

FRACTURE MECHANICS APPROACH TO HYDROGEN ASSISTED CRACKING: ANALYSIS OF THE K -DOMINANCE CONDITION

J. Toribio and V. Kharin

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We summarize the achievements of a major research line at the Department of Materials Science of the University of La Coruña (Spain) in the field of environmentally-assisted cracking in general and hydrogen degradation in particular. We analyze the meaning and significance of the fracture-mechanics approach to hydrogen-assisted cracking and study the problem of K -dominance not only over the mechanical aspects of the phenomenon but also over the environmental (physicochemical) factors affecting the entire coupled process of hydrogenation and failure. Two key factors capable of violating the unambiguous behavior of the kinetic diagram of crack growth $v = v(K)$ are discussed: the role of the far stress-strain field (i.e., the stress-strain field which is not K -dominated) and the effect of the history of hydrogenation and crack growth. For this purpose, we consider the stress-strain-assisted diffusion of hydrogen regarded as a rate-controlling factor of hydrogen-assisted cracking under sustained or quasistatic loads. It is shown that the far field produces a minor effect on the near-tip diffusion of hydrogen. This can only increase the spread in crack growth rates in the near-threshold part of the $v(K)$ -curve. As far as the influence of the history is concerned, we discovered that the processes of hydrogenation and crack growth are coupled, each of them affects the other, and, hence, the kinetic diagram of crack growth $v = v(K)$ is not one-to-one as should be for an intrinsic property of the material. However, there exists a special mode of steady-state crack growth when hydrogen-assisted cracking becomes a K -dominated process and the corresponding plot of the steady-state rate v as a function of K becomes unambiguous (as a characteristic curve of the material) and, thus, can be used in the engineering practice for a more conservative evaluation of the crack-growth resistance of materials and structural integrity.

Introduction

Engineering design frequently deals with the problems of environmentally-assisted cracking (EAC) in materials and structures, a phenomenon appearing in diverse forms such as stress-corrosion cracking, hydrogen-assisted cracking (HAC), liquid-metal embrittlement, etc. In this case, the fracture-mechanics approach proves to be effective for the evaluation of materials and structural-integrity assessment.

Within the framework of linear elastic fracture mechanics, under the conditions of small scale-yielding, the stress intensity factor K is the only parameter governing the stress-strain state in the vicinity of the crack tip. The fracture-mechanics approach to EAC is based on the use of the *kinetic diagram of crack growth* (Fig. 1), i.e., the plot of the crack growth rate v as a function of the stress intensity factor K defined between the threshold value K_{th} (below which the crack growth rate v is equal to zero) and the fracture toughness K_c .

The idea of *unambiguity* of the $v(K)$ -curves and thresholds K_{th} as intrinsic characteristics of material–environment systems forms the basis of the approach and ensures the possibility of its applications in engineering design. The indicated unambiguity guarantees the *similitude* of the behavior of cracks in test specimens and structural components in service, thereby providing the *transferability* of the laboratory experimental data to actual engineering structures.

If the $v(K)$ -curve, including K_{th} , is indeed unambiguous for a given material–environment couple, then any discrepancy between the predicted and actual behavior should be attributed either to the inaccurate analysis or to the spread in the experimental data but not to the concept itself. Otherwise, conceptual weakness makes the predictions less reliable and requires more constraints to be imposed on testing and evaluation to obtain the data on the characteristics of crack-growth resistance in aggressive environments.

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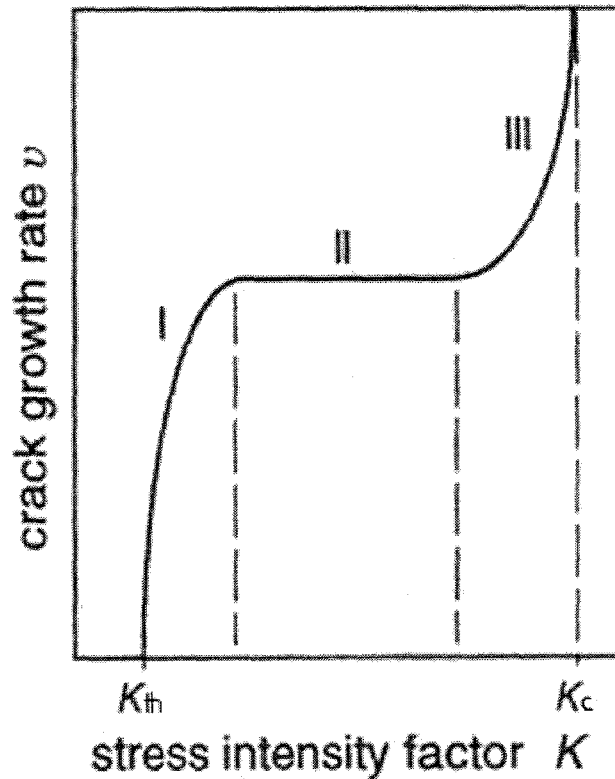


Fig. 1. A typical crack growth rate curve with the near-threshold stage (I), plateau (II), and the stage of mechanical final fracture (III).

The reliability of the fracture-mechanics approach to EAC in engineering design is surveyed in [1], where one can find a rich collection of experimental examples of the ambiguous behavior of the $v(K)$ -curve and the threshold K_{th} . Although these items are supposed to depend solely on the material and environments, they are notably sensitive to the influence of many test and service factors, namely (cf. [1]),

- (i) preloading: fatigue precracking mode and overloads;
- (ii) geometry: crack length, crack bluntness, and the gradient of the stress intensity factor;
- (iii) kinematics: initial loading, tests interruption, and the loading/straining rate.

The results presented in [1] show that the same values of the stress intensity factor does not always result in equal crack-growth rates if all other characteristics of material–environment couples are identical. The observed deviations cannot be related to imperfect testing and are systematic, unlike the obvious statistical spread in the experimental data. This uncertainty of the basic fracture-mechanics characteristics of EAC results in the loss of confidence in the evaluation of materials and structural integrity assessment.

In [2], we partially eliminated the uncertainty of characterization of EAC in a strictly *local* fracture-mechanics approach where both the mechanical and environmental factors are analyzed in terms of local variables related to the crack tip. However, the indicated local interpretation of the kinetic diagram of crack growth still remains incomplete and does not meet all requirements necessary to characterize this diagram as an intrinsic material curve.

In [2], to solve the problem, we proposed a procedure of safe engineering design against EAC. For a given material–environment system, we find the *worst* crack-tip situation producing the fastest crack growth rate v_m attainable at each K . The corresponding master curve $v_m(K)$ is the envelope of all possible $v(K)$ -curves for a given material–environment couple. Moreover, it represents an intrinsic characteristic of the system: its weakest resistance to EAC.

