

A CRITERION FOR HYDROGEN-INDUCED FRACTURE

K. Akhurst

Department of Materials Science and Engineering
University of Pennsylvania
Philadelphia, PA 19104 U.S.A.

ABSTRACT

The achievement of a critical combination of local stress and hydrogen concentration is insufficient alone to explain the existence in high strength steels (> 600 MPa yield strength) of a threshold stress intensity, K_{TH} , below which hydrogen-induced slow crack growth is not observed. Studies of brittle modes of unstable fracture have shown that for fracture to occur a critical stress must be exceeded over a critical distance. This paper considers what behavior would be expected if such a critical criterion is also operative in hydrogen-induced cracking. Equilibrium conditions are assumed at K_{TH} , and the dependence of the critical fracture stress on hydrogen concentration is approximated to a linear relationship. The important material variables are established and the dependence of K_{TH} on external hydrogen pressure (for slow crack growth in gaseous hydrogen) is calculated for various reasonable values of these variables. The results of the calculations compare well with the experimental evidence.

KEYWORDS

Hydrogen-induced cracking; hydrogen embrittlement; brittle fracture; threshold stress intensity; fracture stress.

INTRODUCTION

The embrittling action of hydrogen on steel, often resulting in stable crack growth at stress intensities below K_{IC} , has been recognized for some time. It appears that the presence of hydrogen in some way encourages brittle modes of failure to operate at lower stress levels. The most widespread interpretation is that hydrogen dissolved in the steel reduces the cohesive strength (or cohesive energy) of the Fe-Fe bonds, probably a result of the electrons from the hydrogen atoms entering the electron bands of the metal (Troiano, 1960; Jokl and co-workers, 1980).

Troiano (1960) and his co-workers observed that in notched specimens charged with hydrogen, hydrogen-induced fracture first occurs ahead of the notch in the region where the hydrostatic and tensile stresses are maximum. This is presumably related to the suggestions that hydrogen concentrates in regions of hydrostatic tensile

stress (Oriani, 1969), and that brittle modes of fracture are dependent on the tensile stress perpendicular to the plane of fracture (Knott, 1973). These observations led a number of investigators to propose models for hydrogen-induced fracture in which the threshold stress intensity for stable crack growth, K_{TH} , below which crack advance is not observed, corresponds to the achievement of a critical combination of stress and hydrogen concentration ahead of the crack (Oriani, 1972; Tetelman, 1974; Gerberich, 1974; Van Leeuwen, 1975).

Recent analyses of stress distributions ahead of a loaded crack indicate that the maximum stress is independent of the applied load (Rice and Johnson, 1970; Rice, 1976); the highly stressed region simply expands as the load is increased. Ahead of a crack which is stationary after a sufficiently long period in contact with hydrogen the greatest concentration of hydrogen is at the point of maximum hydrostatic stress. As the load is increased the maximum stress remains constant and so, at equilibrium, does the hydrogen concentration. If stress and hydrogen concentration are the only important factors it is difficult to see why at a certain stress intensity, K_{TH} , the crack should start to grow.

Considering unstable fracture (no hydrogen), Ritchie and his co-workers have shown that for cleavage in mild steel (Ritchie, Knott and Rice, 1973), and for intergranular fracture in an alloy steel (Ritchie, Geniets and Knott, 1973), it is not sufficient simply to exceed a critical stress. The fracture stress must be exceeded over a significant distance in relation to the microstructure (e.g. two grain diameters for the mild steel). This may be interpreted as the distance ahead of the crack tip of the most difficult barrier to the propagation of a freshly nucleated microcrack. If this barrier is very close to the site of microcrack nucleation (e.g. the escape of a microcrack from a carbide particle or an inclusion), then the critical distance would be directly related to the separation of the preferred nucleation sites. Alternatively the stress gradients ahead of a crack tip may, if steep enough, alone be sufficient to arrest a microcrack (Kameda and McMahon, 1980). If this is controlling then the effective critical distance would not be directly related to the microstructure of the steel.

