Hydrogen - Induced Sub - Critical Flaw Growth in Steels under Static and Cyclic Loading Conditions

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The sub-critical flaw growth behaviour in $4\frac{1}{4}\%$ Ni-Cr-Mo steel when exposed to environments containing hydrogen in both the pure molecular and combined forms has been studied under both static and cyclic loading conditions [1,2]. Details of the steel are given in Table 1.

Table 1. Chemical Analysis and Mechanical Properties of 835 M30 Steel

Element, Wt%								0.2% Proof Stress, ksi	K_{1C} ksi $\sqrt{in.}$
C	Si	Mn	S	P	Ni	Cr	Mo		
0.27	0.20	0.53	0.009	0.012	3.93	1.11	0.14	196	69

Heat Treatment: Austenitised 830°C; Oil Quenched; Tempered 200°C.

$\frac{1}{2}$ in. thick compact tension and contoured double cantilever beam test pieces were used. Static load tests were conducted, after fatigue pre-cracking, in environments of aqueous salt solution (3.5% Na Cl by wt.), pure hydrogen gas and dry hydrogen sulphide gas. Both these environments and air were used for cyclic load tests at frequencies of

70 Hz. over a wide range of R values (ratio of minimum to maximum stress intensity). Crack growth rates were determined by an electrical resistance technique.

Figure 1 shows time to failure versus initial stress intensity for static load tests in each of the environments. The threshold stress intensity level, K_{1SCC}, below which no crack growth occurs is independent of environment and is 12 ± 1 ksi $\sqrt{in.}$ This supports earlier work [3] which showed that K_{1SCC} is mechanically, rather than environmentally, controlled and coincides with the formation of a stretch zone at the crack tip. No failure times are shown for tests in hydrogen sulphide because on attaining K_{1SCC} very rapid crack growth produced failure within 10 seconds.

Identical, predominantly intergranular fracture surfaces were produced in each of the environments.

In Figure 2, the crack velocity in each environment is shown as a function of stress intensity. In the gaseous environments a stress intensity-independent crack velocity is rapidly attained which is limited by the embrittling chemical process. In contrast, the crack velocity of 835 M30 steel in the aqueous environment is stress intensity-dependent and is related to the stretch zone size so can be expressed as: $\frac{da}{dt} = f\ (K_1^2 - K_{1SCC}^2)$; that this is not always true for stress corrosion is shown by the results for a 9 Ni 4 Co 0.45 C steel where a steady-state velocity is observed. The most rapid crack velocities occur in hydrogen sulphide and exceed those in hydrogen and salt solution by over 2 and 4 orders of magnitude, respectively.

The influence of temperature on crack velocity in each of the environments is summarised in Figure 3. This indicates that the activation energy, Q, for the cracking mechanism is similar in the gaseous environments ($\simeq 2,000$ cal/g.atom) where the velocity is proportional to the square root of pressure, but is considerably higher in the aqueous environment ($\simeq 8,500$ cal/g.atom). The former value is characteristic of that for the diffusion of atomic hydrogen through the iron lattice while the latter is characteristic of the same process where the diffusion is limited by either partial surface control or a trapping phenomenon.

The addition of as little as 1% oxygen to hydrogen was found to inhibit crack growth but this was not so in hydrogen sulphide.

It is concluded that the hydrogen atom is the embrittling species in each of the environments and that the cracking mechanism involves dissociation of the environment into atomic hydrogen, catalysed by the clean metal surface of the stretch zone, and its subsequent diffusion into the plastic zone where it facilitates microcrack nucleation and

growth. The differences in crack velocity are due to variations in the concentration of atomic hydrogen at the crack tip, being least in aqueous solution where dissociation can only occur at active anodic sites and greatest in hydrogen sulphide which acts as a 'catalytic poison' and diminishes the rate of recombination of hydrogen atoms into molecules.

Figure 4 shows the influence of environment on the relationship between crack growth rate, $\frac{da}{dN}$, and stress intensity range, ΔK, during cyclic loading. The data determined in air, salt solution and hydrogen all fall within the same band between limits defined by the extremes of stress ratio; growth rates increasing with increasing R value. In hydrogen sulphide, however, the crack growth rate is accelerated, particularly at high R values.

Figure 5 shows that the ΔK values required to give specific crack growth rates in air and salt solution can be plotted as a function of the maximum stress intensity during the loading cycle, $K_{f\ max}$. This indicates that a threshold value of stress intensity range, ΔK_{TH}, exists, below which fatigue crack growth will not occur and also that there is a critical maximum stress intensity value for unstable fracture during fatigue, K_C, at which the lines representing specific values of crack growth rate converge. The resulting relationships can thus be written:

$$\frac{da}{dN} = C \left(\frac{\Delta K - \Delta K_{TH}}{K_C - K_{f\ max}} \right)^n$$

where: C and n are constants. Figure 5 confirms that salt solution has little influence on crack growth rates measured in air and this is expected since under static loading the velocity (Figure 2) is generally below 2×10^{-3} in/min which, at a frequency of 70 Hz is equivalent to a crack growth rate below 5×10^{-7} in/cycle.

