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## **Controlling factors and mechanisms of fatigue crack growth influenced by high pressure of gaseous hydrogen in a commercially pure iron**

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### **CRedit author statement:**

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**Abstract:** this paper proposes an extended discussion of experimental results previously published by the authors and from literature about fatigue crack growth influenced by high pressure of gaseous hydrogen in a commercially pure iron. Firstly a summary of these results obtained for different exposure conditions in terms of gas pressure and loading frequency is presented. Two characteristic regimes, the first at low  $\Delta K$  values characterized by a moderated fatigue crack growth enhancement and a nearly fully intergranular mode, and a highly-accelerated regime with a quasi-cleavage failure mode with the formation of coarse striations. The mechanisms controlling the different regimes of Hydrogen-Assisted Fatigue Crack Growth are discussed on the basis of observations of fracture surfaces and of deformation substructures

within the plastic zone while assessing the capability of different models from literature to account for these observations. In a last section, the dependency of the transition between the different regimes as well as the crack growth rate enhancement in the highly-accelerated regime with respect to the hydrogen gas pressure and loading frequency is analyzed.

Keywords: hydrogen embrittlement; dislocations; intergranular fracture; quasi-cleavage fracture; hydrogen gas pressure; loading frequency

## 1. Introduction

It has been established for quite a long while now that Hydrogen Embrittlement (HE) decreases the durability of many structures exposed to environments which can act as a source of hydrogen atoms [1], in particular when they are additionally submitted to a mechanical loading [2, 3]. In an attempt to prevent catastrophic failures and improve the durability of these structures, a certain number of theories have been proposed over the decades to account for these effects of hydrogen on failure of engineering alloys, among which the Hydrogen-Enhanced DEcohesion (HEDE) [4], Hydrogen-Enhanced Localized Plasticity (HELP) [5, 6], the Hydrogen-Enhanced Strain-Induced Vacancies (HESIV) [7] and the Adsorption-Induced Dislocation Emission (AIDE) [8] mechanisms. Nevertheless one has to recognize that none of these theories is the object of a real consensus so far (see for instance [9, 10]) and it is nowadays common to consider, on the basis of experimental observations, numerical simulations or combination of both approaches, that HE results from a combination of some of these different mechanisms are active, either sequentially or in synergy [11-13].

The degradation of material performances exposed to a hydrogen-containing medium can furthermore be amplified in presence of a crack-like defect under cyclic loading. Indeed, it is well established that hydrogen atoms can interact with the cyclic crack tip deformation and the induced damage processes to substantially enhance the Fatigue Crack Growth Rate (FCGR) [14-16]. The issue of hydrogen embrittlement has recently received a renewed attention in the perspective of the development of hydrogen as a clean energy carrier. Indeed, in this framework, the integrity of structural components used in gaseous hydrogen transport and storage is a key issue, in particular for safety reasons. More particularly, regarding the effect of hydrogen gas on the cracking resistance of steels, various studies [17-20] have evidenced a significant increase of the fatigue crack propagation rates in the presence of gaseous hydrogen. This enhancement furthermore depends on loading conditions (value of the applied stress intensity factor range  $\Delta K$ , loading frequency  $f$ , ...) and gas pressure. Meanwhile the observations of the corresponding fracture surfaces generally reveal characteristic changes in fracture modes that provide insights into the role of hydrogen in failure mechanisms at a microscopic scale. Furthermore, the increasing demand for hydrogen-tolerance prognosis and assessment brings to the fore the need of reliable tools for accurate quantitative predictions of the various influences experimentally observed [21]. Such tools rely on the modelling of the various physical processes involved, and therefore require a sound understanding of these mechanisms and of their dependency upon different parameters. However, despite of significant progress on the connection between cyclic crack tip plasticity and the presence of hydrogen, details of the associated failure mode and FCGR enhancement still need clarification. As more specifically concerns  $\alpha$  iron-based materials, one of the key issues is related with possible hardening or softening induced by hydrogen [22]. It seems however that such effects (hardening versus softening) depend on different parameters

such as temperature, applied stress and hydrogen concentration [13, 22-24]. For instance, temperature will alternatively affects the mobility of screw or edge dislocations [22].

The present study was undertaken in an attempt to elucidate some of these issues for focusing on the fatigue crack propagation assisted by gaseous hydrogen at room temperature. A single-phase, fully ferritic microstructure with a good affinity with hydrogen was selected in this aim. Fatigue Crack Growth (FCG) tests were conducted under high pressure of hydrogen gas at various frequencies in order to make the exposure of the crack tip to hydrogen gas vary and evaluate the impact on crack growth resistance. The experimental details, the test results and observations are reported in [25-27] and will be only briefly summarized here. The main purpose of the present paper is to provide a detailed discussion of these findings by integrating the different facts and associated insights. It aims by this means in elucidating the mechanisms of fatigue crack propagation under gaseous hydrogen and its dependency on different parameters, namely hydrogen pressure, frequency and stress intensity range, in particular through a critical assessment the capability of the aforementioned mechanisms to account for the observed phenomena or through the proposal of alternative explanations.