The present paper examines what behaviour would be expected if a critical distance criterion is also operative in hydrogen-induced cracking. Such a requirement would explain why hydrogen-induced crack growth is only observed at stress intensities above K_{TH} , since the distance over which a critical combination of stress and hydrogen concentration is exceeded increases with increasing stress intensity. K_{TH} would be the stress intensity at which this distance is equal to the critical distance.

FORMULATION

It is expected that any changes in the hydrogen concentration do not affect the critical distance, x_c , which is probably related to the microstructure of the steel. The increasing embrittlement with increasing hydrogen concentration is therefore due to a progressive reduction of the critical fracture stress, σ^* . The precise mechanisms of hydrogen-induced fracture are not yet determined, and for the present calculations a simple linear relationship between σ^* and the local hydrogen concentration, C_H , has been assumed:

$$\sigma^* = \sigma_o^* - A' C_H \quad (1)$$

where σ_o^* and A' are constants characteristic of the specific metal (in a specific condition). This assumption is reminiscent of (but different from) the assumption

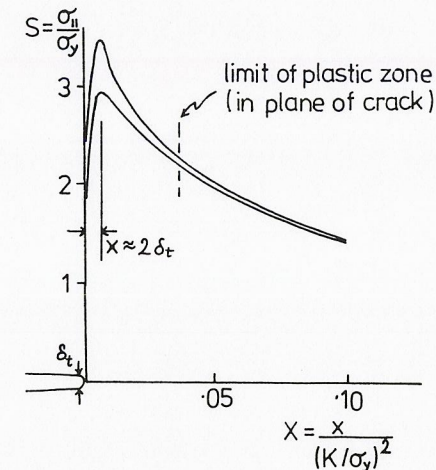


Fig. 1 The distribution of stress ahead of a crack subject to an applied stress intensity K . After Rice (1976).

made by Oriani (1972) of a linear relationship between cohesive strength and hydrogen concentration. The hydrogen concentration, rather than the activity, is chosen because the local density of electrons contributed to the metal by the hydrogen is considered to be the important factor.

For hydrogen-induced cracking in a gaseous hydrogen environment the hydrogen pressure, P_{H_2} , is an important variable, characteristic of the hydrogen activity. The hydrogen pressure can be related to the local hydrogen concentration using Sievert's Law and allowing for the influence of hydrostatic stress (Oriani, 1969). Equation (1) then becomes:

$$\sigma^* = \sigma_o^* - A P_{H_2}^{1/2} \exp \frac{V_H \sigma_{ii}}{3 RT} \quad (2)$$

in which \bar{V}_H is the partial molar volume of hydrogen in the metal, $\frac{\sigma_{ii}}{3}$ is the hydrostatic stress ($\sigma_{ii} = \sigma_{11} + \sigma_{22} + \sigma_{33}$), R is the gas constant and T the absolute temperature. The new embrittlement constant A also includes the Sievert's Law constant and any concentration factor of hydrogen at an interface in the microstructure, if this is where the important cracking event takes place.

The stress distribution resulting from the finite element analysis of Rice and his co-workers (Rice and Johnson, 1970; Rice, 1976) is used in the present calculations, and is shown in Fig. 1. The normalized stress, S , and distance, X , allow for the effects of stress intensity, K , and yield strength, σ_y , on the distribution. In these calculations the value of X for the maximum stress is taken as constant, although in reality it will vary with yield strength, since $x_{max} \sigma \approx 2\delta_t \approx K^2/E\sigma_y$ (Rice, 1976).

It is not thought that this variation will have a large effect upon the results of the calculations, and the yield strength for which Fig. 1 is strictly correct is approximately

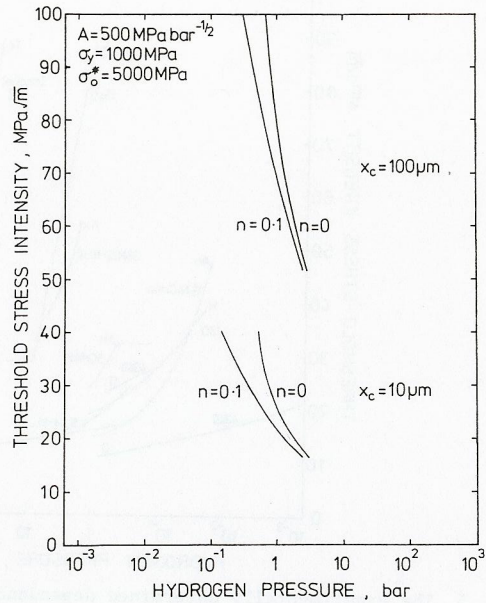


Fig. 2 The influence of strain hardening coefficient, n , on the dependence of K_{TH} on hydrogen pressure, for two values of critical distance, x_c .

in the middle of the range of strengths considered.