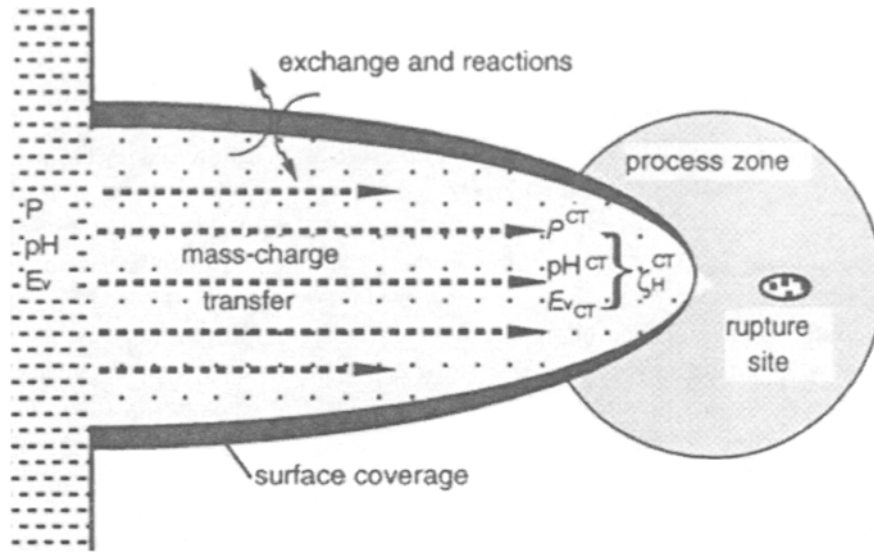


Fig. 2. In-crack environmental currents, the processes of mass and charge exchange, and chemical reactions.

However, the extent to which the $v(K)$ -curve and the threshold K_{th} are properties only of the material and the environment remains an open issue. This uncertainty means that the process, in general, is not exclusively K -dominated, although no attempt was made in the past to elucidate the matter of K -dominance over the entire family of contributing events as the checkpoint of the applicability of the fracture-mechanics approach to EAC.

In the present work, we survey the results of recent research performed by the authors into the meaning and significance of the fracture-mechanics approach to the particular phenomenon of HAC. Our final aim is to clarify the problem of K -dominance not only over the mechanical aspects of the phenomenon but also over the environmental (physicochemical) events affecting the coupled process of hydrogenation and failure.

Meaning and Significance of the Fracture-Mechanics Approach to HAC

Basic Distinctive Features of HAC. The phenomenon of HAC has the following basic distinctive features [3]:

- (i) hydrogen supply to the future fracture nuclei, including hydrogen transport to a metal, penetration into the metal, and transport inside the metal;
- (ii) stress-strain state as a mechanical factor intensifying hydrogen-assisted damage;
- (iii) damage enhancement by hydrogen.

The crack-tip thermodynamic activity of hydrogen (its fugacity) can be represented in terms of the electrode potential E_v^{CT} and the pH^{CT} value of corrosive media in the crack-tip zone. They may significantly differ from the characteristics of the bulk of the environment E_v and pH . The relations for the bulk and local parameters of the environment depend on the in-crack environmental currents, kinetic processes of mass and charge exchange and chemical reactions (Fig. 2). Thus, the local environmental variables depend on the geometry of the crack and time t :

$$pH^{CT} = pH^{CT}(pH, E_v, a, \delta, t) \quad \text{and} \quad E_v^{CT} = E_v^{CT}(pH, E_v, a, \delta, t), \quad (1)$$

where the geometric parameters a (crack depth) and δ (the height of an open crack) represent the characteristic transportation distance from the bulk of the environment to the crack tip (in this case, for the sake of simplicity, we

use only crack depth) and the crack opening displacement under loading, which gives the width of the channel (variable along the crack faces). The right-hand sides of relations (1) are, in general, not plain functions of instantaneous values of displayed variables but should be regarded as functionals over their time histories depending, in particular, on the shapes of the entire trajectories $a(\tau)$ and $\delta(\tau)$ within the time interval $0 \leq \tau \leq t$. This implies the influence of both loading and cracking history and crack geometry outside the K -controlled crack-tip zone on the near-tip environment and, therefore, on the value of v for given K and fixed parameters of the bulk environment.

The phase of hydrogen penetration into a metal includes the processes of physical adsorption of hydrogen-containing species on the metal surface, dissociative chemisorption of atomic hydrogen, and its dissolution in the surface layer. The surface phase of sorption may be the rate-determining step for HAC under the conditions of relatively weak hydrogenation at the crack tip but this is unusual for most practical cases of gaseous or electrochemical (corrosive) hydrogenation when an elevated activity of hydrogen is attained at the sites of its entry (see [3]).

In the phase of hydrogen transport toward the future fracture nuclei, two modes of transportation must be distinguished: *diffusion* and *transport by moving dislocations*. The first is observed under the conditions of both sustained and transient (time-dependent) stress-strain states, has the *instantaneous* level of plastic strains as one of the responsible variables, and evolves toward equilibrium hydrogen distributions. In contrast, the second one is observed exclusively in the process of dynamic plastic straining, has the plastic strain *rate* as the governing variable, and results in nonequilibrium hydrogen distributions (temporal localized oversaturations). They are fed by arriving dislocations that drive hydrogen which escapes by diffusion to restore the thermodynamic equilibrium with local surroundings. After the end of straining, the sites oversaturated with hydrogen relax to the local equilibrium states by short-range (local) diffusion.

The efficiency of the dislocation transport of hydrogen and hydrogen accumulation in the sites of future damage is determined by the competition between the two effects described above. Under sustained or quasistatic loading, local oversaturations with hydrogen supplied by dislocations have time to be reduced by short-range diffusion and, thus, the significance of dislocation transport seems to be negligible. As a result, the (relatively) long-range diffusion driven by the macroscopic stress-strain field becomes the main operative mode of the transport of hydrogen to fracture nuclei in metals. This process is frequently the slowest phase of hydrogen transport and, thus, the kinetics of hydrogen-assisted fracture is often diffusion controlled.

Modeling of the Process of HAC. Hydrogen promotes failure by different physical mechanisms (see [3]). Hence, the elementary events of fracture are associated with certain critical combinations of values of the concentration of hydrogen C and mechanical variables representing the stress-strain state. These combinations enable us to determine the critical concentrations of hydrogen C_{cr} required for local events of fracture to be realized

$$C = C_{cr}. \quad (2)$$

The *critical* concentration is a function of the mechanical (stress-strain) state at a given material point

$$C_{cr} = C_{cr}(\sigma, \varepsilon_p), \quad (3)$$

where $\sigma = \sigma(\vec{r}, t)$ and $\varepsilon_p = \varepsilon_p(\vec{r}, t)$ are the stress and plastic strain tensors, respectively, \vec{r} is a radius vector, and t is time. In the present work, we consider the case of a solid body subjected to *sustained loading*. This means that the stress and strain tensors depend only on spatial coordinates, i.e., $\sigma = \sigma(\vec{r})$ and $\varepsilon_p = \varepsilon_p(\vec{r})$.