## **2. Discussion of Hydrogen-Assisted Fatigue Crack Growth**

### **2. 1. Summary of fatigue crack growth test results**

Figure 1 presents the  $da/dN$  vs.  $\Delta K$  curves established after testing under a gaseous hydrogen pressure of 35 MPa at three different loading frequencies (20 Hz, 2 Hz and 0.2 Hz), compared to the data collected at a frequency of 20 Hz under vacuum, considered as an inert environment, and laboratory air and nitrogen considered as mildly aggressive atmospheres [28].

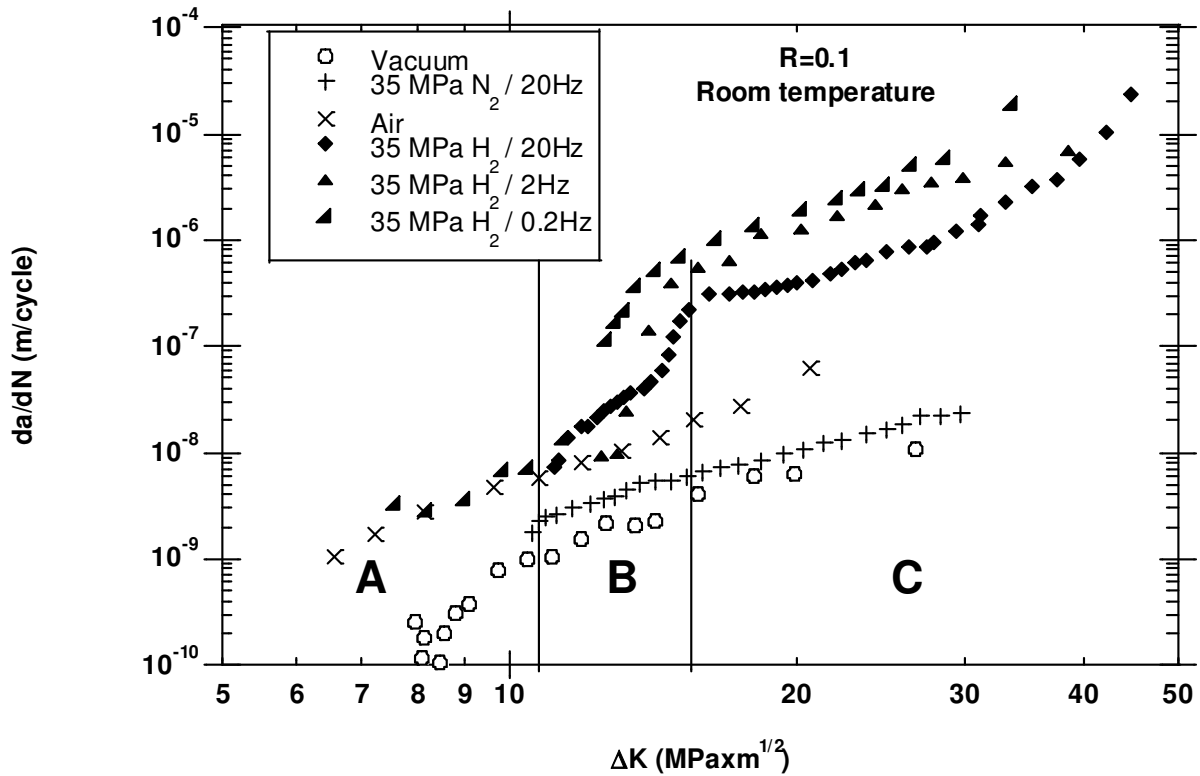


Figure 1. Influence of gaseous hydrogen on FCGRs at different loading frequencies in ARMCO iron (from [25, 27]).

Firstly, it can be noticed that, in the  $\Delta K$  range under consideration, the FCGRs in nitrogen and in air are only slightly enhanced with respect to vacuum. These results are consistent with previous data and the observed enhancement in air and nitrogen can be attributed to the effect of residual moisture [28]. As regards the propagation under high pressure gaseous hydrogen, namely 35 MPa, the FCG curves exhibit a different shape, irrespective of the loading frequency. Indeed, three characteristic propagation regimes can be identified in these curves.

- Regime A (moderately-accelerated regime): At low  $\Delta K$  values ( $\Delta K < 11 \text{ MPa} \times \text{m}^{1/2}$ ), FCGRs in the hydrogen gas are similar to those measured in air, regardless of the loading frequency, and as a consequent only moderately enhanced with respect to nitrogen and

vacuum. Additionally a salient feature of this regime resides in the fact that the fracture surface is almost entirely covered by intergranular facets which are not observed during cracking in air or nitrogen. Another interesting aspect of this regime is related to the presence of regular stripe-like markings crossing the intergranular facets. It has been verified that loading frequency has no effect on the spacing between markings for a given  $\Delta K$  value. In any case, the nearly-constant spacing (about 0.5  $\mu\text{m}$ ) is much larger than the crack advance per cycle [27]. Besides, a significant amount of plastic deformation is accumulated in the grains beneath the intergranular facets. This has been evidenced by the presence of dislocation cell substructure and microvoids immediately beneath the fracture surface as in the case of the more ductile fracture produced in air [26].

