Notch Effects in Corrosive Failure

I. CHATTORAJ
National Metallurgical Laboratory, Jamshedpur- 831 007

ABSTRACT

Notches act as stress raisers in any application. There are a few other detrimental effects of notches when an environment is involved. For a simple corrosive environment, the notch chemistry and electrochemistry are significantly different from that of the bulk environs. When hydrogen embrittlement is a possible failure mode, the presence of notch has an added significance, in defining the hydrogen transport and distribution. This article discusses the notch effects in general as it pertains to corrosive failure and hydrogen embrittlement in specific. The comparative studies on different notch geometries reveal the importance of notch dimensions in the defining the extent and morphology of cracking in the presence of hydrogen. A rationalization has been attempted involving notch hydrogen availability.

INTRODUCTION

The insidious effects of notches as stress raisers are well known. As regards fracture and fracture mode, the presence of a notch is even more significant for defining the stress triaxiality conditions and thereby determining the mode of fracture [1]. These notch effects are worth studying because inadvertently or intentionally notches are present in components. It should be mentioned here that for our purpose, a notch is any local concavity originating at the component surface and protruding into the component body. Notches are hard to account for as they represent a divergence from uniform stress conditions which may be present elsewhere. Analytical solutions for stress distributions in the notch plane and in components containing notches is difficult and Finite Element Modeling (FEM) has to be resorted to.

In an aggressive environment, in addition to being stress raisers, notches are electrochemical and chemical singularities in that they represent zones where the reactions are quite different either in nature or in rate or in both, as compared to the bulk reactions of the component in the particular environment. A notch may be considered to be a crevice for electrochemical purposes, so that the mechanisms of crevice corrosion have to be considered for a component, which may be anodically polarized by intent or accidentally. With regards to the solution chemistry, notches, like crevices, cause solution stagnation and consequent change in local pH. In situations where one of the possible degradation modes is hydrogen embrittlement (HE), it is easy to perceive the significance of notches. HE is a typical illustration of stress-environment synergism, and notches accentuate both. In notches (as in crevices), solution pH tends to decrease causing increased availability of H⁺ ions. Stress
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Triaxiality conditions at notches are such as to normally favor cracking and the hydrostatic stress distribution ahead of the notch enhance hydrogen entry into the component. Thus on all counts notches accelerate HE.

This article will deal with the two prominent effects of notches in aggressive environments, namely, the stress effects and the electrochemical effects and the synergism between the two effects. The specific role of notches in promoting and affecting hydrogen embrittlement will be expounded with reference to different notch geometry.

**General Notch Effects**

**Stress effects of notches**

The distribution of stresses ahead of a notch is a function of the notch geometry. The two important parameters which are definitive of the stress state are the stress intensity factor (denoted as $K_I$ for “mode I”, that is pure tensile loading) and the triaxiality. The first is loosely a measure of the amount of stress enhancement due to the operation of triaxial stress state even when an uniaxial load is applied, due to the presence of the notch or crack. The triaxiality is formally measured as a ratio of the hydrostatic stress to the deviatoric stress. The stress intensity factor is analytically measured for regular notch shapes and different investigators propose different approaches to calculate this value. It is an important fracture mechanics parameter and critical values of $K_I$, also denoted as $K_{IC}$, are characteristic material parameters in component failure by fatigue and stress corrosion fatigue. It is also necessary to talk of notches and cracks emanating from them, in juxtaposition, and not consider notches in isolation since the stress intensification due to the (much smaller tip radii) cracks are higher than that of blunter notches. The stress intensification of notches alone reduces to the case of zero crack length in such situations. The mode I stress intensity factor may be determined from a host of analytical expressions depending on the notch shape and dimensions, for instance for a cylindrical member of gauge diameter ($D$) = 8cm with a circumferential notch (see Fig. 1), the following expression was developed by Tada et al.[2]:

$$K_I = \frac{P}{\pi b^2} \sqrt{\pi b} F_1 \left( \frac{b}{R} \right)$$

where $F_1 \left( \frac{b}{R} \right) = F_1(\beta) = \frac{1}{2} \left[ 1 + \frac{1}{2} \beta + \frac{3}{8} \beta^2 - 0.363 \beta^3 + 0.731 \beta^4 \right] \sqrt{1 - \beta}$ ...(1)

where, $\beta = b/R$, $b =$ uncracked ligament radius, $R =$ the gauge radius, and $P =$ load, kN.

