A SAFE APPROACH TO ENVIRONMENTALLY ASSISTED CRACKING EVALUATION

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Abstract. In another paper in this journal, ample experimental evidence is presented of uncertainty of the threshold stress intensity factor (SIF) and the crack growth kinetics (CGK) curve in environmentally assisted cracking (EAC). Thus the extent to which these items are the properties of *only* the material and the environment becomes an open issue and some problems still need resolution. A rigorous local fracture mechanics approach to EAC —in which all influencing factors are treated autonomously, i.e., in terms of *local* values at the crack tip— is emphasised to advance towards a resolution of these problems. In addition, a *safe* approach is proposed for design against EAC.

Resumen. En otro artículo de este volumen se presenta abundante evidencia experimental sobre incertidumbre en el factor de intensidad de tensiones umbral y en la curva de cinética de crecimiento de fisuras en ambiente agresivo. Hasta qué punto estos parámetros son propiedades *sólo* del material y del entorno electro-químico es una cuestión no resuelta. Se aborda en este trabajo un planteamiento riguroso del problema mediante mecánica de fractura *per sé*, es decir, planteando las variables que influyen en el fenómeno en términos de valores *locales* en el extremo de la fisura. Se sugiere también un método *seguro* para el diseño ingenieril frente a la fisuración en ambientes agresivos.

1. INTRODUCTION

Another paper in this journal [1] gives a collection of manifestations of non-uniqueness of the CGK curve which produce uncertainty in EAC evaluation. This brings doubts concerning the intrinsic character of the basic quantities and demonstrates a shortcoming of current fracture mechanics treatment of EAC. In effect, this shows that the extent to which CGK curve and threshold SIF are the properties of *only* the material and the environment becomes an open issue and some problems on EAC evaluation using fracture mechanics still need resolution.

2. TOWARDS A RIGOROUS FRACTURE MECHANICS TREATMENT OF EAC

Common fracture mechanics treatment to EAC is built up on correlation between crack growth rate (CGR), SIF and bulk environmental characteristics. Strictly speaking, when one relies on the principal fracture mechanics idea of crack tip autonomy and expands this approach into the domain of EAC, *all* the influencing factors should be treated *autonomously*, i.e., in terms of local quantities related just to the crack tip zone. This procedure would exclude a high degree of uncertainty in the analysed concepts of CGK curve and threshold SIF.

With regard to mechanical concepts of a kinematic nature, it should be noted that the global or externally-applied displacement rate (or loading rate) is only a control variable in EAC tests. The relevant reference variable is the *local* strain rate at crack tip (or, equivalently, the rate of CTOD or the SIF rate $K^{\bullet}$), since this is the exact location where all EAC events proceed, as discussed in a previous work [2].

In the matter of electrochemical aspects, a proper characterisation of the environment requires the use of its *local* characteristics in the near-tip region, too. In particular, with regard to EAC under corrosion conditions in aqueous electrolytes, it is well documented that parameters of bulk environment such as hydrogen ion exponent pH, electrode potential E_V, activities (concentrations) of influencing environmental species c_i (i=1,...), *etc.*, can differ significantly from their local counterparts at the crack tip (cf. [3,4]).

The relations between *bulk* and *local* (crack-tip) environment characteristics are governed by kinetic processes of mass-charge transfer and chemical reactions, and by environmental currents [4-8]. Thus, local environment state depends on time t, mechanical variables (stress-strain state), crack geometry (crack length and width) and kinematic variable (the rate of strain or CTOD). Evidences of distinct in-crack electrochemistries dependent on crack length a are reported in [9]. One key factor of a geometric nature is the opened crack profile as the width of the mass-transfer canal represented by the crack opening displacement (COD) δ over the whole crack area. Diverse alterations of pH^{CT} and $E_V{}^{CT}$ in specimens with stationary crack at different load levels —and correspondingly crack stretchings δ— are notified in [4]. The value of CTOD rate (or $K^{\bullet}$ for small scale yielding) must be considered to reflect the influence of kinetic physico-chemical processes (surface passivation, hydrogenation etc.) and strain-dependent dynamics affecting crack-tip physico-chemistry (oxide film creation/rupture, bare metal exposure, *etc.*).