- Regime B: In a quite narrow  $\Delta K$  range, typically for  $11\text{MPa} \times m^{1/2} < \Delta K < 14\text{MPa} \times m^{1/2}$ , and for the pressure under consideration, an abrupt transition is noticed in the  $da/dN$  versus  $\Delta K$  curves, in association with a sharp FCGR enhancement dependent on the frequency but of at least one order of magnitude. The propagation then returns to a purely transgranular mode near  $\Delta K = 11\text{MPa} \times m^{1/2}$ , that means just before the sharp increase in FCGRs.
- Regime C: Beyond this transition, the FCGRs achieved are approximately 10 to 30 times higher than in air, depending on loading frequency with a Paris law exponent similar to the ones observed under vacuum, nitrogen and air. The fracture surfaces are nearly fully transgranular in nature, with the progressive apparition of particularly well-defined, coarse striations at low frequency. The striation spacing is furthermore consistent with the macroscopic FCGR.

The same conclusions qualitatively hold for different pressure values (typically 3.5 MPa) [29], but the  $\Delta K$  value at the transition and the FCGR in the highly accelerated regime are affected. The different results of fatigue crack properties and failure modes under gaseous hydrogen are summarized in Table 1 a for  $P_{H_2}=35MPa$  and Table 1 b for  $P_{H_2}=3.5MPa$  by organizing the results in terms of various values of  $\Delta K$  and  $f$ . The unknown information are shown as blank in this table.

The following sections aim in analyzing the hydrogen-related mechanisms controlling these different regimes (A, B and C) and the role played by different test parameters such as pressure and frequency.

*Table 1: Summary of fatigue crack growth properties under gaseous hydrogen at various  $\Delta K$ ,  $P_{H_2}$  and  $f$  (data from [25-27, 29]).*

(a)  $P_{H_2} = 35$  MPa

| Regime<br>( $\Delta K$ range<br>[MPa $\times$ m <sup>1/2</sup> ])             | Non-<br>accelerated<br>( $\Delta K < 12$ )  | Transition<br>( $12 < \Delta K < 15$ ) | Accelerated ( $15 < \Delta K$ )                         |                                     |
|---|---|--|---|-------------------------------------|
|   |   |  | $f \geq 0.2$ Hz   | $f = 0.02$ Hz                       |
| FCGR  | Not enhanced<br>(or only slightly enhanced) | Enhanced                               | Enhanced  | Less enhanced                       |
| Fracture mode   | IG  | IG + QC                                | QC  | QC with larger cleavage-like facets |
| Cyclic crack tip plasticity<br>(compared to the one in the inert environment) | -   | Reduced                                | Reduced   | No change                           |
| Dislocation structure   | Cell structure<br>(2 Hz)                    | -                                      | Dislocation tangles +<br>Dislocation walls connected to | Cell structure                      |



|  |  |  |                         |  |
|--|--|--|-------------------------|--|
|  |  |  | striation<br>(20, 2 Hz) |  |
|--|--|--|-------------------------|--|

(b)  $P_{H_2} = 3.5$  MPa

| Regime<br>( $\Delta K$ range<br>[MPa $\times$ m <sup>1/2</sup> ])             | Non-accelerated<br>( $\Delta K < 15$ ) | Transition<br>( $15 < \Delta K < \text{Unknown}$ )                        |                          | Accelerated<br>(Unknown<br>< $\Delta K$ ) |
|---|--|---|--------------------------|---|
|   |  | $f \geq 2$ Hz   | $f \leq 0.2$ Hz          |   |
| FCGR  | Not or slightly enhanced               | Enhanced  | Not or slightly enhanced | -   |
| Fracture mode   | IG + Ductile TG                        | QC  | Ductile TG               | -   |
| Cyclic crack tip plasticity<br>(compared to the one in the inert environment) | -                                      | Reduced   | No change                | -   |
| Dislocation structure   | -                                      | Dislocation tangles +<br>Dislocation walls connected to striation (20 Hz) | Cell structure (0.02 Hz) | -   |

(IG: Intergranular, QC: Quasi-cleavage, TG: Transgranular, -: Unknown)

## 2. 2. Mechanism of hydrogen-induced intergranular fracture in the moderately-accelerated regime (regime A)

It has to be reminded that in regime A the FCGRs are almost identical to the ones determined in air, and are only moderately enhanced with respect to nitrogen or vacuum, thereby suggesting a limited effect of hydrogen on deformation and damage mechanisms taking place at the crack tip. However this is somehow contradicted by the drastic change in fracture mode, shifting from fully transgranular in nitrogen to almost entirely intergranular in hydrogen. In addition intergranular failure as observed in hydrogen gas might advocate for a prevailing role of decohesion

presumably induced by hydrogen. However, on the basis of molecular dynamics simulations, Wang et al. [30] concluded that the reduction in the cohesive strength of the grain boundary cannot account by itself for intergranular failure that would require a contribution from additional mechanisms. However some other research works [31, 32] pertaining to hydrogen embrittlement in nickel indicate that grain boundary decohesion can indeed be achieved. One of the major differences in the computations presented in [31] is to consider the formation of a 3 atomic layer structure, instead of 1 layer in [30], in the H-enriched region at the crack tip.