The *actual* concentration depending on the specific location of the material point and time is also a function of the stress-strain state, namely,

$$C = C(\vec{r}, t; \sigma, \varepsilon_p). \quad (4)$$

The process of hydrogen penetration can be characterized by the equilibrium value C_Γ of hydrogen concentration in the stressed and strained metal on the surface of penetration Γ (metal–environment interface):

$$C(\Gamma, t) = C_\Gamma. \quad (5)$$

The driving force of the diffusion of hydrogen \bar{X}_D is determined via the gradient ∇ of its chemical potential μ_H as follows:

$$\bar{X}_D = -\nabla\mu_H, \quad (6)$$

and the latter is expressed via the coefficient of solubility of hydrogen in the metal K_S (the density of available sites) according to the formula

$$\mu_H = RT \ln\left(\frac{C}{K_S}\right), \quad (7)$$

where R is the universal gas constant and T is absolute temperature. The coefficient of solubility K_S depends on temperature, the level of *hydrostatic stresses* σ , the microstructure of an alloy, its chemical and phase composition, and the density of hydrogen traps (traps for hydrogen in metals are formed by lattice imperfections; dislocations are, as a rule, the strongest kind of traps but not the only one). The overall density of traps depends on the level of plastic strains, which may be represented via the second invariant of the plastic strain tensor: the *effective* or *equivalent plastic strain* ε_p . In addition, plastic strains may affect the phase composition of the alloy, thereby causing variations in the solubility of hydrogen, as in austenitic steels, via the strain-induced $\gamma \rightarrow \alpha$ transformation. Thus, parallel with hydrostatic stresses and temperature, the level of plastic strains is also a variable affecting the solubility of hydrogen in metals, namely,

$$K_S = K_S(\sigma, \varepsilon_p, T). \quad (8)$$

This quantity can be represented as a product of the factor depending on the level of plastic strains $K_{S\varepsilon}$ by the function of hydrostatic stresses as follows (cf. [3]):

$$K_S(\sigma, \varepsilon_p, T) = K_{S\varepsilon}(\varepsilon_p, T) \exp(\Omega\sigma), \quad \text{where} \quad \Omega = \frac{V_H}{RT} \quad (9)$$

and V_H is the partial molar volume of hydrogen in the metal.

The gradient (inhomogeneity) of any solubility-affecting factor can induce a diffusion flux. Under the assumption that the *distribution of temperature in the solid is uniform* (a hypothesis accepted throughout the present work), the diffusion flux \bar{J} can be expressed as follows:

$$\bar{J} = \frac{DC\bar{X}_D}{RT} = -DC\nabla \ln\left(\frac{C}{K_S}\right), \quad (10)$$

where D is the diffusion coefficient of hydrogen in the metal. Actually, the diffusivity should be regarded not as a constant but as a function of the level of plastic strains, i.e., $D = D(\varepsilon_p) \neq \text{const}$, to reflect the influence of the variable phase composition or the density of traps on the averaged (macroscopic) mobility of diffusing species (cold-work effect) in addition to their effect on the solubility of hydrogen reflected by Eqs. (8) and (9). Substituting relation (9) in (10), we obtain

$$\bar{J} = -D(\varepsilon_p) \left\{ \nabla C - C \left[\nabla(\Omega\sigma) + \frac{\nabla K_{S\varepsilon}(\varepsilon_p)}{K_{S\varepsilon}(\varepsilon_p)} \right] \right\}. \quad (11)$$

The principle of mass balance gives the following diffusion equation in terms of concentration:

$$\frac{\partial C}{\partial t} = -\operatorname{div} \bar{J}, \quad (12)$$

which enables one to determine the evolution of concentration in time t . According to (11) and (12), the equation of stress-and-strain-assisted diffusion for concentration takes the form

$$\frac{\partial C}{\partial t} = D[\nabla^2 C - \bar{M} \cdot \nabla C - NC] + \nabla D \cdot [\nabla C - \bar{M} C], \quad (13)$$

where the dot \cdot denotes the scalar product and, for the coefficients \bar{M} and N , we have

$$\bar{M} = \nabla \ln K_S(\sigma, \varepsilon_p) \quad \text{and} \quad N = \nabla^2 \ln K_S(\sigma, \varepsilon_p). \quad (14)$$

The process of penetration of hydrogen into the metal is characterized by the *boundary condition* (5) for diffusion with $C_\Gamma = C_0 K_S(\Gamma)$, where C_0 is the equilibrium concentration of hydrogen specified by the environment in the bare metal (free of stresses and plastic strains). In view of (9), this yields

$$C_\Gamma = C_0 K_S(\Gamma) = C_0 K_{S\varepsilon}(\varepsilon_p(\Gamma)) \exp(\Omega \sigma(\Gamma)). \quad (15)$$

For solids, under the conditions of uniform environmental activity of hydrogen characterized by an equilibrium concentration $C_0 = \text{const}$, it is easy to get the exact *steady-state solution* of the equation of stress-strain-assisted diffusion (13) asymptotically attained as $t \rightarrow \infty$. This corresponds to the equilibrium state in which the diffusion flux (10) is absent or, equivalently, the diffusion driving force (6) vanishes. According to expression (10), this is true if $C/K_S = \text{const}$. Thus, taking into account relation (9), for the steady-state solution, we can write

$$C_\infty(r) = C_0 K_S(r) = C_0 K_{S\varepsilon}(\varepsilon_p(r)) \exp(\Omega \sigma(r)). \quad (16)$$

For $\varepsilon_p = 0$ and $K_{S\varepsilon} = 1$, this expression coincides with the well-known formula for stress-only driven concentration.

Fracture-Mechanics Approach to HAC. The basic concept of mechanical autonomy of the crack-tip region (K -dominance) is the keystone of the approach of linear elastic fracture mechanics [3]. It can be interpreted as follows: there is a region of characteristic size R_{SIF} (Fig. 3) around the crack tip where the elastic stress-strain state is K -dominated, i.e., adequately represented *solely* by the universal singular term $r^{-1/2}$ of the complete solution in the form of a series. This is the asymptotic term σ_a of hydrostatic stresses if we focus our attention on this component (the relevant component of the diffusion of hydrogen).

In addition, a nonlinear region exists in the vicinity of the crack tip subjected to microscopic damage (the fracture process zone of size R_{FPZ}). As a rule, it is surrounded by a plastic region of size R_Y . The entire inelastic zone (the fracture process zone plus the plastic region) may be so small that it does not sensibly disturb the linear elastic solution (*small-scale yielding* condition). If this happens, then the K -dominated annular elastic region still exists at distances from the crack tip $R_Y < r \leq R_{\text{SIF}}$. Outside this annular domain (for $r > R_{\text{SIF}}$), the remote stress-strain field (*far-field*) is neither governed by K nor is its hydrostatic component σ_f .