The distribution of hydrostatic stress ahead of a loaded crack is, to the author's knowledge, not available in the published literature. The value of σ_{ii} for plane strain conditions can be approximately related to the tensile stress, σ_{11} , normal to the crack plane, assuming Tresca's yield criterion and a material with little strain hardening (Akhurst; to be published);

$$\sigma_{ii} = (2 \sigma_{11} - \sigma_y) (1 + \nu^*) \quad (3)$$

ν^* is the effective Poisson's ratio, which is taken as 0.3 in the present analysis since ahead of the peak in the stress distribution, in the plane of the crack, the strain is predominantly elastic even in the plastic zone (McMeeking, 1977). Variation of ν^* between 0.3 and 0.5 probably does not, in any case, greatly affect the results.

Combining equation (2) and (3) and putting $\nu^* = 0.3$;

$$\sigma^* = \sigma_o^* - A P_{H_2}^{1/2} \exp \frac{\bar{v}_H (2.6 \sigma_{11} - 1.3 \sigma_y)}{3 RT} \quad (4)$$

This relates the critical stress for fracture to the hydrogen pressure, P_{H_2} , the tensile stress perpendicular to the crack plane, σ_{11} , the temperature, T , and the material variables, σ_o^* , A , \bar{v}_H , and σ_y .

We can find the distance ahead of the crack over which the critical stress is exceeded

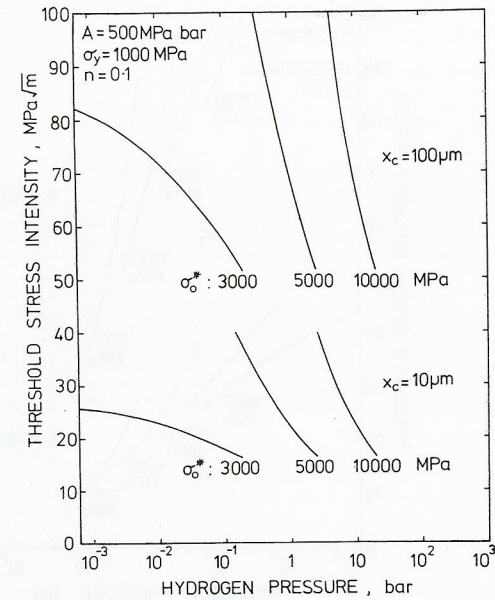


Fig. 3 The influence of σ_o^* on the dependence of K_{TH} on hydrogen pressure, for two values of critical distance, x_c .

(i.e. for which $\sigma_{11} > \sigma^*$) by solving this equation for $\sigma^* = \sigma_{11}$ and finding the position of the resultant stress ahead of the peak of the stress distribution in Fig. 1, $X_{\sigma_{11} = \sigma^*}$. The true distance, $x_{\sigma_{11} = \sigma^*} = X_{\sigma_{11} = \sigma^*} (K/\sigma_y)^2$, increases with increasing stress intensity, and the threshold stress intensity corresponds to the stress intensity at which this distance reaches a critical value, x_c .

$$\text{i.e. at } K_{TH}; x_{\sigma_{11} = \sigma^*} = x_c \quad (5)$$

This is the critical distance criterion discussed in the introduction.

THE INFLUENCE OF HYDROGEN PRESSURE AND MATERIAL VARIABLES ON K_{TH} .