In an attempt to clarify this point, the mechanism responsible for this hydrogen-induced intergranular fracture without significant effect on FCGR is discussed in this section. On the basis of different observations, a scenario of the hydrogen-induced intergranular fatigue crack growth, schematically represented in Figure 2, is proposed as follows.

1. During cyclic loading, hydrogen molecules are adsorbed at the crack tip. After dissociation, solute hydrogen atoms diffuse in the volume ahead of the crack tip but can also alternatively be dragged along slip planes by dislocations put in motion during loading (Figure 2a).
2. Dislocations accumulate ahead of the crack tip during cyclic deformation, partly due to the relatively low FCGR so as to form a characteristic cell structure. Meanwhile, since the grain boundaries may act as a barrier for the dislocation mobility [33], some of the mobile dislocations carrying hydrogen atoms can be blocked and then pile-up at the intersections of the dislocation walls and the grain boundary. This could be the cause for a local hydrogen enrichment along grain boundaries (Figure 2 b).

3. The highly accumulated dislocations and hydrogen atoms additionally induce the nucleation of vacancies at the grain boundary, for instance by the HESIV mechanism [34]. Such an aggregation of the vacancies in turn generates microvoids, as evidenced analytically [34-36] and experimentally on mating surfaces [37] and as Figure 2c.
4. Eventually, the presence of microvoids and of segregated hydrogen atoms at the grain boundaries weaken the bonding energy of the grain boundary, favoring a failure along the grain boundary by decohesion and microvoid coalescence with respect to transgranular cracking. This type of grain boundary decohesion process has been highlighted by atomistic simulations [38, 39]. It is noteworthy that the microvoids are supposed to be linearly arranged in the depth-direction of this illustration since the intersection of slip plane and grain boundary would be a line parallel to the crack front edge. Therefore, the trace of the microvoids is possibly observed as stripe-like markings perpendicular to the crack growth direction on the intergranular facets (Figure 2 d).