As far as this K -dominated ring completely shields the inelastic zone from any other external influence except that provided by K , the state of the entire inelastic near-tip region including the fracture process zone depends solely on the value of K and the material, i.e., is also autonomous and, thus, the stress intensity factor K is the parame-

ter governing the mechanical predamage state of the crack tip despite the lack of the explicit analysis of the nonlinear behavior and microfracture events in the fracture process zone.

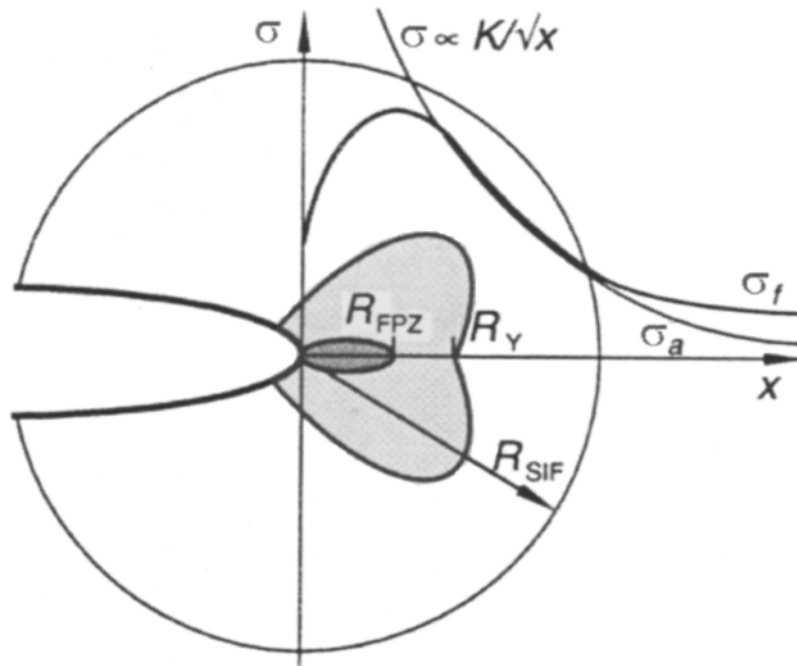


Fig. 3. Specific zones and stresses in the vicinity of the crack tip.

In the case of HAC where a crack of depth a appears in the material, the criterion of hydrogen-assisted fracture (2) remains valid. For the K -dominated stress-strain state in the vicinity of the crack tip, the *critical* concentration (3) is a function of the stress intensity factor K , i.e., $C_{cr} = C_{cr}(\sigma(K, \bar{r}), \varepsilon_p(K, \bar{r}))$ and, for the actual concentration (4), we can write $C = C_{cr}(\bar{r}, t; \sigma(K, \bar{r}), \varepsilon_p(K, \bar{r}))$.

By using only independent variables and a local coordinate x with origin at the crack tip (see Fig. 3), we obtain

$$C_{cr} = C_{cr}(K, x) \quad \text{and} \quad C = C(x, t; K). \quad (17)$$

Therefore, to guarantee the K -dominance over the entire process of HAC and, thus, the uniqueness of the crack growth kinetics curve $v = v(K)$ as a characteristic of a given material–hydrogen system, the following two preliminary conditions must be satisfied:

1. The K -controlled uniqueness of the critical concentration of hydrogen C_{cr} that must be attained at some point of the fracture process zone to cause local fracture and crack advance.
2. The K -dominance over the process of hydrogenation in the fracture process zone ahead of the crack tip, i.e., the uniqueness of the evolution of the distribution of hydrogen concentration $C(x, t)$.

According to the failure criterion (2), the curves specified by the right-hand sides of Eqs. (17) must “meet” at some point to cause crack propagation. To attain the exclusive K -dominance over the solution of the problem of intersection of these two curves (of the *critical* and *actual* concentrations of hydrogen), they must be K -controlled in a close vicinity of the instantaneous crack tip.

Since the critical concentration C_{cr} in the vicinity of the crack tip inherits the property of K -dominance from the stress-strain fields, the preliminary conditions 1 and 2 formulated above are equivalent to the following ones:

1*. K is the sole variable that controls the near-tip stress-strain fields (i.e., $\sigma = \sigma(K, \bar{r})$ and $\varepsilon_p = \varepsilon_p(K, \bar{r})$) in a domain covering the physical process zone and, thus, dominates over the mechanical aspects of both predamage and stress-strain affected hydrogenation.

2*. In addition, K also governs the parameters of the environment that control hydrogenation in the very close vicinity of the crack tip (*local* parameters of the environment) determining the evolution of the concentration of hydrogen $C(x, t)$ in the fracture process zone.

Finally, the indicated preliminary conditions also admit the following formulation in terms of the concepts of fracture mechanics:

1**. The K -controlled *mechanical autonomy* of the crack tip region, i.e., the K -dominance over the stress-strain field, which is the keystone of linear elastic fracture mechanics under the conditions of small-scale yielding.

2**. The K -controlled *environmental autonomy* of the crack-tip region, i.e., the K -dominance over the physicochemical events, namely, the boundary conditions and the diffusion of hydrogen in the vicinity of the crack tip.

It is clear that the first preliminary condition is always satisfied within the framework of linear elastic fracture mechanics under the conditions of small-scale yielding but the validity of the second condition is not always guarantee because there are many factors that can destroy K -dominance in the process of HAC (see [3]) and, thus, the uniqueness of the kinetic curve of crack growth $v = v(K)$. In what follows, the effects of the far field and history are discussed in more details.

Despite the fact that the $v(K)$ -curve is not always K -dominated (the second preliminary condition may be not true), under the conditions of sustained loading (suggested in the present work), the threshold K_{th} always satisfies both preliminary conditions of K -dominance because the limit of crack nonpropagation is associated with a unique steady-state distribution of concentration $C_\infty(r)$ near the tip of a stationary crack attained as $t \rightarrow \infty$. This stationary solution of the equation of stress-strain-assisted diffusion is given by (16) and possesses the same properties of self-similarity as the stress-strain field. Therefore, only the first preliminary condition (mechanical autonomy) is necessary to guarantee the uniqueness of the threshold state, which is always K -dominated in the case of linear elastic fracture mechanics, small-scale yielding, and sustained loading.

Effect of the Far Field on the Phenomenon of K -Dominance in HAC

Effect of the Far Field on the Process of Stress-Strain-Assisted Diffusion. The phenomenon of K -dominance over the diffusion of hydrogen in the near-tip region is discussed in [4]. This is the problem of accuracy of an approximate distribution of hydrogen concentration C_a governed by the K -dominated component of the near-tip stress-strain field (i.e., by the *asymptotic* term σ_a) in representing the actual concentration C_f specified by the total mechanical field containing the entire expansion in a series (i.e., affected by the nonautonomous *far field* σ_f). To this end, the difference between the two distributions of concentration $\chi = C_a - C_f$ is analyzed to estimate the effect of the far field (the remote stress-strain field which is not K -controlled) on the process of hydrogenation of the fracture process zone.