The stress intensity factor is shown as a function of a progressing crack for a shallow and a deep notched cylindrical member, in Fig. 1. This illustrates the dynamic nature of stress intensification during the life of a component (or of a sample in a monotonic loading situation). It also shows the importance of notch geometry: the notch depth difference causes significant difference in the $K_I$ for any given load level.
While $K_1$ is strictly representative of the notch root or the crack root, the stress distribution throughout the component cross section is altered by the presence of a notch. The stress distribution for the three principal stresses, the effective stress (Von-Mises stress) or the hydrostatic stress can all be calculated by FEM for the component cross section for components of reasonable complexity. The nature of fracture, that is the preponderance of ductile or brittle mode, is often determined not by the absolute value of the principal stresses but by the relative values of the hydrostatic and the deviatoric (or von-Mises stress) stresses. The ratio of these two stresses is the triaxiality and it is often representative of a materials propensity to brittle cracking. The triaxiality across a notched cylindrical sample is shown for different crack extents in Fig. 2. The dynamic nature of the triaxiality and its variation with radial distance are to be noted.

**ELECTROCHEMICAL EFFECTS OF NOTCHES**

The electrochemistry of a notch should in many ways be similar to that of a crevice and like the latter it should also have the following electrochemical effects:

i. solution stagnation

ii. different rates of electrochemical reaction compared to the bulk solution

The first effect leads to a depletion of mobile ions (cations or anions) leading to a preponderance of slower ions within the notch so that a differential electrochemical cell is created between the notch and the rest of the component. When the environment
is inherently corrosive, the notch, just like a crack, would corrode autocatalytically. The presence of applied stress and its intensification at the notch would naturally enhance stress corrosion cracking (SCC), however the treatment of SCC must take into account that the notch geometry keeps changing with corrosion and so does the stress profile even for a constant applied stress.

\[ \begin{align*}
\text{Normalized radial distance} & \quad 0.1 \quad 0.2 \quad 0.3 \quad 0.4 \quad 0.5 \quad 0.6 \quad 0.7 \quad 0.8 \quad 0.9 \quad 1 \\
\text{fig. 2: The variation of triaxiality with crack progression in shallow notched (solid lines) and deep notched (broken lines) samples. The radial extent of crack in each case is shown by the crack schematic and the vertical line.} \\
\end{align*} \]

The situation is quite different when the component is cathodically protected or when the notch electrochemistry is such as to accelerate hydrogen production instead of corrosion. The effect of hydrogen is substantially sub-surface as compared to corrosion, which is a superficial phenomenon. While the production of hydrogen may be enhanced (compared to the rest of the component) in notches, what is more important is the dynamic interaction of the hydrogen with the stresses in the notch plane.

**NOTCH EFFECTS IN HYDROGEN EMBRITTLEMENT**

**Hydrogen distribution ahead of a notch**

As indicated earlier a stress profile ahead of the notch root is generated on application of load to the component. Hydrogen, which is an interstitial solute in steels, responds to the stress state. The hydrogen distribution in the absence of stress is given by the solution of Fick's law, which for flat members (square/rectangular cross section) involve an error function solution and a bessel function solution for cylindrical members [3]. The influence of stress on hydrogen diffusion is incorporated in our analysis by using the relationship for modified hydrogen concentration in the presence
of a hydrostatic stress. Three situations need to be considered in generating the hydrogen concentration profiles:

i. *Stress insensitive situation*: where the hydrogen profile within the sample is generated purely under a chemical potential gradient.

ii. *Equilibrium situation*: where the hydrogen permeation is much faster than the imposed strain rates or in case of cracked samples, than the crack growth rates. This would be applicable for very slow strain rate experiments and very slow crack growth rate situations.

iii. *Frozen-in situation*: This is a compromise situation between the above two conditions. The hydrogen concentration is frozen in at values corresponding to a particular stress distribution, and subsequent change in the stress states of the notch plane does not cause changes in the hydrogen redistribution, except for the additional influx with time.