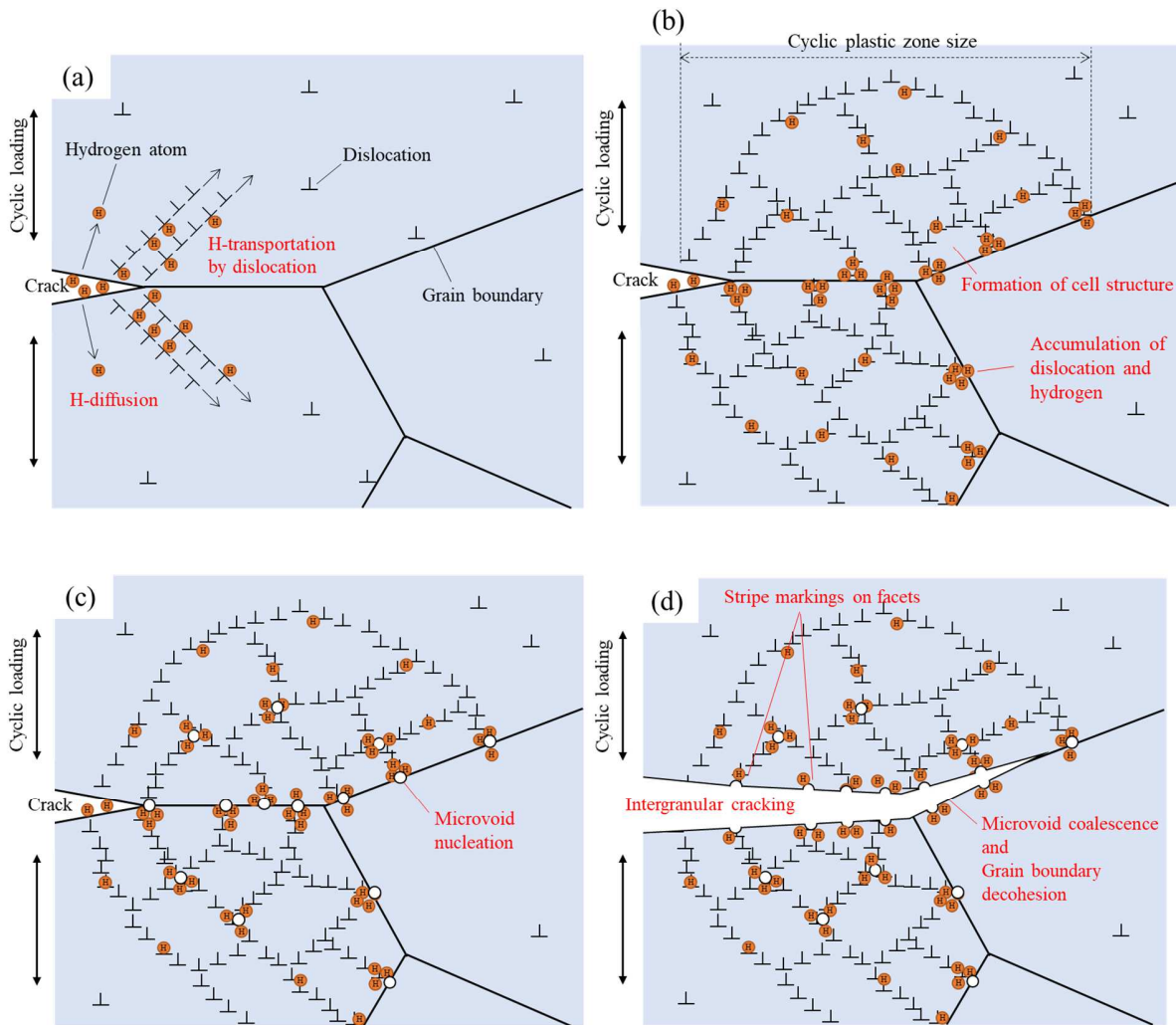


Figure 2: Schematic illustration of the proposed model of hydrogen-induced intergranular fracture mechanism (inspired from [40], see the text for detailed interpretation).

A similar approach has recently been proposed by Ogawa et al. [40] to account for this intergranular failure regime on the basis of experimental results in pure iron which are mostly consistent with this study. In particular they observed a dislocation structure beneath intergranular fatigue fracture surface in pure iron by STEM in the same way, and confirmed the presence of dislocation cell structures and microvoids [40, 41], in accordance with the results obtained in the present study [26]. It is also noteworthy that such dislocation cells have been

reported in the vicinity of a fatigue crack by Awatani et al. [42]. However, a change in the dislocation cell size induced by hydrogen, such as suggested by Ogawa et al. [40, 41] or Wang et al [43] , was not clearly confirmed in the present STEM observations. Actually, it is difficult to conclude about a global characteristic of dislocation structure by referring to a limited number of STEM observations because of the small size of STEM observation area. The dislocation structure observed within this very limited area is typically related to a single grain with a given orientation, grain size, and so on. Ogawa et al. [24, 25] additionally provide the Grain Reference Orientation Deviation (GROD) mapping near the crack path by means of the EBSD analysis so as to analyze the plastic strain distribution in the scale of hundred microns. The results indicate that the extent of plastic strain distribution near the intergranular crack path in hydrogen is almost the same as in air, and in any case not clearly greater. A salient feature of this regime is the formation of markings on the intergranular facets, even though it is difficult to state on whether the markings are associated with the root cause of intergranular failure, and therefore related to hydrogen, or just revealed by the intergranular failure and in that case not directly affected by hydrogen. Nishikawa et al. [37], established in the case of a low carbon steel a relation between slip bands induced by intragranular slip, and the presence of striation-like stripes on intergranular facets as observed here in pure iron. According to these authors, intragranular slip might be influenced by hydrogen, but it remains that it is difficult to definitely conclude about a possible intragranular plasticity enhancement inducing intergranular cracking. On the basis of in-situ diffraction measurements, Connolly et al. [44] attributed a difference in the peak broadening to the formation of dislocation pile-ups along the grain boundaries that would be induced by a HELP mechanism, leading to a depletion in the dislocation density in the grain interior with respect to the situation in air. The intergranular cracking process itself would be however controlled by a HEDE mechanism, designated as “IG-HEDE”, but could be regarded as a HELP+HEDE

synergistic action [11] of a basically HEDE process mediated by intragranular plasticity enhanced by HELP as suggested in [45, 46]. However, again, the activation of such an “IG-HEDE” mechanism would conduct to much higher FCGRs which are not observed here. Nishikawa et al. [37] noticed that such stripes present a “peak-to-valley” correspondence on mating surfaces, which, according to these authors, support a role of intragranular slip on the formation of these traces. Similarly Wang et al. [43], on the basis of the dislocation cell structure analysis beneath an intergranular fracture surface in hydrogen-charged pure iron, proposed the fracture model based on “hydrogen enhanced plasticity-mediated intergranular decohesion”. It is worth noticing that they did not observe stripe-like markings on the intergranular facets similar to the ones observed in the present study and also observed in hydrogen-assisted intergranular fracture of nickel [47]: however the severe electro-charging may have erased such markings initially present on the facets [48]. They argued that the stripe-like markings are produced as a result of extrusions at the grain surface due to slip band formation in the grain interior, that is different from the present argument and the one proposed by Ogawa et al. [40]. As the STEM observations performed in the present study [26, 27] did not confirm a presence of ladder-like dislocation structure which is a typical microstructure of the persistent slip bands (PSBs), the proposal of “hydrogen-induced plasticity-mediated intergranular decohesion process” by Wang et al. [43] is not fully supported by the present results. Recent findings by Harris et al. [49] on intergranular fracture in nickel may also advocate against a contribution of hydrogen-dislocation interactions to intergranular fracture. Indeed they showed that intergranular decohesion is also observed in tensile failure of precharged samples at 77K, that means under conditions where interactions between mobile hydrogen atoms and moving dislocations are inactive. However it has to be pointed out that, prior to testing, the precharged samples were maintained at room temperature so as to ensure equilibrium hydrogen concentrations at grain boundaries, which