Relations between *bulk* and *local* (crack tip) environment characteristics may be expressed as follows:

$$pH^{CT} = pH^{CT}(t, pH, E_V, c_j, a, \delta, K^{\bullet}) \quad (1)$$

$$E_V{}^{CT} = E_V{}^{CT}(t, pH, E_V, c_j, a, \delta, K^{\bullet}) \quad (2)$$

$$c_i{}^{CT} = c_i{}^{CT}(t, pH, E_V, c_j, a, \delta, K^{\bullet}) \quad (3)$$

$$(i, j=1,...;\ i \neq j)$$

where the superindex CT indicates the crack tip values. As a matter of fact, the right hand parts of these relations are not functions of the instantaneous values of displayed variables but rather functionals over their time histories, in particular over the trajectories $a(t)$ and $\delta(t)$. In general, crack tip environmental parameters (1)-(3) usually vary along a specific path at every particular run of EAC for nominally the same couple material-environment in terms of its bulk parameters (cf. [4]). The total process time and particular loading/cracking history both influence crack tip environment, which follows its own way of variation whilst EAC proceeding renders some CGK curve (Fig. 1). It is clear that instantaneous CGR at a given SIF must then correspond just to instantaneous values of local environment parameters [4].

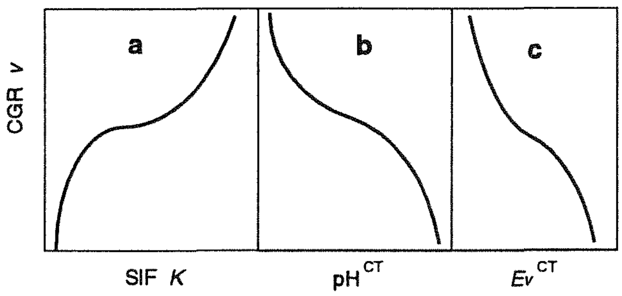

Fig. 1. Trends of variation of CGK and crack tip environment parameters during EAC tests under corrosive conditions in changeless bulk environment.

This implies that there is no reason to expect uniqueness of fracture mechanics characteristics of EAC for couples ⟨*material*; *bulk environment*⟩ in general, since EAC is governed by crack tip environmental variables which have their own histories of evolution (1)-(3). Apparently, EAC may be related directly to bulk environment characteristics only for gases of rather low viscosity (e.g., hydrogen) or at sufficiently high pressure (e.g., for water vapour or hydrogen sulphide) so that bulk and crack tip activities, i.e., partial pressures, of responsible species can be practically identical [7,8]. Thus uniqueness of the whole CGK curve —and of the threshold SIF in particular— may be expected only at fixed crack-tip straining dynamics with respect to the couple ⟨*material*; *local environment*⟩ which presumes control of the second constituent (the environment) in the vicinity of crack tip. Since the latter is variable and difficult to monitor in practice, these legitimate fracture mechanics characteristics of EAC seem to lose importance in engineering.

However, given a bulk environment, all conceivable evolutions of the EAC process surely lie within some closed region in the space of the complete set of directly governing variables, i.e., crack tip mechanical (K and $K^{\bullet}$) and physico-chemical (pH^{CT}, $E_V{}^{CT}$ and $c_i{}^{CT}$, *etc.*) ones. With regard to evaluation of environmental degradation of materials and assessment of structural performance, K-slices of this domain are of interest, where the worst combination of the remaining variables with regard to EAC facilitation can be found (*the worst state*). This worst situation may happen in various ways, e.g., it can be established asymptotically as a steady-state or achieved temporarily at intermediate times.