In accordance with the general form of the equation of stress-strain-assisted diffusion (13), the equations for the far-field-affected (exact) concentration C_f and the asymptotic near-tip (approximate) concentration C_a have the form

$$\frac{\partial C_f}{\partial t} = D[\nabla^2 C_f - \bar{M}_f \cdot \nabla C_f - N_f C_f] + \nabla D \cdot [\nabla C_f - \bar{M}_f C_f], \quad (18)$$

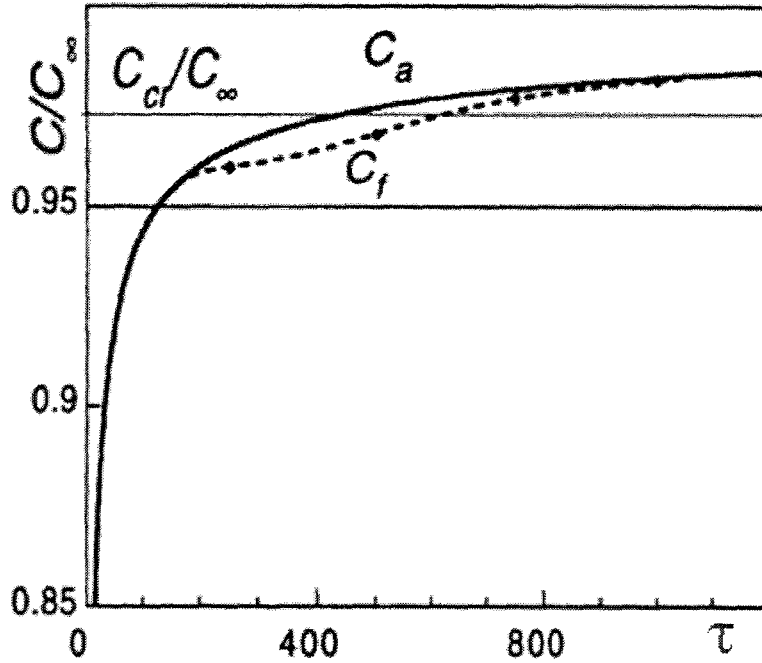


Fig. 4. Time evolution of the concentration of hydrogen: the asymptotic (K -controlled) concentration C_a (solid line) and a representative of the family of far-field-affected concentrations C_f (dashed line). An example of the near-threshold critical level of concentration C_{cr} below the steady-state concentration C_∞ for K_{th} is also shown.

$$\frac{\partial C_a}{\partial t} = D[\nabla^2 C_a - \bar{M}_a \cdot \nabla C_a - N_a C_a] + \nabla D \cdot [\nabla C_a - \bar{M}_a C_a], \quad (19)$$

where the coefficients \bar{M} and N with subscripts f and a are given by formulas (14) with the corresponding mechanical fields (total or asymptotic, respectively).

In view of the small-scale yielding condition, in the vicinity of the crack tip, there is a K -dominated region ($r < R_{SIF}$), where the indicated two elastoplastic stress-strain fields coincide. In addition, plasticity is assumed to be associated solely with the crack-tip region and no other plastic zones exist. Hence, the inelastic behavior is always K -governed and plastic strains ε_p do not appear in Eqs. (18)–(19) as a matter of distinction. Thus, the difference is attributed to the discrepancy between the two hydrostatic stress fields: the far field σ_f and the asymptotic field σ_a for $r > R_{SIF}$.

Subtracting one of the equations presented above from the other, we arrive at the following equation for the difference between concentrations:

$$\frac{\partial \chi}{\partial t} = D[\nabla^2 \chi - \bar{M}_f \cdot \nabla \chi - N_f \chi] + \nabla D \cdot [\nabla \chi - \bar{M}_f \chi] + Q \quad (20)$$

with an additional source-type term (cf. [4])

$$Q = \begin{cases} D \Omega \nabla(\sigma_f - \sigma_a) \cdot \nabla C_a \neq 0 & \text{for } r > R_{SIF}, \\ 0 & \text{for } r \leq R_{SIF}. \end{cases} \quad (21)$$

Expression (21) represents the source-type term for the diffusion of the difference χ between the approximate K -driven distribution of concentration and the exact distribution affected by the far field. For the case of trivial initial and boundary conditions for χ , its absolute value increases from zero as a function of time since the source Q

produces a fictitious “diffusing substance” in the solid. The “error” generated by the source Q operating for $r > R_{\text{SIF}}$ diffuses from this region toward the fracture process zone. The effect of the far field on the K -dominance over the accumulation of hydrogen in the fracture process zone becomes more pronounced when a greater amount of the “error” χ reaches the region $r < R_{\text{FPZ}}$ in the process of diffusion from the distant source (21) located at $r < R_{\text{SIF}}$.

Assessment of the Conditions of K -Dominance. If we estimate the sizes of the crack-tip zones (Fig. 3) and perform the theoretical analysis of the near-tip diffusion of hydrogen (for details, see [4]), then we can describe the time evolution of the asymptotic (K -driven) concentration C_a on the outer boundary of the fracture process zone (Fig. 4), where the effect of the source Q is detected earlier than anywhere, i.e., at $x = R_{\text{FPZ}}$, as

$$C_a(x = R_{\text{FPZ}}, t) = C_a(\tau) = C_\infty(R_{\text{FPZ}}) \operatorname{erfc}[(2\sqrt{\tau})^{-1}], \quad (22)$$

where $\operatorname{erfc}(\cdot)$ is the complementary error function and τ is dimensionless time defined as

$$\tau = \frac{Dt}{R_{\text{FPZ}}^2}.$$

For about $\tau \geq 130$, the concentration C_a in the fracture process zone (i.e., for $x < R_{\text{FPZ}}$) exceeds 95% of the steady-state level C_∞ . From this time on, its subsequent variation goes within a 5% scatter band near the indicated limit of hydrogenation, i.e., an increase in the K -driven concentration in the fracture process zone lies within this 5% interval from the time t_{ss} (where the subscript “ss” stands for the steady state) given by the formula

$$t_{\text{ss}} = 130 \frac{R_{\text{FPZ}}^2}{D}.$$

On the other hand, for the time t_Q^* when the source Q becomes noticeable, we have [4]

$$t_Q^* \geq 0.00386 t_{\text{ss}} \left(\frac{R_{\text{SIF}}}{R_{\text{FPZ}}} \right)^2. \quad (23)$$

Estimating the ratio $R_{\text{SIF}}/R_{\text{FPZ}}$ on the basis of the assumptions of fracture mechanics, we obtain $t_Q^* > t_{\text{ss}}$ for $E/\sigma_y > 161$, where E is Young’s modulus and σ_y is the yield stress of the material.

