CHALLENGES IN CHARACTERIZING THE CRACK-TIP ENVIRONMENT AS A BASIS FOR PREDICTION OF CRACK GROWTH KINETICS

Alan Turnbull

National Physical Laboratory, Teddington, Middlesex, TW11 0LW, UK.

ABSTRACT

The challenges in improved mechanistically-based prediction of crack growth kinetics due to hydrogen embrittlement are discussed in relation to the local crack-tip environment, which, in context, embraces crack-tip chemistry and the hydrogen distribution ahead of the tip. Important advances have been made in modelling crack-tip electrochemistry and considerable insight obtained but the need for an electrochemical database of input parameters is paramount to ensure confidence in prediction. In modelling the crack-tip hydrogen distribution the use of generalised boundary conditions which link electrochemical processes and hydrogen atom transport in the crack-tip region has been an important advance but must be coupled to more realistic crack-tip stress and strain models. A validated model of this form linked with criteria for crack advance incorporating material property and microstructural parameters is a necessary precursor to meaningful quantitative crack growth prediction.

KEYWORDS

Environment assisted cracking, crack-tip environment, hydrogen embrittlement, modelling.

INTRODUCTION

Stress corrosion cracking and corrosion fatigue (collectively environment assisted cracking, EAC) pose major challenges in prediction because the interaction of the environmental, mechanical and material variables responsible for cracking occurs at a highly localised level. Cracks tend to initiate at microstructural and microchemical inhomogeneities, at stress concentrators, and at sites of local solution chemistry change. The latter is reflected for example in the importance of pitting, crevice attack, or intergranular corrosion as precursors to EAC for corrosion resistant alloys. Once a crack has initiated, the growth rate is determined or influenced strongly by the crack-tip environment and electrochemical kinetics. This applies also to hydrogen embrittlement, but here the concept of the crack-tip environment must be expanded to include the distribution of hydrogen atoms in the crack-tip process zone.

There is no mechanistic model for crack growth in aqueous solutions which properly accounts for the range of service variables and their time variation in a coherent manner although the simplest models based on slip-dissolution have had some limited engineering application, albeit with partial fitting [1,2]. Predicting threshold and crack growth kinetics for hydrogen embrittlement in an engineering context is a particularly formidable challenge [3]. In most service applications, transient variations in stress, temperature or environment chemistry will occur as part of normal operational service or be induced by scheduled excursions (e.g. shutdown) or unintentional fluctuation in system control (e.g. contamination); the character of the metal surface may change with time of operation (e.g. precipitation of a scale or deposit) and welding quality may be variable. These pose a challenge to service prediction and would require extensive input data gathering representative of the change of conditions. It is perhaps best not to envisage mechanistic model development being undertaken for direct engineering prediction. Engineers will base predictions mainly on laboratory testing and field experience/measurement. Nevertheless, the value of modelling will be in sensibly interpreting short term data, in ensuring that testing is conducted with an informed awareness of the impact of operational variables and in providing some framework for prediction when test data are limited. To instil confidence in the industry, modelling has to improve and rigorous validation must be undertaken.

The component features of hydrogen embrittlement models are clear: crack-tip electrochemical kinetics, hydrogen transport in the stress/strain field at the crack tip, the interfacing between electrochemistry and transport, and a crack advance or failure criterion. These are interdependent to a large extent and a crack growth model must embrace all aspects in an integral fashion. A brief summary of the present position and the challenges in raising such models to the next level of sophistication is now described.

CRACK-TIP ELECTROCHEMISTRY

Characteristics

Conceptually, the crack electrochemistry system is now well understood and the principle processes are illustrated schematically for a Mode I crack in Figure 1. For completeness, the dissolution of alloying elements and the solubility limit for dissolved metal cations would also be included. Depletion of reactive species such as oxygen confines reduction of this species mainly to the external surface. Under open circuit conditions, the net anodic current emerging from the crack causes a depression in the corrosion potential in order to provide the balancing net cathodic current on the external surface. The key requirement for EAC prediction is to quantify the transient electrode kinetics for the partial anodic dissolution and cathodic hydrogen generation reactions at the crack tip. These cannot be determined directly but the functional dependency of the parameters, viz. maximum current density on bare surface and the refilming kinetics, can be determined from electrochemical experiments in simulated crack-tip environments and the values then used as input to the crack electrochemistry model.