represents a clearly different situation from the one envisaged here. Regardless of the previous considerations, a key question remains: despite such a drastic shift in the fracture mode from transgranular to intergranular due to the presence of hydrogen, the FCGRs are not drastically changed as compared to air in regime A. One possible explanation for this is that the same level of crack-tip strain energy, as characterized by the deformation substructure, might be required for triggering both types of cracking. It is noteworthy that similarly, in the near-threshold regime in air, a variation in the percentage of intergranular facets which are not observed in vacuum, has no effect on FCGRs [50-52], even though in such cases the percentage is far less than 100%. Again, the TEM observation of dislocation structures [26] indicates that the same degree of plastic strain was imparted to the material during the crack propagation, which is consistent with the similarity in FCGRs, while it is still difficult to determine which point is the consequence of the other one. On the other hand, Ogawa et al. [40] explained this issue by referring a competition of two different effects of hydrogen: material softening (resulting in FCG deceleration) and material hardening (resulting in the FCG acceleration), occurring at the same time. More recently, Ogawa et al. [53] revisited this issue by considering the impact of temperature variation on this regime. It is shown that the FCGR enhancement in regime A is actually mitigated by temperature but closely related to the amount of intergranular facets. According to the authors, the degree of enhancement would be related to the coverage rate of grain boundaries by hydrogen atoms. It could also be argued that the global crack growth response exhibited in this hydrogen-assisted regime is the balance between fatigue crack growth enhancement induced by gaseous hydrogen and enhanced crack-tip shielding by roughness-induced crack closure due to intergranular fracture. For instance Esaklul et al. [54] report that the effect of internal hydrogen in the low  $\Delta K$  range is only sensible when crack-closure effects are taken into account. In the present study,

crack-closure effects were not continuously monitored but the data available do not indicate any substantial difference with respect to air

### 2. 3. Mechanism of hydrogen-induced QC fracture in the accelerated regime

The mechanism of hydrogen-induced QC fracture in the accelerated regime (regime C in Figure 1) is discussed in this section. The important features of this fracture mode as characterized in [26, 27] are summarized as follows.

- The brittle QC fracture occurs at relatively high  $\Delta K$  values, depending on the hydrogen gas pressure;
- The FCGR in hydrogen is highly enhanced as compared to the one observed in air (Figure 1);
- This FCGR enhancement is accompanied by a significant reduction in cyclic crack tip plasticity in particular evidenced by the reduced plastic deformation near the crack path [27] and the dislocation structure, with a random distribution of dislocation tangles immediately beneath the fracture surface. Typically, according to Awatani et al. [42], no significant change is expected in the near-tip dislocation structure in air when the  $\Delta K$  value is raised in air, which suggests that the observed structure is a consequence of the presence of hydrogen. However it should be pointed out that these findings are different from those reported by Wang et al. [55] indicating that the same mechanism than in air is operative in presence of hydrogen which enhances the formation of the structure.

Based on these experimental facts, a scenario of brittle QC fracture in the accelerated regime schematically described in Figure 3 is proposed as follows.



1. Before the loading increases, hydrogen atoms are absorbed from the crack surface and diffuse ahead of the crack tip (Figure 3 (b-1)).
2. Once the mechanical loading is raised, intense slip deformation of the crack tip causes crack tip blunting accompanied by plastically deformed zone ahead of the crack tip in vacuum, but also at a lower extent in air and nitrogen (Figure 3 (a-2)) [56, 57], leading to the formation of ductile striations [58]. In contrast, in the presence of hydrogen, the solute hydrogen atoms concentrated at the crack tip, for instance in high hydrostatic stress field [59], inhibit the plastic deformation at the crack tip. The mechanism could be a suppression dislocation nucleation [60, 61] and mobility [22, 23, 61-64] by hydrogen, but could also be associated with a contribution of the AIDE mechanism [9, 58, 65] (Figure 3 (b-2)). In any case, the crack tip is maintained sharp due to the crack tip plasticity reduction. The hydrostatic stress intensity ahead of the crack tip is further enhanced due to the sharp crack tip, inducing higher hydrogen concentration. In a synergy effect, hydrostatic stress and hydrogen concentration could thus rapidly enhance each other. The same effect may hold when considering the AIDE mechanism [8], which, due to the slip localization at the crack tip, induces a greater crack-growth increment per cycle and a reduced crack-tip blunting during loading in conjunction with the formation of 'brittle' striations [58].
3. When critical conditions are satisfied at the crack tip, in particular in terms of stress intensity and hydrogen concentration, , crack growth takes place by a cleavage-like fracture process (Figure 3 (b-3)). Such a process is supported by a molecular dynamics simulation by Matsumoto et al. [22]. The cleavage fracture takes place along {100} plane in case of BCC lattice because it is the weakest plane. It continues until the crack tip advances to the place containing insufficient amount of hydrogen concentration to maintain the atomic decohesion. By such, and by the consideration of critical concentration, this step can be classified as a

HEDE-dominated of possibly (HELP+HEDE) effects according to [11]. Similarly it could be consistent with the so-called “T-HEDE” (Transgranular HEDE) mechanism described by Connolly et al. in [44]. Indeed, from in-situ measurements of dislocation density at the crack, they derive an estimation of the effective stress intensity factor which exhibits a sharp variation consistent with the modification of the crack tip sharpness evidenced by in-situ observations and the variation of fatigue crack growth rates as influenced by H<sub>2</sub>. This T-HEDE process reflects a transgranular decohesion cracking process induced by the hydrogen environment.