Thus, the far field can affect the K -driven hydrogenation of the fracture process zone well after the transient concentration falls within a 5% scatter band near the steady-state distribution of hydrogen in this area. Within this narrow 5%-wide strip in the vicinity of the steady-state limit C_∞ that defines K_{th} according to criterion (2), the hypothesis of K -control over the diffusion of hydrogen may be incorrect as shown in Fig. 4, where the dashed line schematically represents one of the possible C_f -curves. This may affect the $v(K)$ -curve only in its near-threshold part but without affecting the threshold K_{th} (see [4]).

Effect of History on the Phenomenon of K -Dominance in HAC

The processes of crack propagation and hydrogen diffusion should in no case be considered separately because the motion of a crack tip is explained by the accumulation of hydrogen in the fracture process zone. In terms of the theory of boundary-value problems, this situation is qualified as diffusion with moving boundary. Thus, the crack-growth *history* should be regarded as a factor capable of affecting the process of near-tip diffusion and, hence, the kinetics of HAC parallel with the stress-strain field represented by K . This also makes the idea of exclusive K -dominance over the process of HAC doubtful.

The effect of history of the coupled process of hydrogenation and cracking on K -dominance during HAC is studied in our previous research work [5, 6]. In [5], we develop the theoretical bases and perform a qualitative analysis demonstrating that the processes of hydrogenation and crack growth are coupled so that the crack growth rate in HAC is generally governed not only by K . The quantitative consideration is given in [6], where the condition of K -dominance is analyzed showing the significance of the effect of history that destroys K -control over the crack growth rate, although a special mode of steady-state crack growth is seen to exist for which HAC becomes a K -dominated process.

Coupling of Hydrogenation and Crack Growth. In this section, the process of HAC is analyzed in a *moving crack*. As in the remaining part of the work, we consider the case of sustained or quasistatic loading. The small-scale yielding condition near the crack tip is assumed to be valid for the entire process of cracking and, hence, the K -controlled mechanical autonomy of the near-tip region is supposed to be constantly preserved in the process of crack growth. Within the framework of the diffusion theory of HAC outlined in the previous sections, the analysis is restricted to the case of *stress-strain-assisted* diffusion regarded as the factor responsible for HAC.

We consider two approaches to the analysis of the process of cracking. According to the first approach, the crack grows discontinuously by a series of jump-like steps. The time intervals Δt between the discrete increments of crack length Δa are just the periods of accumulation of the amount of hydrogen required to satisfy criterion (2) in the fracture process zone. The crack growth rate is defined as

$$v = \frac{\Delta a}{\Delta t}.$$

According to the second approach, the crack grows continuously provided that criterion (2) is constantly satisfied at a distance x_c . In this case, the instantaneous crack growth rate is defined as

$$v = \frac{da}{dt}. \quad (24)$$

The jump-like and continuous approaches are usually regarded as essentially different from the viewpoint of the background physics. Despite numerous speculations trying to support one or another approach on the basis of physical reasoning, none is generally accepted as adequate to represent the process of crack growth.

Jump-Like (Discontinuous) Modeling of Crack Growth. This approach is used in Fig. 5, where we present schematic representations of the curves of hydrogen concentration near the crack tip after successive increments of crack length. The critical point x_c is supposed (for definiteness) to coincide with the place where the hydrogen concentration and stresses are maximum. The critical concentration must be attained at this point to produce a local event of rupture causing a jump-like crack increment. All variables are assumed to be determined *solely* by the material properties and K , i.e., remain constant if $K = \text{const}$. The process of crack propagation consists of a series of the following loops (cycles): “hydrogen accumulation–local rupture–crack advance.”

In each cycle of hydrogenation and fracture, certain amounts of hydrogen reach sites of possible future fracture process zones. Thus, the initial conditions for the diffusion of hydrogen within each particular loop are, in general, different from the preceding and subsequent cycles (Fig. 5). This shows that the diffusion of hydrogen is coupled with the process of crack growth. The near-tip diffusion of hydrogen depends on the entire history of HAC and, in particular, on the behavior of the crack size $a = a(t)$ and the time evolution of the stress intensity factor $K = K(t)$. Thus, K -dominance fails in the process of HAC because, for every instant value of K , the near-tip diffusion runs along its specific path originating at the beginning of a particular event of HAC.

Smooth (Continuous) Modeling of Crack Growth. This approach is useful for the analytic evaluation of the role of the history of coupled processes of hydrogenation and cracking in the K -control over all crack tip events.

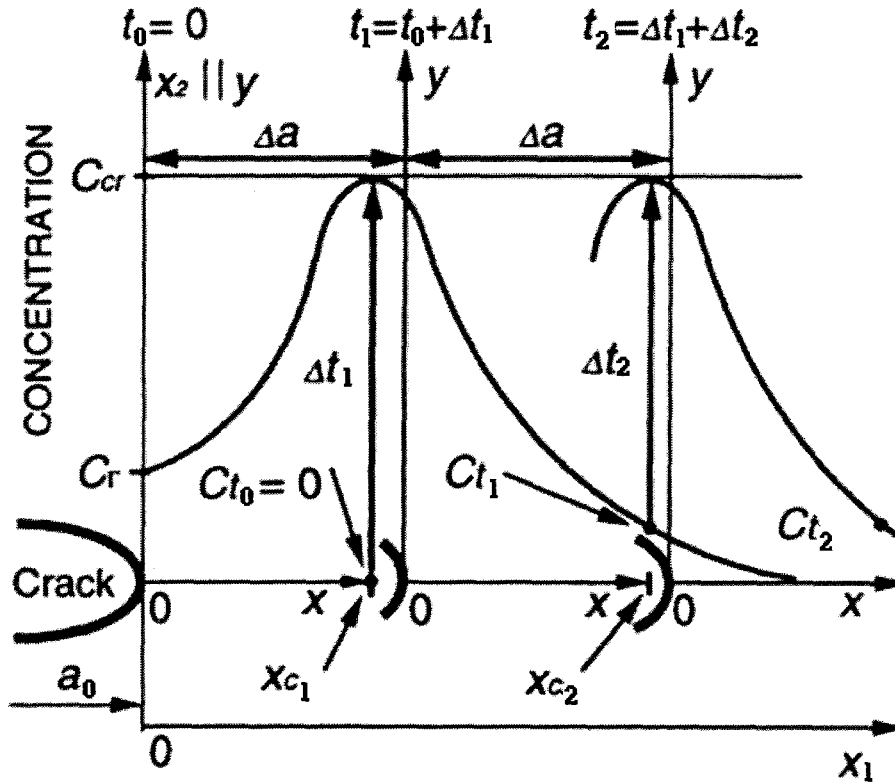


Fig. 5. Schematic diagram of the process of hydrogenation of the metal in the vicinity of the crack tip demonstrating that the processes of hydrogenation and crack growth are coupled.