Both temperature and hydrogen pressure are explicitly mentioned in equation (4). The temperature can influence the material variables, and so its effect on K_{TH} is difficult to establish. The hydrogen pressure, on the other hand, is expected to have little or no influence on the material variables, although it may effect plastic flow in a way which is not yet completely clear. Assuming it has a negligible effect on the flow stress in the plastic zone, equations (4) and (5) can be used together with the curves in Fig. 1 to calculate the expected dependence of K_{TH} on the hydrogen pressure for materials with various combinations of properties, characterised by the values of \bar{v}_H , σ_y , x_c , σ_o^* , n and A . In the present calculations \bar{v}_H was taken to be the partial molar volume of hydrogen in iron; $2.0 \times 10^{-6} \text{ m}^3/\text{g atom}$ (Oriani, 1969). A range of

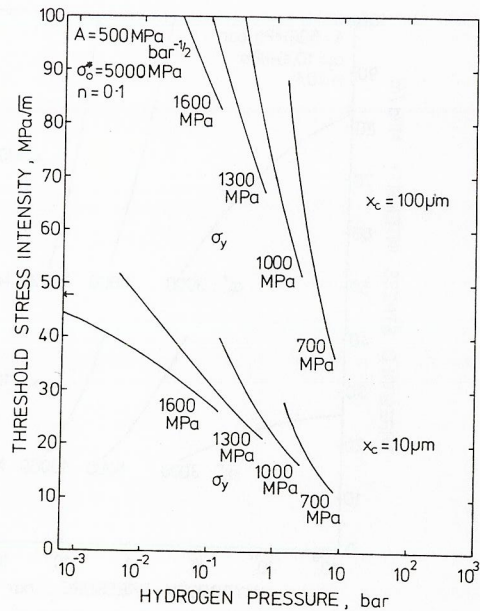


Fig. 4 The influence of yield strength, σ_y , on the dependence of K_{TH} on hydrogen pressure, for two values of critical distance, x_c .

yield strengths (700 MPa - 1600 MPa) was considered which covers most of the steels which exhibit hydrogen-induced slow crack growth, and strain hardening coefficients of 0 and 0.1 were used, the majority of calculations being for $n = 0.1$. The variables x_c , σ_o^* and A refer to the specific mode of hydrogen-induced cracking and no practical technique for measuring these has yet been developed. In the calculations ranges of x_c and σ_o^* were chosen by analogy with brittle modes of unstable fracture (Akhurst, to be published), the σ_o^* values being somewhat higher than measurements of σ^* for cleavage in mild steel and silicon iron (Knott, 1973), as seems fitting for relatively tough high strength alloy steels. It is not clear how appropriate this analogy is. The only variable which was chosen to fit the experimental evidence was the embrittlement constant A , as there was no apparent method to estimate it a priori.

The results of the calculation are shown in Figs. 2-4 for a variety of steels at 25°C. Considering first the influence of the various material variables; K_{TH} at a particular hydrogen pressure is seen to decrease as x_c or σ_o^* are decreased, or n or σ_y are increased. The influence of yield strength is consistent with the experimental evidence, which is well documented. If, as seems reasonable, impurity segregation to prior austenite grain boundaries reduces σ^* for hydrogen-induced intergranular fracture, then the observation of a fall in K_{TH} accompanying this segregation (Jokl and co-workers, 1980) is consistent with the present calculations. However, it should be noted that it is doubtful whether a single material variable can be changed, e.g., by heat treatment, without affecting the other variables to some extent. In particular, the microstructural refinement which often accompanies increases in strength might result in a reduction in the critical distance, x_c .

