CURRENT ISSUES IN HYDROGEN EMBRITTLEMENT

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An overview is given of current issues in evaluating the likelihood of hydrogen embrittlement. Further confirmation of the validity of the recently standardised electrochemical method for hydrogen permeation measurement is illustrated by good agreement in hydrogen content estimated by the permeation technique and by the total hydrogen extraction method. However, use of hydrogen probes for quantitative assessment of hydrogen content in ***service*** is more questionable. The primary development in mechanical testing is the resurgence in use of dynamic straining tests. A major European interlaboratory study has shown that K_{ISCC} may be lowered by dynamic straining and test times reduced relative to static load tests. The application of ripple loading is expected to gain extended use as a method of determining K_{ISCC} and σ_{SCC}.

INTRODUCTION

Hydrogen atoms are generated by corrosion, by galvanic interaction between dissimilar metals, by cathodic protection and by welding. Cracking occurs when critical combinations of local hydrogen content, stress, strain, and microstructural sensitivity are achieved. Hydrogen embrittlement has been a major source of failure of engineering structures and components in most industrial sectors including oil and gas, petrochemical, aerospace, marine and construction. The extent of these problems presents challenges to the materials and engineering community in predicting when hydrogen cracking is likely to occur and in avoiding its occurrence. Two key elements in that prediction process which have stirred most controversy are how best to evaluate and monitor hydrogen uptake and which test/test method best reflects likely behaviour in service.

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MEASUREMENT AND MODELLING OF HYDROGEN UPTAKE AND FLUX

Measurement of hydrogen uptake

Techniques for measuring hydrogen uptake and characterising its distribution in metals include hydrogen permeation, total hydrogen extraction, and thermal desorption methods. Measurement of hydrogen permeation by the electrochemical method is the most common approach to quantifying hydrogen concentrations and diffusivity in laboratory testing but the results have been variable in many cases and the validity of the results often not demonstrated. Issues affecting measurements were articulated by Turnbull (1) and this article provided the basis for the development of the recent BSI standard (BS 7886, 1997). Validation of the results is achieved by repeating the measurement with samples of different thickness and demonstrating consistency when the data are normalised with respect to thickness. Nevertheless, partly due to the inconsistent measurement derived from poorly conducted testing, the technique has not always generated confidence in comparison to the method of total hydrogen extraction, particularly for corrosion resistant alloys. To resolve this concern, a comparison of hydrogen permeation and total extraction methods for determining hydrogen content has been undertaken recently using 22Cr duplex stainless steel (DSS). The comparison is not trivial since steady-state conditions are not achieved in the rod specimens used for total hydrogen extraction. Nevertheless, using existing knowledge of the diffusivity of hydrogen in this alloy, the sub-surface hydrogen atom concentration can be calculated from the total hydrogen extraction data. The results for the two techniques are compared in Fig. 1. Good agreement is apparent, confirming the applicability of the hydrogen permeation method.

The hydrogen permeation technique can be used also to characterise parameters for hydrogen trapping. The same claim has been made for the use of the thermal desorption technique (2) in which the time evolution of the hydrogen evolved from a sample subjected to a temperature ramp is measured. The real concern here has been the simplistic basis of the analytical framework used, in most cases, to extract information about trapping. Recent numerical modelling (3) based on more rigorous principles has shown that such simple models have very limited validity and has thrown into question much of existing analysis.

Field monitoring of hydrogen flux

Monitoring of the hydrogen flux in service applications has been ongoing for many years but there has been a proliferation of devices of late and much controversy with respect to the efficacy and limitations of these methods. The hydrogen probe is clamped onto the vessel or pipeline and the flux of hydrogen monitored either as an electrochemical current as with the permeation technique or with respect to the change in pressure.

Quantitative estimation of the sub-surface hydrogen concentration from the measured flux can be uncertain and dependent on the device used. A fundamental concern is the extent to which attachment of the device alters the pre-existing flux of hydrogen. Generally, the external surface of the steel pipe or vessel will have rust products. Hydrogen egress is then dependent on the efficiency of hydrogen transport through this surface and the rate of recombination of hydrogen atoms to form and evolve molecular hydrogen. This process can be sufficiently slow that concentration profiles in the material may be small. If the surface is cleaned and a probe attached, the flux will increase due to the cleaner surface and also in response to lateral transport to the probe region. In addition, when using electrochemical probes, with the steel surface as the anode, the application of an oxidation potential will force the hydrogen concentration to zero, which will not reflect actual behaviour. For those probes which use a palladium interface, hydrogen atoms recombine at the steel metal surface and then dissociate on the palladium surface before diffusing through the palladium membrane and being detected. It is possible for the molecular hydrogen to be lost laterally between the palladium and the steel and for the medium interfacing the palladium and steel to affect recombination, rendering the results uncertain.