The crack size is assumed to be a smooth function of time $a = a(t)$ and the crack growth rate is defined as its ordinary derivative (24). The concentration of hydrogen throughout the fracture process zone $C(x, y, t)$ is determined by the process of stress-strain-assisted diffusion. In an arbitrary fixed coordinate system (x_1, x_2) connected with the solid, it obeys the equation

$$\frac{\partial C}{\partial t} = -\nabla \cdot \left(\frac{D\bar{X}_D C}{RT} \right) \quad (25)$$

which follows from (10) and (12) with the vector of the driving force of diffusion given by (6) and (7), namely,

$$\bar{X}_D = -RT \nabla \ln \frac{C}{K_S} \quad (26)$$

If we consider the case of a moving crack, then it is convenient to study the problem of diffusion in a moving coordinate system (x, y) connected with the crack tip, i.e., $x = x_1 - a(t)$ and $y = x_2$. This results in a transformation of the diffusion equation (25) written in the coordinate system (x_1, x_2) connected with the solid. Thus, for the total time derivative of concentration, we get

$$\frac{d}{dt} C = \frac{\partial C}{\partial t} - \frac{da}{dt} \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} - v \frac{\partial C}{\partial x} \quad (27)$$

Substituting relation (27) in the left-hand side of Eq. (25), we arrive at a modified equation of stress-strain-assisted diffusion in moving coordinates in the form slightly different from the original one (25), namely,

$$\frac{\partial C}{\partial t} = -\nabla \cdot \left[\left(\frac{D\bar{X}_D}{RT} - \bar{v} \right) C \right], \quad (28)$$

where the vector $\bar{v} = v\bar{j}_x$ is independent of spatial coordinates and parallel to the x -axis [\bar{j}_x is its unit vector; in this case, $\nabla \cdot (\bar{v}C) = \bar{v} \cdot \nabla C = v\partial C/\partial x$].

By analogy with the actual thermodynamic force, the *fictitious driving force* of diffusion can be formally introduced in Eq. (28) as follows:

$$\bar{X}_D^* = \bar{X}_D - \frac{RT\bar{v}}{D}. \quad (29)$$

In view of expression (26), this yields

$$\bar{X}_D^* = -RT\nabla \left[\ln \frac{C}{K_S} + v \left(\frac{x}{D} \right) \right] = -RT\nabla \ln \frac{C}{K_S^*}, \quad (30)$$

where the formal solubility-like term has the form

$$K_S^* = K_S^*(\sigma, \varepsilon_p, v) = K_S(\sigma, \varepsilon_p) \exp\left(-\frac{vx}{D}\right). \quad (31)$$

To obtain solutions helpful for the analysis of the effect of history in the closed form, we simplify the equation under consideration by *neglecting the spatial variability of the coefficient of hydrogen diffusion* $D = D(\varepsilon_p)$, i.e., by assuming that D is a constant equal to the average value of $D(\varepsilon_p)$ over the zone of interest. As a result, the terms with ∇D in the diffusion equation vanish and we find

$$\frac{\partial C}{\partial t} = D[\nabla^2 C - \bar{M}^* \cdot \nabla C - N^* C] \quad (32)$$

with the following vector and scalar coefficients: $\bar{M}^* = \nabla \ln K_S^*(\sigma, \varepsilon_p, v)$ and $N^* = \nabla^2 \ln K_S^*(\sigma, \varepsilon_p, v)$.

Since the components of the near-tip stress-strain field are controlled by K , these coefficients depend not only on the spatial coordinates but also on K and the crack growth rate v regarded as parameters, i.e.,

$$\bar{M}^* = \bar{M}^*(K, v) \quad \text{and} \quad N^* = N^*(K, v). \quad (33)$$

Therefore, the solution of this problem depends not only on K but also on the crack growth rate v , namely, $C = C(x, t; K, v)$. The concentration of hydrogen in the vicinity of the crack tip is determined by the equation of stress-strain-assisted diffusion (32) with the following *boundary condition*: $C(x, t)|_{x=0} = C_\Gamma$, where the surface concentration $C_\Gamma = C_0 K_S|_{x=0} = \text{const}$. Moreover, the *initial condition* has the form $C(x, t)|_{t=0} = C_{t0}(x)$.

The crack growth rate v becomes an additional unknown variable that must be found from the solution of the *coupled* problem of hydrogen diffusion and crack growth. To complete the system of equations for this coupled process of diffusion and cracking, we use the criterion of crack growth (2). By using the distance x_c , for the *critical* and *actual* concentrations (17), we get

$$C_{\text{cr}} = C_{\text{cr}}(K, x_c) \quad \text{and} \quad C = C(x_c, t; K, v) \quad (34)$$

and the crack-growth criterion takes the form

$$C(x_c, t; K, v) = C_{cr}(K, x_c). \quad (35)$$

This formulation of the problem of diffusion and cracking is completely closed if the stress intensity factor K is known in a certain sense. In this case, if C is a solution of the diffusion equation (32) and depends on the crack growth rate v as a parameter, then the latter can be found from Eq. (35) as $v = v(K, t)$, i.e., the crack growth rate is a function not only of K but also of the total duration of the process of HAC t .

However, in most practical situations, K depends not only on the applied load but also on the crack length, i.e., $K = K(a)$ and, hence, the same is true for the coefficients (33) of Eq. (32). Hence, the crack length a turns out to be an additional unknown variable that should be determined from the solution of the coupled problem. The differential equation (24) for the crack size has the following obvious solution:

$$a(t) = a_0 + \int_0^t v dt. \quad (36)$$

The problem is reduced to the same equation as in the case $K = \text{const}$ but now Eq. (35) for the crack growth rate with $K = K(a)$ becomes not a function depending on v as a parameter but a functional of the entire *history* of the process. Similarly, the crack growth rate determined as a solution of this coupled problem of diffusion and cracking also becomes a functional depending on a certain history of the process with its individual $K(a)$ -variation. The variability of the crack growth rate for the same value of K is thus inevitable.