Present position in prediction

Over the last two decades, the capability of modelling the various reaction processes in a crack together with mass transport by diffusion, ion migration and in the case of corrosion fatigue, fluid flow, has been established [4]. Models of crack chemistry of varying level of complexity exist for systems such as low alloy carbon steels in seawater, nickel-base alloys and stainless steels in nuclear environments, nickel in H_2SO_4. In relation to hydrogen embrittlement the advances made have led to clarification of several issues.

What we have learned

Relevance of bulk environment

- The bulk environment composition, including the species indicated in Figure 1 (O_2, H_2S, H^+ etc) will have an effect on the corrosion potential which can influence crack chemistry and potential for that reason, but, depending on crack size may not have a direct effect on crack chemistry because reactive species are consumed before they enter far into the crack.
- In very low conductivity chloride solutions, the potential drop in the bulk solution is often significantly greater than in the crack itself since dissolved metal ions increase the crack solution conductivity. A crack size effect on crack-tip conditions is predicted for low conductivity solutions but associated with the impact of crack depth on net current flow from the crack and the potential drop induced in the bulk solution [5].

Crack size effects

- In corrosion fatigue of low alloy high strength steels in seawater, acidic pH values of 4 can be achieved in short cracks compared to near neutral values for long cracks [4]; enhanced crack growth of the short crack would then be predicted and has been reported [6].
- Depletion of reactive species from the bulk solution such as H_2S will be greatest for deep cracks. For corrosion resistant alloys in the passive state, this may lead to a decrease of crack growth with increase in crack size, although testing remains to be done. For steels in the active state, this may result in bulk charging becoming the dominant source of hydrogen atoms for deep cracks [3].

Localised charging vs bulk charging

- As noted above, for alloys in the active state, bulk charging can become the predominant source of hydrogen atoms controlling crack growth when reactive species such as H_2S or H^+ in acid solutions are present in the bulk at significant concentrations but consumed readily in the crack and do not reach the crack tip. Bulk charging will also tend to be important under cathodic polarisation conditions because the potential drop and high pH in the crack limit hydrogen atom generation at the crack tip [4].
- For corrosion resistant alloys in the passive state, the oxide film is a major barrier to hydrogen entry at ambient temperatures. For that reason, hydrogen entry will be favoured where localised straining ruptures the film or where localised corrosion creates a local acidic metal chloride solution and correspondingly dissolves the film barrier. In the latter case, cracking may not ensue unless the critical pitting or critical crevice temperature is exceeded; simpler tests can then be used as a preliminary indication of cracking likelihood.

Fluid flow induced by cyclic loading

Fluid mixing induced by cyclic loading will result in dilution of the crack solution and generally permit more influence of bulk solution reactants. Even at a low frequency of 0.1Hz, fluid flow can result in a decrease in crack-tip metal ion concentration by more than two orders of magnitude [4]. Because of the lower conductivity, anodic polarisation will tend to be more difficult in a corrosion fatigue crack compared to a stress corrosion crack (assuming no major change in fracture mechanism which affects crack opening). In seawater, cathodic polarisation will be more difficult as buffering species are pulled into the crack by the fluid mixing and reduce the beneficial effect of high pH on the ease of polarisation.

Advances required

The limitation in modelling the crack-tip environment and predicting crack-tip kinetics for many systems is primarily the limited availability and quality of input parameters, including the transient electrode kinetics on initially bared surfaces which must be derived from separate electrochemical experiments using fast fracture or guillotine techniques. The establishment of an electrochemical database is essential and validation of model predictions by crack-tip chemistry and potential measurements is important. However, in some systems the crack-tip reactions may not have a significant effect on the local potential and chemistry and demonstration that the predicted crack tip reaction kinetics are valid may not be possible.