As a tool for indicating that the hydrogen flux has changed significantly, eg due to depletion of inhibitor or excursion in chemistry, hydrogen probes can be effective. However, they should not be relied upon for accurate estimation of hydrogen uptake.

TEST METHODS FOR HYDROGEN EMBRITTLEMENT

The main concern with respect to laboratory testing is to predict the likelihood of failure in service on the basis of accelerated or short term testing. The timescale o hydrogen uptake, the importance of dynamic straining and the significance o notches or crack-like defects provide the major uncertainties.

Time-dependence of hydrogen uptake

A fundamental question is how long should a laboratory test be to ensure that hydrogen uptake is sufficient in reflecting behaviour in service, for which exposure times are of the order of years.

For alloys in the *active* state, with no protective passive film, hydrogen entry is not limited to local sites but can occur over the whole surface, particularly under cathodic protection conditions. Consequently, when utilising fracture mechanics specimens, for example, laboratory exposure times should be sufficient to allow transfer of hydrogen along the crack front. For low alloy high strength steels, the latter can be up to a year depending on the specimen thickness (4). The importance of long term exposure is highlighted by the results of Fig. 2 which shows the corrosion fatigue crack growth rates for AISI 4340 steel exposed for different periods in simulated marine environments at a loading frequency of 0.167Hz and stress ratio 0.25 (4). Clearly, short term tests, as conventionally conducted would be inadequate.

The effect of pre-exposure on environment assisted cracking of *corrosion resistant alloys* is a matter of some uncertainty and of controversy. Diffusion coefficients are particularly low for most austenitic and ferritic-austenitic alloys and the time to charge up a specimen to steady state is very long, except at high temperatures. However, in corrosion resistant alloys, cracking is not necessarily dependent on general hydrogen charging unless crack initiation is at internal microstructural sites or defects. The presence of an oxide film has a major retardation effect on hydrogen entry at ambient temperatures. If the oxide can be broken, hydrogen uptake will be relatively large locally. Consequently, hydrogen cracking is most likely when localised corrosion in pits or crevices causes dissolution of the film or when the film is mechanically ruptured due to mechanical straining. For corrosion resistant alloys at their free corrosion potentials, cracking may not ensue unless a pit develops. Correspondingly, the critical temperature for cracking would be expected to exceed that for localised attack. The importance of pitting is illustrated for duplex stainless steel in simulated downhole environments (Fig. 3). At low levels of H_2S, no pitting was observed under open circuit conditions (charging current of about 2 μAcm^{-2}) at the strain rate of 10^{-6} s^{-1} and the normalised plastic strain to fracture was not less than one. However, when the solution was H_2S saturated, pitting and cracking ensued.

Clarification of the relative role of "bulk" charging of hydrogen and localised hydrogen uptake can be obtained by comparing hydrogen uptake measurements from permeation measurements with cracking behaviour. Hydrogen uptake data for a duplex stainless steel at 80°C in a range of environments under cathodic polarisation conditions (5) are shown in Fig. 1. It is evident that there is no effect of H_2S on hydrogen entry until quite high charging currents. At charging currents less than 100 μAcm^{-2}, the cracking susceptibility should be unaffected by the presence of H_2S if determined only by bulk charging through the passive oxide film. In practice, cracking susceptibility is greater in the H_2S environment (Fig. 3). This result demonstrates that hydrogen uptake is occurring locally, enhanced perhaps by the effect of H_2S in retarding refilming rates on freshly produced surface.

Dynamic straining

The importance of dynamic straining for hydrogen embrittlement is not a new concept but has received recent impetus in the desire to ensure that laboratory tests can adequately account for failures in service for which dynamic straining has been implicated. The slow strain rate test is commonly used as a useful sorting test but is considered too severe as a design basis. However, there is current interest in methods of measuring threshold stress under dynamic straining conditions using pre-cracked, notched or plain specimens.

The impact of the load-line displacement rate on the threshold stress intensity factor for cracking (K_{ISCC}) of AISI 4340 steel corroding in seawater at 20°C (Fig. 4) illustrates the significance of dynamic straining. This study was undertaken as part of a European round-robin on accelerated test methods for determining

K_{ISCC}. The time for testing can be reduced significantly relative to the 3000 hour test recommended under static load conditions but the important feature is that the value of K_{ISCC} can be reduced also relative to the static load test. In using this dynamic straining technique, caution should be exercised with respect to the extent of hydrogen uptake during the test period. For the tests of Fig 4, the steel was at open circuit for which the most significant hydrogen entry is via the straining crack tip. Under cathodic protection conditions, pre-exposure may be required to achieve the required level of hydrogen uptake.

