_2 are constants. At $t = 0$, $P_s = 1$ thus $c_1 = 0$ in Equation 6. At $t = t_1$, P_s in Equations 6 and 7 is the same, thus

$$c_2 = (x_2 - x_1)\, t_1$$

and Equation 7 now becomes

$$\ln (P_s) = (x_2 - x_1)\, t_1 - x_2 t \quad (9)$$

The values of x_1, x_2 and t_1 can be determined by plotting a graph of $\ln (P_s)$ against t, and calculating the gradients.

4. Results

The charging conditions for all the rolled steels were standardized, and applied to each specimen prior to

TABLE II Material properties

	X65–A	X65–B	X65–C	X65–D	X65–E	X52–L	X52–M
Yield strength, σ_Y, (MPa)	490	430	468	481	530	472	520
Grain size, $\bar{d}\alpha$, (μm)	3.9	3.9	3.9	3.9	3.9	3.9	3.9

TABLE III Failure times of X65–A specimens (seconds)

3.5	164.5	229.4	443.4	80.8	145.7	76.5
140.0	3.6	NF	599.6	3.4	235.3	216.5
7.0	NF	608.7	589.9	830.2	4.3	236.0
352.1	667.0	223.2	NF	5.7	2019.6	209.1
388.8	288.0	129.3	5.1	3.7	NF	NF
NF	282.0	23.7	203.0	3.6	1673.6	10.5
149.5	230.7	21.6	NF	6.8	195.2	4.5
509.1	–	–	–	–	–	–

TABLE V Failure times of X52–M specimens (seconds)

60.6	65.8	114.3	408.3	111.1	72.6	71.9
731.6	397.1	NF	984.7	382.4	26.4	462.0
369.6	2986.9	81.4	14.6	15.5	102.8	23.8
11.0	3487.2	1142.9	421.2	108.6	18.7	92.7
799.2	1991.2	3.2	183.8	160.0	10.1	189.9
14.4	2361.3	889.6	1229.9	8.5	110.5	1477.6
261.0	3.0	248.3	342.8	76.5	77.4	57.3
28.0	–	–	–	–	–	–

testing in the delayed failure mode. The X65 rolled steels were tested at a stress level of 1.05 times their respective yield strengths. The X52 rolled steels were tested at a stress level of 1.10 times their respective yield strength, in order to obtain comparable failure times with the X65 rolled steels. Each set of delayed failure tests consisted of fifty individual tests, though not all the tests resulted in failure. Some specimens did not fail even after 1 h of testing; in such cases the tests were stopped and noted as no failure (NF). The results of delayed failure tests are given in Tables III, IV and V for the X65-A, X65-B and X52-M steels, respectively.

Histograms of the failure times showed that the majority of failures occurred within the first 10 min of testing [10]. The delayed failure results were analysed using the statistical analyses described.

5. Discussion

All tensile specimens were made with their longitudinal axis transverse to the rolling direction of the slabs, because this direction generally exhibits lower tensile properties and a greater susceptibility to hydrogen embrittlement due to anisotropy [12]. Several delayed failure tests were conducted at varying applied stresses to determine the minimum threshold stress below which no failure would occur. These preliminary tests showed that delayed failure did not occur at an applied stress below the yield stress of the material, in specimens charged under the standardized conditions. At the yield stress of the material or above, all the rolled steels exhibited delayed failure behaviour.

The results were initially analysed using the statistical analysis proposed by Yokobori [11]. The results showed that the analysis required modifying to predict more accurately failure times of hydrogen-charged specimens subjected to delay failure tests. The Yokobori analysis assumes that the probability per unit time of a crack occurring of sufficient size to cause failure remains constant during the duration of the test, and is thus independent of time. For failure to occur in hydrogen-charged specimens sufficient hydrogen must accumulate at a defect site to initiate and propagate a crack [6]. This process is controlled by the rate of diffusion of hydrogen and is thus time dependent. Also, as the test proceeds hydrogen diffuses out of the test specimen and the longer the test the less hydrogen available to cause failure. Therefore, because both processes are time dependent, it is assumed in the proposed analysis that the probability per unit time of a crack occurring of sufficient size to cause failure will also be time dependent; this is the argument in the time-step modification.

The probability of specimens surviving failure at any given time during testing is shown in Fig. 2 for the X-65 steel. This type of distribution was also exhibited by the X65-D, X65-E and X52-M steels. It can be seen that Yokobori's prediction is not in very good agreement with the experimental result. There was better agreement with the X65-B, X65-C and X52-L steels, as shown by Fig. 3. When the results are replotted using the modified statistical analysis as shown in Fig. 4, the predicted values of survival probabilities at any given time agree very well with the experimental results. The gradients x_1 and x_2 can be obtained from Fig. 4 and used to predict the probabilities of specimens surviving at any time up to and beyond the maximum failure time encountered during testing.