The hydrogen concentration profiles under the three conditions mentioned above are shown in Fig. 3. Evidently the hydrostatic stress causes significant increase in the hydrogen content throughout the samples.

**Fig. 3**: The hydrogen distribution ahead of a crack (length = 255 microns) using different approaches. Note the significant enhancement in hydrogen due to hydrostatic stresses in the notch plane.

The hydrogen distribution is therefore a function of the environmental reaction, pertaining to the notch tip or crack tip environment, and of the instantaneous hydrostatic stress profile ahead of the notch (or crack) tip. Different notch geometries affect hydrogen distribution in two ways:

i. By providing different hydrostatic stress profiles (which is a function of notch dimensions like notch radii, depth, etc.)

ii. By causing hydrogen starvation
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Our results suggest that a frozen concentration is imposed in deep notched specimens only, and never for a shallow notched specimen. The shallow notched samples show an equilibrium hydrogen concentration even at the tip of long cracks. It is easy to visualize that for the shallow notch where the notch is flush on the surface of the sample itself, there is no chance of “hydrogen starvation”, which would be a possibility when the solution has to be channelled to reach the notch tip as in the deep-notched cases. The latter would, therefore, encounter hydrogen deprivation practically as soon as the crack grows. This geometrical effect on solution and therefore on hydrogen transport, has not been given due consideration in the treatment of hydrogen effects on crack growth.

CRACKING AND FRACTURE MORPHOLOGY

Circumferentially notched cylindrical tensile samples were subjected to electrochemical hydrogen charging while monotonic loading. Brittle cracking was observed at slow strain rates. In the embrittled samples there was a clearly defined and symmetrical annular brittle zone which has been variously referred to as the “hydrogen process zone” or the “tearing topography surface” [4], the latter nomenclature due to the presence of quasi cleavage facets as opposed to classical cleavage. Morphologically and functionally this outer annulus represents a brittle fracture, and is referred to as the brittle zone in this article. The demarcation of this zone from the central ductile zone (characterised by microvoids or dimples) is abrupt and sharp, and the brittle zone remained well defined in all the tests. The brittle zone was confined to the notch plane while the dimpled ductile central region was often undulated due to the manifestation of “cup & cone” failure. The notable difference between the shallow-notched and deep-notched specimens was in their extent of cracking measured in absolute terms. The extent of cracking is shown for shallow notched as well as deep notched samples in Fig. 4.

RATIONALIZATION OF THE NOTCH EFFECT IN HE

The overall influence of notches along with the variations due to the dimensional effects on HE can be summarized as due to the following:

i. Notches define the stresses available for crack growth, thus they are of singular importance in deciding the crack initiation conditions, namely $K_{IC}$. The imposed hydrostatic stress also defines the equilibrium hydrogen distribution.

ii. The notch dimensions define the triaxiality conditions ahead of the notch and any emanating crack. The extent of brittle cracking is defined by the zone with triaxiality favourable for brittle cracking. Thus the extent of cracking and the onset of ductile failure is linked to notch dimensions.

iii. The notch depth is often instrumental in defining the availability of hydrogen at the notch/crack tip, thereby influencing any hydrogen transport mechanism.
Fig. 4: The fracture surface of embrittled samples. (a) Shallow notched samples (notch depth=0.5 cm, gauge diameter=8 cm) show a much wider brittle outer annuli compared to (b) deeper notched samples (notch depth=1.5 cm, gauge diameter=8 cm). The central zone is dimpled ductile region for both samples.
iv The notch is the catchment area for hydrogen. The local electrochemical reaction is at variance with the bulk reaction; this variance is an indirect function of the notch shape and size.

CONCLUSIONS

The significance of notches in corrosive failure has been discussed. The primary effects in general corrosive situations are due to the imposition of a stress profile and triaxiality, and due to the different electrochemistry inside notches. When the corrosive situation is such as to encourage hydrogen production and absorption by the component, the primary notch effects lead to several manifestations. Notch plane hydrostatic stresses define the distribution of hydrogen ahead of the notch and/or crack, while the notch depth may decide the availability of hydrogen at the notch/crack root, thereby influencing the hydrogen transport mode into the specimen. Macroscopically these effects enforce a very different cracking rate and fracture morphology for different shapes and sizes of notches.

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