The use of ripple loading in determining the likelihood of cracking is gaining further attention. Perceived as providing a more severe ranking test than constant load testing (6), but with more modest plastic straining compared to the slow strain rate technique, it may also provide a basis for evaluating threshold stress for both plain and pre-cracked specimens. The primary virtue for many applications is the continuation of dynamic straining without increasing significantly the mean stress level. Only a limited number of cycles can be applied as material modification means that the extent of plastic straining will eventually diminish to zero. Used as a sorting technique, the stress range has been typically 80%-100% of $\sigma_{0.2}$ (6). However, at NPL the impact of smaller amplitude ripple loading in determining the threshold stress/strain is being evaluated. Preliminary results indicate that such ripple loading can reduce the threshold stress/strain.

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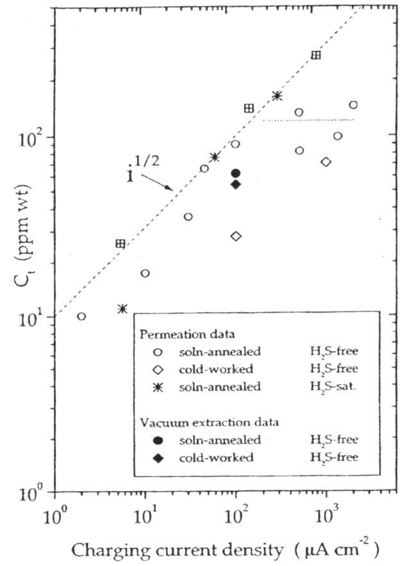

Figure 1 Hydrogen uptake of DSS in acid brine at 80 °C.

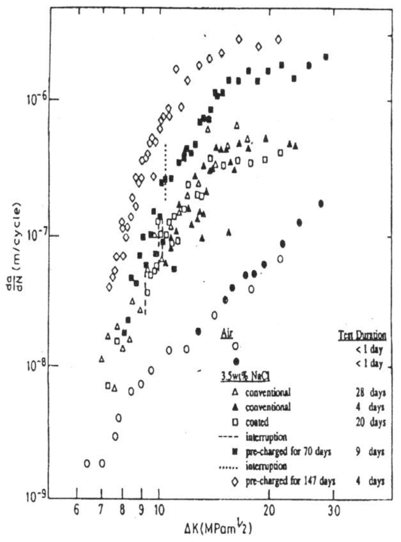

Figure 2 Corrosion fatigue of 4340 steel in 3.5 wt% NaCl; E = -1100 mv (SCE)

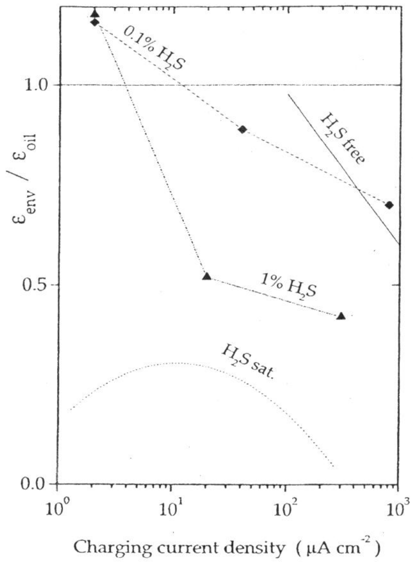

Figure 3 Impact of H_2S on cracking of DSS in acid brine at 80°C.

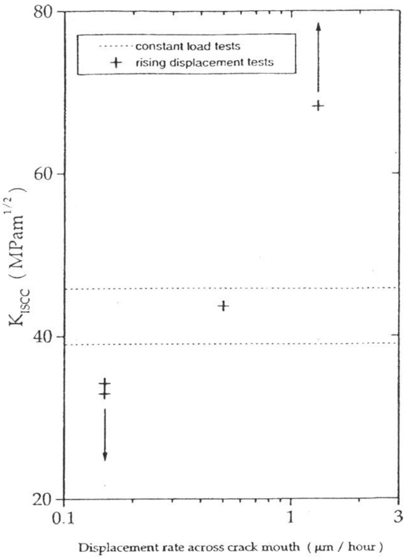

Figure 4 K_{ISCC} vs load-line displacement rate for 4340 steel in sea water.