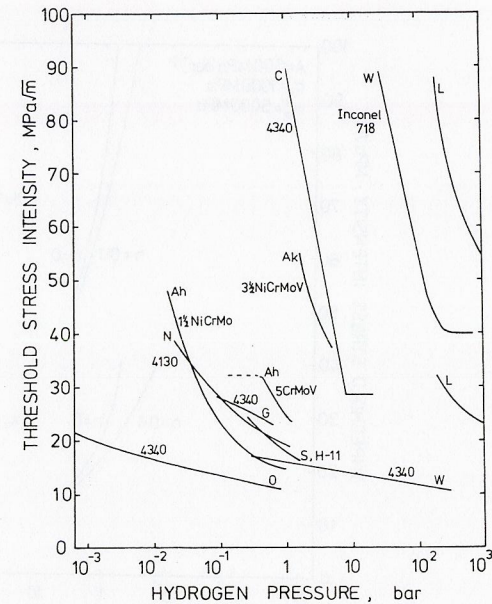


Fig. 5 The experimentally determined dependence of K_{TH} on hydrogen pressure for a variety of steels, and InconelTH 718. Letters by curves correspond to sources listed below: Ah; S. A. Ahmad, D. A. Ryder & T. J. Davies (1975). *Eng. Fract. Mech.*, **7**, 357-365. Ak: K. N. Akhurst, to be published. C: W. G. Clark, Jr. (1975). Westinghouse research laboratories, scientific paper 75-1E7-MSLRA-Pl. G: W. W. Gerberich, J. Garry & J. F. Lessar (1976). In *Effect of Hydrogen on Behavior of Materials*, AIME, New York, pp. 70-82. L: A. W. Loginow & E. H. Phelps (1975). *Trans ASME*, Feb. 1975, 274-282. N: H. G. Nelson and D. P. Williams (1977). In *Stress Corrosion Cracking and Hydrogen Embrittlement of Iron Base Alloys*, NACE, Houston, pp. 390-404. O: R. A. Oriani and P. H. Josephic (1974). *Acta Met.*, **22**, 1065-1074. S: V. R. Sawicki, Jr. (1971) Ph.D. Thesis. Cornell Univ. W: R. J. Walter & W. T. Chandler (1973). NASA Report CR-124410.

The influence of the embrittlement constant, A , on the results is not illustrated in Figs. 2-4. In two steels with different values of A , A_1 and A_2 , and all other material variables the same, equation (6) shows that these will "behave" as if they had the same A but were at hydrogen pressures different by a factor of $(A_2/A_1)^2$. In other words a change in A from A_1 to A_2 has the effect of shifting the $K_{TH}/\log P_{H_2}$ curve along the pressure axis by $2 \log (A_1/A_2)$, without changing the gradients or the range of K_{TH} .

Turning to the influence of the hydrogen pressure itself, Figs. 2 - 4 show that K_{TH} decreases with increasing hydrogen pressure, the gradients of the curves generally decreasing as K_{TH} falls. Steels with higher values of K_{TH} tend to have steeper curves and, except in steels with curves at very low pressures (i.e. with high σ_y and low σ_o^*) steels with similar values of K_{TH} at different pressures have curves with quite

similar gradients. These general trends are not strongly affected by any changes in A , for the reasons discussed above.

Because of the difficulties in measuring x_c , A and σ_0^* , it is not possible to compare one particular calculated curve with its experimental equivalent. However, by studying the results for a variety of steels it is possible to compare the general trends with those expected from the analysis. The results for a number of steels at temperatures close to 25°C are shown in Fig. 5; these compare well with the general trends expected from Figs. 2-4. In fact the actual gradients of the curves in similar ranges of K_{TH} and P_{H_2} agree reasonably well. These similarities are not the result of fitting the calculated curves to the experimental data, and the only fitted variable, A , does not strongly influence similarities observed.

The results presented in Figs. 2-4 are restricted to situations for which the plastic zone size in the crack plane is greater than the critical distance, x_c . This is the region in which the analysis can be applied with most confidence since dislocation motion assists hydrogen diffusion (Tien & co-workers, 1976) and crack nucleation probably requires plastic flow. Limitations of space prevent a full discussion of the behavior expected beyond the ends of the calculated curves (Akhurst, to be published). At low pressures unstable fracture may intervene (e.g. the curve for 5 Cr MoV steel in Fig. 5); at high pressures K_{TH} may eventually become controlled by the plastic strain necessary for microcrack nucleation ahead of the main crack tip. Such a limit is suggested by the behaviour of 4340 steel (curve C) and Inconel 718 shown in Fig. 5. The way in which the results for Inconel 718 fit in with the general trends for steels suggests that hydrogen acts in a fundamentally similar way in this nickel-based alloy.