The modified analysis is an alternative treatment of hydrogen-induced delayed failure behaviour than the Yokobori analysis, and more accurately predicts delayed failure times. The analysis also provides the basis for qualitatively comparing the susceptibility of different steels to hydrogen embrittlement by comparing the constants evaluated from Equation 9 for the different steels.

6. Conclusions

The susceptibility of steels to hydrogen embrittlement can be compared in a qualitative manner by analysing

TABLE IV Failure times of X65–B specimens (seconds)

185.0	237.6	1437.0	3.9	789.2	264.8	486.7
303.0	209.0	NF	510.7	954.5	3.3	3.0
247.5	546.7	316.8	730.1	238.8	3.4	1587.1
NF	605.2	NF	NF	153.8	117.8	1863.7
73.2	1430.2	20.1	2132.6	2076.4	2129.3	254.4
406.3	580.6	2142.5	5.8	721.3	271.2	NF
162.1	5.8	NF	108.2	715.4	2494.8	5.5
845.9	–	–	–	–	–	–

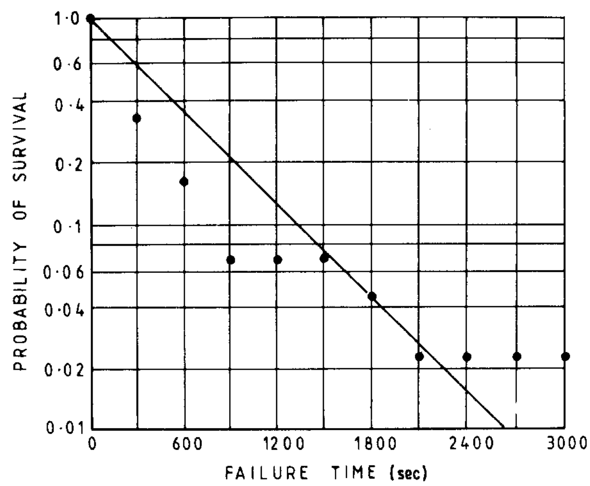

Figure 2 Analysis of failure times, X65-A steel. (●) Experimental values, (——) Yokobori [11].

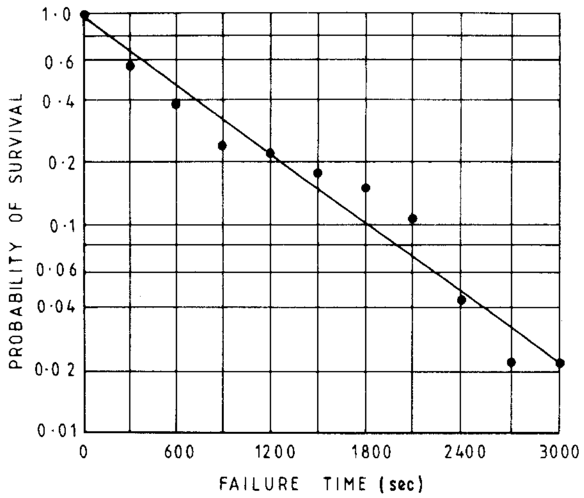

Figure 3 Analysis of failure times, X65-B steel. (●) Experimental values, (——) Yokobori [11].

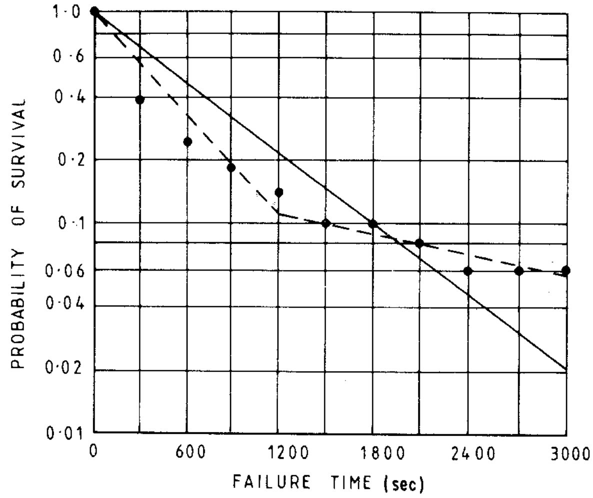

Figure 4 Analysis of failure times, X52-M steel. (●) Experimental values, (——) Yokobori [11], (– – –) step function.

the failure times of specimens tested in the delayed failure mode. The proposed statistical analysis is more representative of the hydrogen-induced delayed failure behaviour than the Yokobori analysis, and more accurately predicts failure times.

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