Revision of K -Dominance. By using the same formalism as for a stationary crack under sustained loading, expressing this solution in terms of the solubility coefficient K_S , and replacing this quantity by its analog $K_S^* [\sigma(x; K), \epsilon_p(x; K), v] = K_S^*(x; K, v)$, we construct an approximate solution for the process of diffusion near a moving crack tip as follows:

$$C(x, t; K, v) = C_0 K_S^*(x; K, v) \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right). \quad (37)$$

Taking into account the expression (31) for K_S^* , we get

$$C(x, t; K, v) = C_0 K_S(x; K) \exp \left(-\frac{vx}{D} \right) \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right). \quad (38)$$

In view of the criterion of crack growth (35), we arrive at the following equation that can be used to determine the crack growth rate v for a given value of K :

$$v(K, t) = -\frac{D}{x_c} \ln \left\{ \frac{C_{cr}(K, x_c)}{C_0 K_S(x_c, K) \operatorname{erfc} [x_c (2\sqrt{Dt})^{-1}]} \right\}. \quad (39)$$

This equation is physically meaningful only after a certain incubation period t_{in} , i.e., for $t \geq t_{in}$. For earlier times $t < t_{in}$, it gives negative values of the crack growth rate if the expression in braces in relation (39) is greater than one. This happens for the following incubation time:

$$t_{in} = \frac{1}{4D} \left[\frac{x_c}{\operatorname{erfc}^{-1}(C_{cr} C_\infty^{-1})} \right]^2, \quad (40)$$

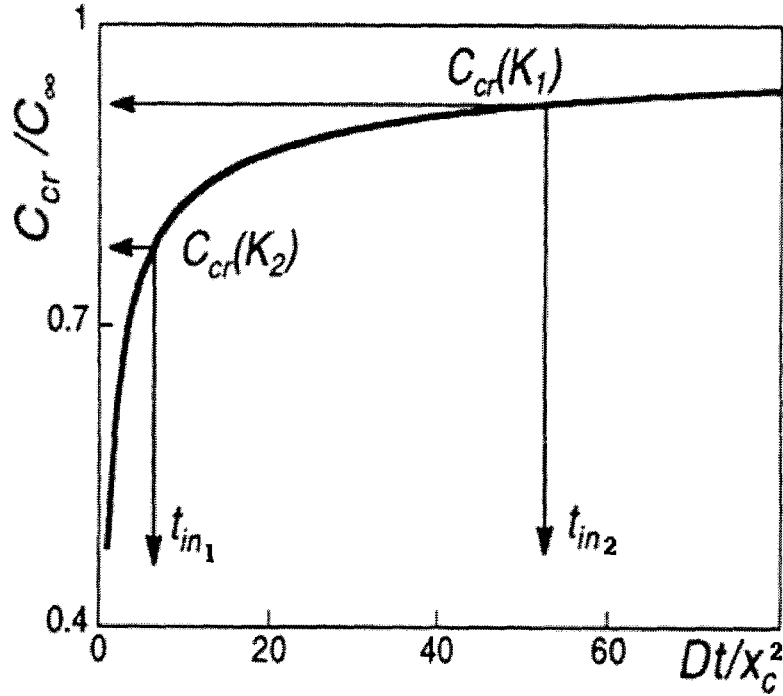


Fig. 6. Accumulation of hydrogen in a near-tip fracture site according to the solution of the diffusion problem for a stationary crack and a schematic diagram used to explain the behavior of the values of C_{cr} and t_{in} as functions of K (here, $K_2 > K_1$).

where $\operatorname{erfc}^{-1}(\cdot)$ is the function inverse to $\operatorname{erfc}(\cdot)$ and $C_\infty = C_0 K_S(x_c, K)$ is the exact steady-state solution for hydrogen diffusion near a stationary crack attained for a long period of time (as $t \rightarrow \infty$).

Within the range $K_{th} \leq K < K_c$ in the $v(K)$ -curve depicted in Fig. 1, we have $C_{cr}(K) \leq C_\infty(K)$, i.e., the argument of the function $\operatorname{erfc}^{-1}(\cdot)$ in (40) always varies between 0 and 1 where this function is defined. This is because, for HAC to occur, the critical concentration of hydrogen C_{cr} must be attained sooner or later and the steady-state concentration C_∞ is the maximum concentration that can ever be asymptotically attained for fixed K near a stationary crack.

In Fig. 6, we describe the time evolution of the concentration of hydrogen (38) for an initially immobile crack ($v = 0$). By applying criterion (2), or (35) with $v = 0$, to determine the time of the onset of crack propagation, we obtain exactly the same result as in (40) for t_{in} . Thus, the time limit at which the solution for the crack growth rate in the coupled problem of diffusion and cracking exists is equal to the incubation period prior to the onset of HAC.

It follows from relation (39) that the crack growth rate for fixed K is an increasing function of time which begins to grow from $v = 0$ at $t = t_{in}$ and asymptotically approaches the *steady-state* value v_{ss} as $t \rightarrow \infty$:

$$v_{ss} = -\left(\frac{D}{x_c}\right) \ln \left[\frac{C_{cr}(K)}{C_0 K_S(K)} \right] = \left(\frac{D}{x_c}\right) \ln \left[\frac{C_\infty(K)}{C_{cr}(K)} \right]. \quad (41)$$

Despite the approximate character of the analysis of the coupled problem of diffusion and cracking, it readily proves the intrinsic variability of values of the crack growth rate for fixed K described by relation (39). Hence, in general, the crack growth rate is not a single-valued function of K and the $v(K)$ -curve is not unique for a given material–environment system.

As for the *steady-state* mode of crack growth, all near-tip processes are time independent for the observer placed in the coordinate system moving with the crack tip. This obviously happens in the process of HAC due to the existence of the steady-state solution (with $\partial C / \partial t = 0$ and $\partial v / \partial t = 0$) of the coupled problem of diffusion and cracking considered above for constant K . The exact steady-state solution of Eq. (32) for a moving crack can be

obtained by the same method as in the case of a stationary crack, simply by equating the “fictitious driving force” (29) to zero. This gives

$$C_{ss}(x_c; K, v) = C_0 K_S^*(x_c; K, v). \quad (42)$$

By comparing this formula with estimate (37) of the nonstationary solution of the same equation, we conclude that the approximate solution (37), at least, approaches the exact steady-state distribution of concentration in the vicinity of a moving crack tip as $t \rightarrow \infty$. This means that the formal approximation of the nonstationary solution (39) is characterized by the correct asymptotic behavior.

For a given material–environment (material–hydrogen) couple, the steady-state crack growth rate (41) is a single-valued function of K and, thus, the kinetic curve of crack growth, as a plot of v_{ss} vs. K , possesses the uniqueness of a characteristic curve of the material. This stage of the process of HAC, i.e., the steady-state crack growth, appears to be indeed K -dominated.

CONCLUSIONS

The meaning and significance of the approach of linear elastic fracture mechanics to hydrogen-assisted cracking were revised for the case small-scale yielding and stationary cracks under sustained or quasistatic loading.

The influence of the *far field* on the near-tip diffusion of hydrogen is of minor importance. Actually, it may affect only the near-threshold part of the $v(K)$ -curve but has no effect on the threshold itself governed by K .

The effect of *history* appears in the form of coupling of the processes of hydrogen diffusion and crack growth and is accompanied by the loss of K -dominance over the crack growth rate v , although the K -controlled steady-state value v_{ss} exists.

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