An explanation of this matter can be found in the data of EAC studies for metals in aqueous environments, shown in Fig. 2 (cf. [4]). Given a specified couple ⟨*material*; *bulk environment*⟩, from the data about actual variation of crack tip environment characteristics pH^{CT} and $E_V{}^{CT}$ (Fig. 2a) the intensity of hydrogen evolution (*hydrogenation index*) at the crack tip may be estimated using the shift of electrode potential [4]:

$$\Delta_{HE}E_V{}^{CT} = E_V{}^{*}(pH^{CT}) - E_V{}^{CT} \quad (4)$$

which relates local electrochemical variables with the thermodynamic stability border for water given by the equation of Nernst line (referred to the crack tip):

$$E_V{}^{*} = \alpha + \beta\, pH^{CT} \quad (5)$$

$$(\alpha = -0.014V,\ \beta = -0.059V)$$

It was found (cf. [4]) that the index of hydrogenation $\Delta_{HE}E_V{}^{CT}$ during EAC tests of steels approaches asymptotically the most negative level $(\Delta_{HE}E_V{}^{CT})_{min}$, (see Fig. 2b), which provides the most severe hydrogenation. Therefore, this case yields the example of the worst steady-state attained in EAC promoted by metal hydrogenation from a corrosive environment.

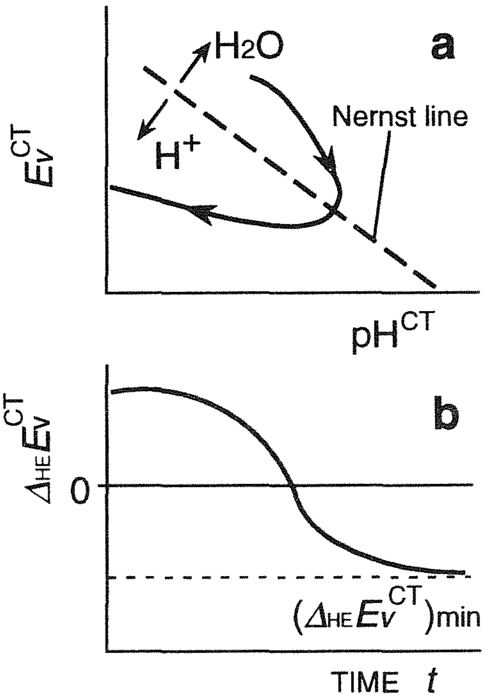

Fig. 2. Typical progress of crack tip conditions in EAC: (a) progress of crack tip electro-chemistry as the crack grows; (b) progress of hydrogenation index with time.

On the other hand, the transient worst state may occur resulting from the competition of the rates of passivation reaction, liquid diffusion and deformation-controlled film rupture which all affect EAC in certain systems [10]. There crack tip strain rate (CTOD-rate or $K^{\bullet}$) becomes the relevant process variable responsible for maximum facilitation of EAC.

Thus the *worst state* seems to be indeed the intrinsic attribute of the material-environment system (the latter considered in a global sense, i.e., as bulk environment). Accordingly, the same may be expected with regard to fracture mechanics characteristics of EAC process: the threshold SIF and the CGK curve as a whole.

3. AN APPROACH TO SAFE EVALUATION OF EAC

The above considerations suggest the modification of the customary concepts of EAC threshold and CGK curve. A first conceptual item emerges regarding discrimination between the *conventional threshold* for which crack extension does not occur for "infinite" time (i.e., reasonably long in practice) and the *true (physical) threshold* as the limit below which crack extension is impossible in a given system ⟨*material*; *bulk environment*⟩. The latter meaning refers to the weakest resistance against local rupture at the crack tip provided either by steady state equilibrium in the kinetic process of metal-environment interaction or by the maximal degree of attainable environmental degradation of the material. The first one is familiar to hydrogen assisted cracking where the threshold corresponds to maximum hydrogenation of metal when equilibrium hydrogen concentration in metal is reached [11]. The other may occur "instantaneously" under dynamic loading conditions when the notion of equilibrium is not relevant. For whichever case, the true (physical) threshold may be defined as follows:

The EAC threshold is the minimum SIF (lower limit) at which EAC ever starts for the worst stationary or transient crack tip state.