More attention to the crack-tip shape and opening for moving cracks and for intergranular cracks would add refinement. Concentrated solutions still pose some uncertainty in modelling; nevertheless, progress in being made. Modelling is still accessible to only a comparative few because of the complexity of development. A future can be envisaged where such models are accessed through the internet and run remotely with an individual’s own dataset. Such schemes are already in place for other material performance models.

HYDROGEN TRANSPORT AND TRAPPING AT A CRACK TIP

Characteristics

The kinetics of hydrogen generation and entry will be varying around the crack tip from the highly reactive tip area to the crack walls and will be undergoing a complex time variation in response to film rupture and repair.

The hydrogen atoms generated will be absorbed and transported into the metal by lattice diffusion, grain boundary diffusion and by dislocation transport. Although there is some indication of enhanced grain boundary diffusion in pure nickel, for most commercial alloys the presence of impurities and precipitates at the grain boundary will provide local traps and hinder grain boundary diffusion. Dislocation transport of hydrogen certainly occurs but the relative significance is more hotly debated. However, the effectiveness of this process is inevitably constrained by microstructural barriers limiting the mean free path. Long range transport is not readily feasible but short range redistribution of hydrogen with possible dumping of hydrogen from dislocations to grain boundaries or to interfaces is likely. The hydrostatic stress field at the crack tip will create a gradient in chemical potential which will provide a driving force for localisation of hydrogen in the lattice. Trapping at microstructural trap sites will influence the diffusion rate through the matrix and may play a critical role in the fracture process. In addition, differential strain in the crack-tip region will create variations in dislocation trap density, and the varying plastic strain rate in the process zone will determine dislocation trap generation kinetics and dislocation transport kinetics.

In some systems, hydrogen atoms absorbed from the external surface will be diffusing to the crack-tip region. If that were not complicated enough, the crack advance process will result in a redistribution of crack-tip conditions. Cyclic loading will cause dynamic fluctuations in local entry kinetics, through the effect on crack-tip reduction kinetics and film rupture rate, and will affect the local concentration through the cyclic variation in hydrostatic stress.

Present position in prediction

Modelling of the time variation of the hydrogen distribution at a crack tip is a formidable problem but major advances have been achieved through the work of Sofronis and McMeeking [7,8], Turnbull et al [9], and Krom et al [10]. The modelling of Sofronis and McMeeking and of Krom et al represented a important step forward insofar as the models were two-dimensional, included elastic-plastic analysis combined with diffusion and trapping and accounted for trap generation associated with crack-tip straining. Simplified boundary conditions were used with no specific account of the distribution of the electrochemical kinetics between the tip and walls. Trapping of hydrogen was dealt with only in relation to low occupancy conditions. Also using a two-dimensional model, more appropriate boundary conditions were established by Turnbull et al which for the first time united the transport and electrochemical processes explicitly by including the reaction processes on the crack tip and walls in a generalised flux expression with no *a priori* assumption about surface or diffusion control of entry and transport. Reversible traps of varying occupancy and irreversible trapping were included. The other virtue of the model of Turnbull et al was the exploration of the imbalance between crack-tip charging rates and bulk charging rates. However, although a two-dimensional approach was used, an important limitation was the simplified Prandtl stress field used. The assumed crack-tip mechanics model has a critical impact on predictions and contrasting approaches such as that of Lii et al [11] based on a discretised dislocation model indicate the potential for very much larger hydrostatic stresses, at least in the single crystal system studied

What we have learned

Hydrogen localisation

Hydrogen atoms in the lattice are localised due to hydrostatic stress but the magnitude of the effect is modest for a blunting crack. However, since the crack-tip opening displacement for propagating cracks and for intergranular cracks tends to be smaller than predicted by the blunting model, the latter will tend to underestimate the crack-tip stresses and localised lattice hydrogen content. Nevertheless, the trapped hydrogen content ahead of the crack tip will be large. The trap binding energy will always lead to a local concentration significantly in excess of the lattice value, up to trap saturation level. Also, for hydrogen trapped at dislocations, the highly deformed nature of the crack-tip region means high trap densities.