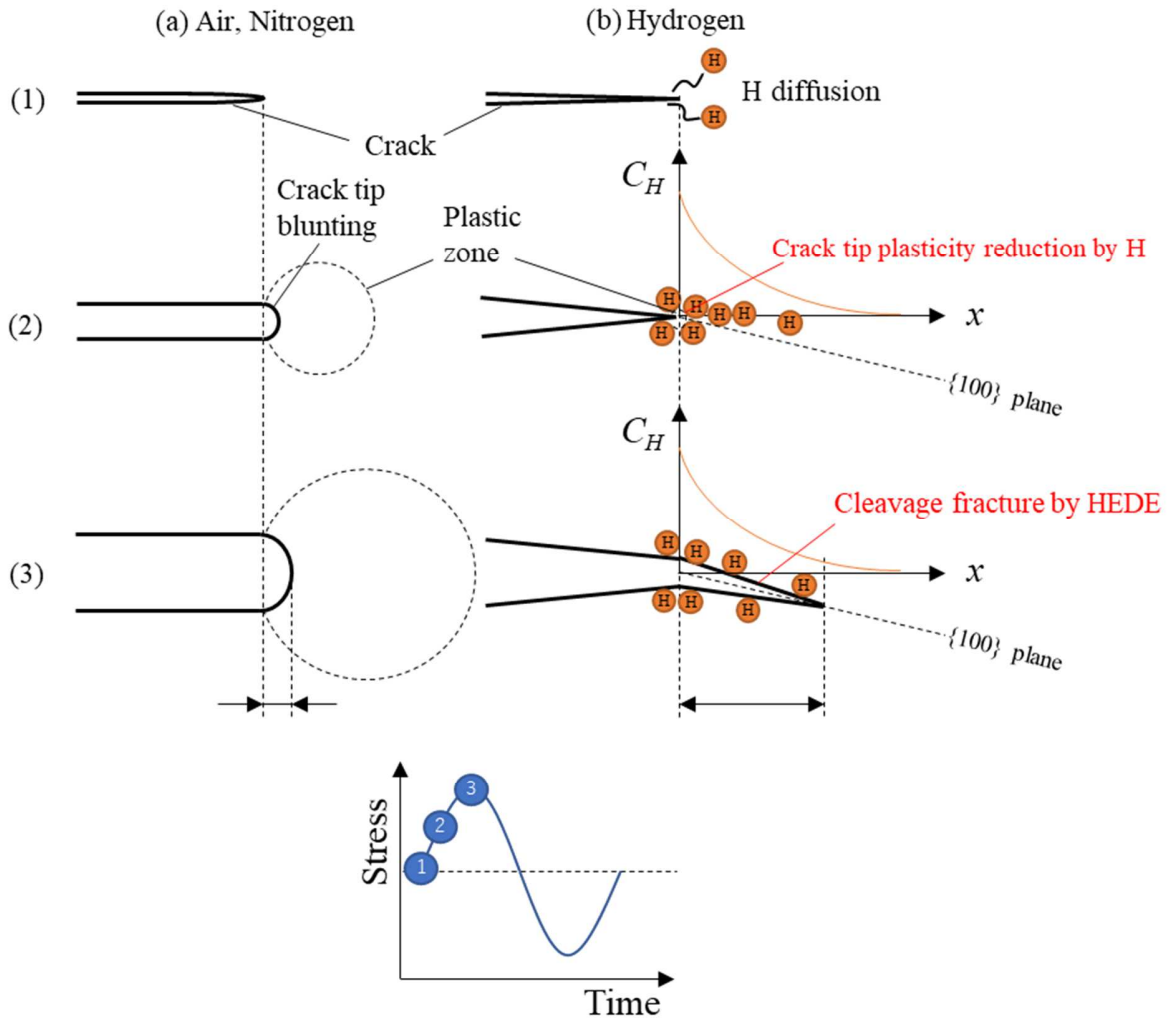


Figure 3: Schematic illustration of standard FCG model in air or nitrogen (a) and the present model of hydrogen-induced cleavage-like fracture mechanism (b).

Different models of the hydrogen-induced QC fracture have been proposed to account for the hydrogen-induced quasi-cleavage crack growth, as summarized for some of them in [66].