Such a lower limit bounds the set of all *apparent* threshold values which could be experienced. An equivalent definition may also be stated if one would like to emphasise the upper limit at which no EAC occurs, accordingly, as follows:

The EAC threshold is the maximum SIF (upper limit) at which EAC never occurs for the worst stationary or transient crack tip state.

Then the threshold level can be viewed as the lower limit when environment induced CGR $v > 0$ is possible or the upper limit to preserve $v = 0$ despite a possible harmful environment. Given a stationary crack tip state, the term "infinite time" may be used instead of "never", with the meaning of "reasonably long" from the engineering point of view (conventional threshold).

The definition of CGK curve as the intrinsic characteristic of the couple ⟨*material*; *bulk environment*⟩ also requires the use of limits to bound the region (in the v-K space) of all possible CGR values of EAC that can happen for different SIF levels, as follows:

The CGK curve is a plot representing the maximum instantaneous CGR (upper limit) at a given SIF.

The concept of the worst state is implicitly involved in this definition since the maximum is considered, and this *worst state* is characterised by the whole set of variables representing crack tip environment as well as the crack tip strain rate (CTOD rate or $K^{\bullet}$) when dynamics of competing processes may be essential. Then the *material's* CGK curve is the *envelope* of all possible CGK curves for a given ⟨*material*; *bulk environment*⟩ system. Thus it can be considered as a *master curve* or *reference curve*, as shown in Fig. 3. It can be used in engineering design against EAC to provide reliable conservative estimations of performance (*safe approach*) in the framework of engineering fracture mechanics.

Correspondingly, EAC testing techniques should involve artificial maintenance of these most severe crack tip interactions which provide the strongest EAC impact. Clearly, this implies incorporation of the bounding procedures to establish the proper limits for crack tip mechanics and physico-chemistry to evaluate the weakest EAC resistivity. In this way, the basic EAC characteristics for a given material-environment system can be obtained, thus providing conservative evaluation of EAC resistance of materials and structures [4]. Obviously, this requires more extensive testing to find the worst among all possible behaviours. This could be reduced by proper modelling and development of prediction techniques regarding involved interactions.

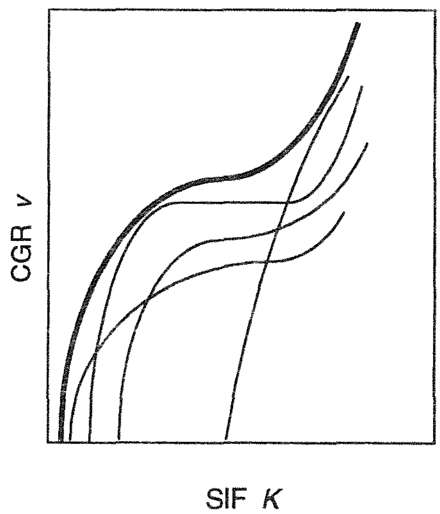

Fig. 3. The *worst* CGK curve (bold) for the couple ⟨*material*; *bulk environment*⟩ as the *envelope* of all possible CGK curves (*reference curve* or *master curve*).

4. CONCLUSIONS

Some deal of uncertainty of EAC characterisation caused by complicated inter-relations of local (crack-tip) and bulk environmental parameters is eliminated by a rigorous fracture mechanics approach which is essentially *local*, and thus both mechanical and environmental EAC-factors must be treated in terms of local values related to the crack tip.

Rigorous definitions of threshold SIF (for both stationary and transient conditions) and CGK curve are provided on the basis of the concept of the *worst state* at the crack tip, towards a *safe approach* to EAC in the framework of engineering fracture mechanics.

The concept of the worst state is implicitly associated with a *material's* CGK curve as the *envelope* of all possible CGK curves for a given ⟨*material*; *bulk environment*⟩ system. It can be used in engineering design against EAC to provide reliable conservative estimations of performance.

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