Strain rate effects

A key conclusion from the work of Krom et al [10] and of Sofronis et al [8] was the demonstration that straining the material will cause depletion of lattice hydrogen because diffusion of hydrogen from the source at the tip is not fast enough to replenish hydrogen atoms lost to the newly created traps. This dilution of hydrogen atom concentration would lead to the expectation of a reduced crack growth, which would be accentuated by increased strain rates. Krom et al give emphasis to the reduced lattice hydrogen concentration and models based on such in predicting the influence on cracking but inevitably the local trapped hydrogen concentration would be reduced also and a trapping-based model could not be excluded. Also, dislocation transport would provide an explanation for the strain rate behaviour but its inclusion in continuum models is difficult because it is inherently an inhomogeneous process. Correspondingly, there will always be uncertainty in the local distribution of hydrogen atoms at the microstructural level.

Surface reaction vs diffusion control

In alloys of low lattice diffusivity for hydrogen atoms, e.g. nickel-based alloys, entry and transport is inevitably diffusion control because the diffusion flux of hydrogen will be small compared to the charging and recombination fluxes at the crack tip. For iron-based ferritic alloys for which the lattice diffusivity is high, it is less apparent and conceptually, it would be expected to depend more critically on the concentration gradient. The particular advance of the model of Turnbull et al [9] was to show that the concentration gradient was high (and hence the flux high) because of the significant gradients in hydrogen induced by the marked difference in hydrogen generation kinetics between the crack tip and adjacent crack walls. Thus, the prediction was that crack growth would be surface reaction controlled, although a cautionary comment is required because of the simplified stress-strain model adopted. Since many of the models developed for crack growth kinetics are based on low alloy steel and often invoke diffusion control using a one-dimensional model this was an important step forward.

Bulk charging

The generalised boundary conditions adopted by Turnbull et al, which incorporated desorption fluxes as well as absorption fluxes, allowed exploration of the effect of pre-charging. In this case, significant *loss* of hydrogen atoms via the crack tip and walls can occur if the charging conditions at the tip are less significant than that associated with the precharging and especially so when testing in air. The latter deduction raises uncertainty in the interpretation of crack growth kinetics on cadmium-coated specimens once cracking has commenced and the coating barrier film locally damaged. Bulk charging is an important issue. Long term (150 days) pre-exposure of an AISI 4340 steel cathodically protected in seawater indicated corrosion fatigue crack growth rates much faster than obtained from conventional test (20 days) [3].

Advances required

There has to be integration of the best features of the models of Turnbull et al and those of Sofronis et al and of Krom et al but with crack-tip mechanics models more appropriate to growing stress corrosion and hydrogen embrittlement cracks. Multi-disciplinary interaction is required. A further step is to deal with the transient electrochemical parameters associated with a refilming material (rather than average crack-tip values). This is not so difficult to incorporate into a model but obtaining experimental data on the effect of refilming on the absorption and desorption input parameters, which determine C_0, presents a major challenge. In principle, it should not prove overly difficult to model some features of the effect of cyclic loading on hydrogen atom distribution provided we can define the impact on the stress and strain distribution on individual cycles and the cumulative impact. However, this would be on the basis of a non-propagating crack.. The biggest challenge is to account for the crack growth process itself, assuming that a criteria for the onset of cracking and for crack arrest (if crack growth is not a continuous process) has been established. With crack extension, new surface is created generating more hydrogen. The crack will have to be treated as a moving boundary and the evolution of the hydrogen distribution progressively recalculated. All of these steps are foreseeable with focused resource. Perhaps the greatest fundamental difficulty will be the incorporation of inhomogenous localised dislocation transport of hydrogen into the model.

These represent some of the challenges in improved modelling. Experimental validation is critical in models of such complexity and with so many variables. Direct measurement of crack-tip hydrogen concentration, lattice and trapped hydrogen, very close to the crack tip would be a fundamental test but presents major technical difficulties. Within the bounds of current test methods it is not easy to envisage how this might be achieved at the spatial resolution required.