A similar plot in Figure 6 shows accelerated crack growth in hydrogen when $\frac{da}{dN}$ exceeds 10^{-6} in/cycle and in hydrogen sulphide when $\frac{da}{dN}$ exceeds 10^{-7} in/cycle. However, the extent of this is less than expected

since, for example, static load results predict growth rates exceeding 10^{-3} in/cycle in hydrogen sulphide whereas even when the minimum fatigue stress intensity exceeds K_{1SCC} the rate is only 10^{-5} in/cycle. Cyclic loading can, therefore, attenuate the static load crack velocity and it is thought that this is due to the introduction of restraint into the plastic zone during the decreasing load part of the cycle. Figure 6 also shows that in hydrogen sulphide crack growth is accelerated even when $K_{f\ max}$ is below K_{1SCC}. This is because cyclic loading can expose a fresh metal surface on which hydrogen can be adsorbed at stress intensities below that for stretch zone formation under static load.

These observations prevent the application of a superposition model[4] to environmentally enhanced fatigue crack growth in which the separate contributions of fatigue and the aggressive environment are treated additively. This is confirmed by the fractographic observation that the normal transgranular fatigue surface produced in air changes to one which is predominantly intergranular at the lower fatigue stress intensities in the other environments, even at $K_{f\ max}$ values below K_{1SCC}.

1. P. McIntyre and A. H. Priest, B.S.C. Corporate Laboratories. Report MG/23/72.

2. C. E. Nicholson, P. McIntyre and A. H. Priest, B.S.C. Corporate Laboratories. Report MG/22/72.

3. A. H. Priest and P. McIntyre; AGARD Conf. Proc.: AGARD-CP-98 Paper 13 (1972).

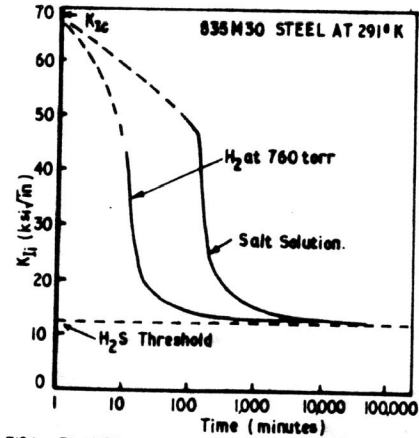4. R. P. Wei and J. D. Landes; Mat. Res. and Stds.; 9 (1969) 25 - 28.

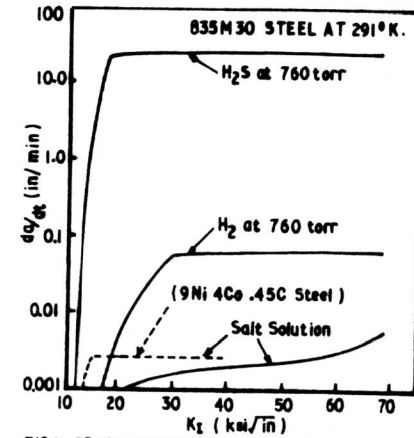IV - 441

FIG 1. FAILURE TIME vs INITIAL STRESS INTENSITY.
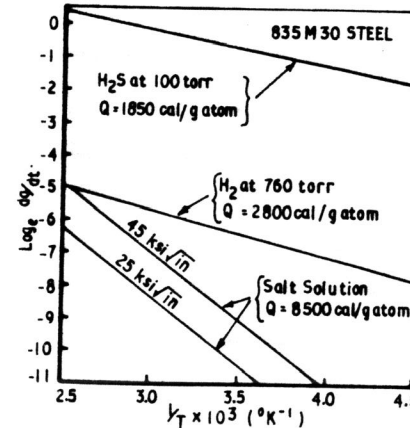
FIG 2. CRACK VELOCITY vs STRESS INTENSITY
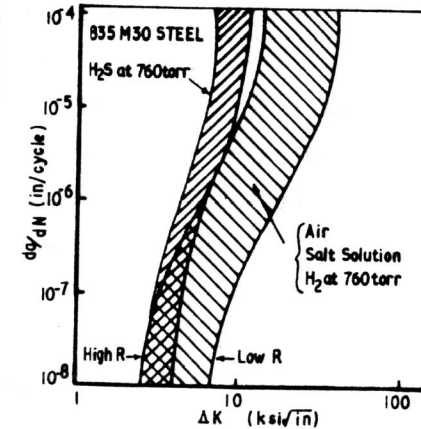
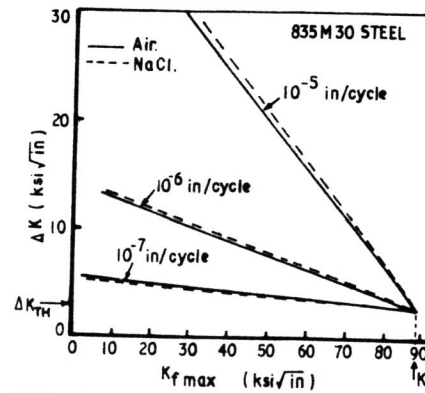FIG 3. CRACK VELOCITY AS A FUNCTION OF TEMPERATURE.

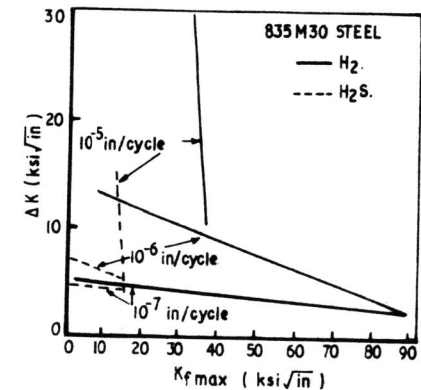FIG 4. CYCLIC LOAD TEST RESULTS.

FIG 5. FATIGUE IN AIR AND SALT SOLUTION

FIG 6. FATIGUE IN H_2 AND H_2S.