FURTHER WORK

Rice (1976) has suggested testing notched specimens in equilibrium with hydrogen of known activity. This would enable measurement of σ_0^* as a function of hydrogen activity which allows determination of σ_0^* and A . Using the values of K_{TH} in the same steel, x_c could then be found and the assumptions used in the present analysis verified or refuted. The problem in such tests is to achieve equilibrium concentrations of hydrogen and maintain them as the load is increased. Diffusion distances from the surface are larger in notched specimen than in precracked specimens, and there is less plastic strain to assist diffusion. Surface oxide barriers can further slow diffusion, and methods of avoiding these barriers, such as pre-charging or testing in H_2S , have problems in determining the hydrogen activity. The possibility of testing Pd coated specimens in hydrogen is being investigated at present. A palladium coating should allow more rapid entry of hydrogen into the metal (Kumnick and Johnson, 1975).

CONCLUSIONS

The expected dependence of K_{TH} on hydrogen pressure has been determined assuming (i) that equilibrium arguments can be used in the interpretation of K_{TH} , (ii) that the critical fracture stress is reduced by an amount proportional to the hydrogen concentration, and (iii) that this stress must be exceeded for a critical distance ahead of the crack tip for fracture to occur. The results of the calculations compare well with the experimental evidence.

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REFERENCES

Gerberich, W. W. (1974). Effect of hydrogen on high-strength and martensitic steels. In I. M. Bernstein & A. W. Thompson (Eds.) *Hydrogen in Metals*, ASM, Metals Park, Ohio. pp 115-147.

- Jokl, M. L., Jun Kameda, C. J. McMahon, Jr. and V. Vitek (1980). Solute segregation and intergranular brittle fracture in steels. *Metal Science*. In press.
- Kameda, Jun and C. J. McMahon, Jr. (1980). Solute segregation and brittle fracture in an alloy steel. *Met. Trans.*, **11A**, 91-101.
- Knott, J. F. (1973). *Fundamentals of Fracture Mechanics*. Butterworths, London.
- Kumnick, A. J. and H. H. Johnson (1975). Steady state hydrogen transport through zone refined irons. *Met. Trans.*, **6A**, 1087-1091.
- van Leeuwen, H. P. (1975). Embrittlement by internal and external hydrogen. *Corrosion-NACE*, **31**, 154-159.
- McMeeking, R. M. (1977). Finite deformation analysis of crack tip opening in elastic-plastic materials and implications for fracture. *J. Mech. Phys. Sol.*, **25**, 357-381.
- Oriani, R. A. (1969). Hydrogen in metals. In R. W. Staehle, A. J. Forty and D. Van Rooyen (Eds.), *Fundamental Aspects of Stress Corrosion Cracking*, NACE, Houston. pp 32-50.
- Oriani, R. A. (1972). A mechanistic theory of hydrogen embrittlement of steels. *Ber. Buns.-Gesell. fur Phys. Chem.*, **76**, 848-857.
- Rice, J. R. (1976). Note: some mechanics research topics related to the hydrogen embrittlement of metals. *Corrosion-NACE*, **32**, 22-25.
- Rice, J. R. and M. A. Johnson (1970). The role of large crack tip geometry changes in plane strain fracture. In M. F. Kanninen et al. (Eds.), *Inelastic Behavior of Solids*, McGraw Hill, New York. pp 641-672.
- Ritchie, R. O., L. C. E. Geniets and J. F. Knott (1973). Effects of grain-boundary embrittlement on fracture and fatigue crack propagation in a low alloy steel. In *The Microstructure and Design of Alloys*, Inst. of Metals and ISI, London. pp 124-128.
- Ritchie, R. O., J. F. Knott and J. R. Rice (1973). On the relationship between critical tensile stress and fracture toughness in mild steel. *J. Mech. Phys. Sol.*, **21**, 395-410.
- Tetelman, A. S. (1974). Recent developments in classical (internal) hydrogen embrittlement. In I. M. Bernstein and A. W. Thompson (Eds.), *Hydrogen in Metals*, ASM, Metals Park, Ohio. pp 17-33.
- Tien, J. K., A. W. Thompson, I. M. Bernstein and R. J. Richards (1976). Hydrogen transport by dislocations. *Met. Trans.*, **7A**, 821-829.
- Troiano, A. R. (1960). The role of hydrogen and other interstitials in the mechanical behavior of metals. *Trans. ASM*, **52**, 54-80.