CONCLUDING REMARKS

The potential exists for significant progress in modelling crack-tip electrochemistry and hydrogen transport in an integrated manner but as the complexity increases and the input database enlarges it becomes more important to seek direct experimental methods of validation such as crack chemistry or crack-tip hydrogen atom concentration measurement. Clearly, an integrated hydrogen generation and transport model will be a necessary input to models of cracking (although such modelling will inevitably be numerically based) but we have to build a more effective description of the failure process and its relationship to material properties and microstructural parameters.

REFERENCES

1. F. P. Ford and P.L. Andresen (1988). In: *Environmental Degradation of Materials in Nuclear Power Systems*, p 789, J.L. Theus, J.R. Weeks (Eds), The Metallurgical Society, Warrendale, PA.
2. Engelhardt, G.R., Macdonald D.D., and Urquidi-Macdonald, M. (1999), *Corros. Sci*., 41, 2267.
3. Turnbull, A. (2001), In: *Ageing Studies and Lifetime Extension of Materials*, L.G. Mallinson (Ed.), p. 397, KA/PP, New York, NY.
4. Turnbull, A. (2001) *Corrosion*, 57, 175.
5. Turnbull, A.(2001), In: *Corrosion 2001*, Paper no. 01237, NACE, Houston, Tx.
6. Gangloff, R.P (1985). *Metall. Trans. A ,* 16A, 953.
7. Sofronis, P. and McMeeking, R.M (1989). *J. Mechanics and Physics of Solids*, 37, 317.
8. Sofronis, P, and Taha, A. (2000). In: *Environmentally Assisted Cracking: Predictive Methods for Risk Assessment and Evaluation of Materials, Equipment and Structures*, p. 70, R.D. Kane (Ed.), ASTM 1401, West Conshohocken, PA.
9. Turnbull, A., Ferriss, D and Anzai., H. (1996). *Mater.Sci. Eng.,* A206, 1.
10. Krom, A.H.M., Koers. R.W.J. and Bakker, A.(1999). *J. Mechanics and Physics of Solids*, 47, 971.
11. Lii, M., Foecke, T., Chen. X., Zieliski W. and Gerberich, W.W., (1989) *Mater. Sci. Eng.*, A113, 327.

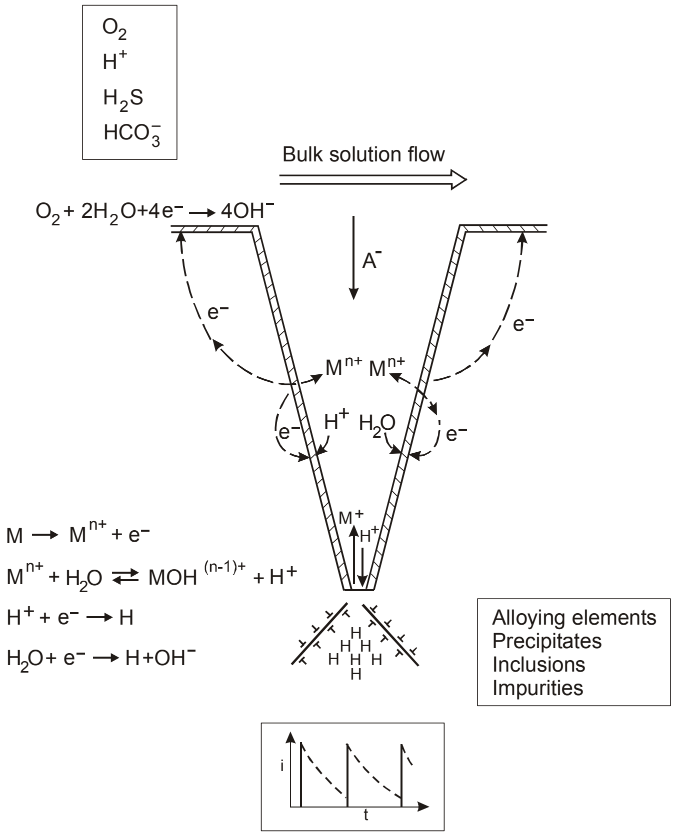

Figure 1: Schematic illustration of crack electrochemistry system indicating reactions in crack, transient current densities associated with film rupture at the tip, the possible impact of local material composition in determining kinetics (and fracture path) and accumulation of hydrogen ahead of the crack tip.