Thus, in the HESFCG model proposed by Matsuoka et al. [67, 68], the localization of plastic deformation near the crack tip is associated with the FCGR enhancement in hydrogen-charged

austenitic stainless steel and low carbon steel, by observing the suppression of slip deformation near the crack path and the presence of brittle-like striation on the fracture surface. Based on these experimental results, the proposed scenario of FCG with the presence of hydrogen assumes that during loading stage of cyclic loading, hydrogen diffused from the crack tip is concentrated in the high hydrostatic stress field ahead of the crack tip. Highly accumulated solute hydrogen then enhances the localization of slip deformation within the limited zone ahead of the crack tip, which is much smaller than the case in air, resulting in the inhibition of extended crack tip blunting like in vacuum. Consequently, the sharp crack tip continuously advances by intense slip deformation during the rising part of cyclic loading. From this point of view this model is not fundamentally different from the AIDE mechanism [9, 58, 65], except that the localization is induced by hydrogen trapped in a few subsurface layers instead of accumulated in the high hydrostatic stress field at the crack tip. It is noteworthy that a significant FCGR enhancement at high  $\Delta K$  values, similar from a phenomenological point of view to the behavior observed in HAFCG here, and accompanied by a modification of the fracture mode and the disappearance of intergranular fracture, has been observed in the case a martensitic steel fatigued in a liquid lead-bismuth eutectic at 300°C [69].

In the hydrogen-induced cyclic cleavage model proposed by Marrow et al. [70], it is assumed that when the applied loading is raised, dislocations are emitted from the crack tip and the crack tip starts blunting. As a consequence, a high hydrostatic stress field with a high dislocation density is formed in front of the crack tip. Subsequently, the diffusing hydrogen atoms are intensely trapped within this field. The highly accumulated hydrogen atoms reduce the lattice cohesive energy, and consequences a cleavage fracture by a HEDE-type mechanism. This model states that an intense plastic strain field ahead of the crack tip is required to achieve the high

hydrogen concentration, even though the basic cracking mechanism is atomic decohesion without accompanying the plastic deformation of the crack tip.

The hydrogen-induced void-coalescence model was proposed by Nishikawa et al. [71]. This model assumes that, when the loading is applied, the interaction between hydrogen and the plastically deformed zone ahead of the crack tip generates a high density of microvoids by the HESIV mechanism. Consequently, ductile tearing occurs between the microvoids, leading to microvoid coalescence and crack growth. Although the hydrogen-induced cyclic cleavage model by Marrow et al. [70] involves the same fracture process, i.e. cleavage, it assumes the plastically deformed zone with high density of dislocation ahead of the crack tip as a trapping site of hydrogen, which contradicts the observation in this study in that sense that the dislocation density is not high. Takahashi et al [72] furthermore discard the “cyclic cleavage” wording, in particular by showing that the flat facets separating the tips of brittle striation are not crystallographically related with {100} cleavage planes.

On the other hand, Birenis et al. [66, 73] have recently proposed a hydrogen-induced cyclic cleavage model driven by the reduction of crack tip plasticity, which is very similar to the present one. They identified the crack tip plasticity reduction due to hydrogen by a fractography and analyses of plastic strain distribution around the crack by EBSD and STEM. The main difference between their model and the present one is that their model does not involve the bonding energy reduction of matrix atoms by the HEDE mechanism while the present one does. At the moment, it cannot be clearly concluded whether the HEDE mechanism is operating or not. Since the activation of HEDE mechanism requires very high hydrogen concentration and stress concentration [26], in order to clarify the involvement of the HEDE mechanism, it may be

effective to investigate quantitatively whether such condition is satisfied at the actual fatigue crack tip.

Finally, as pointed out in [11], the dominance of a HEDE mechanism in no way allows to prejudge about the activity of the other plasticity-enhanced mechanisms mentioned in the introduction. Typically, the scenario presented in Figure 3 for cleavage-like fracture with a reduction in crack tip blunting is also to some extent consistent with the AIDE mechanism, without excluding additional contributions from the HELP or HEDE mechanisms [74]. The AIDE mechanism is based on the effect of hydrogen adsorbed at the surface or located in the interstitial sites of the first few atomic layers from the surface. It assumes that these two groups of hydrogen atoms locally weaken the interatomic bond and therefore and promote the dislocation emission from the crack tip. This is different from the classical ductile cracking process where dislocations are essentially emitted from the volume of the material by Frank-Read sources to produce blunting but only a small proportion of them interact with the crack front to cause a fracture or the void nucleation. Besides, the nucleation of microvoids ahead of the crack is facilitated and it assists the crack propagation. The microvoid coalescence produces small dimples on the fracture surface. Typically, the dislocation structure observed in this highly-assisted regime is much less developed than in air while FCGRs are much higher. This structure can be envisaged as a preliminary stage in the formation of the cell structure observed in air. The completion of the development of this cell structure would in that case be prevented by some premature failure at the crack tip, for instance by a HEDE process, or by a higher efficiency of the crack-tip dislocation activity in terms of crack advance as advocated by the AIDE mechanism. The interesting point is that when FCGR is highly enhanced by hydrogen gas, especially at high

frequency, the crack advance per cycle is so large that it might be difficult to envisage how hydrogen could influence the failure process over such a large distance only by diffusion.

#### 2. 4. Transition from intergranular to transgranular fracture

Although the mechanisms controlling the two main types of HAFCG have been discussed in the previous sections, an inevitable question is related to the huge FCGR enhancement associated with a drastic change in the fracture mode from the intergranular fracture to the transgranular one in a narrow  $\Delta K$  range. A possible clue to answer this question is the presence of two different hydrogen effects: in the moderately-accelerated regime, no clear modification of the crack tip plasticity by hydrogen was observed whereas, in the highly-accelerated regime, a reduction of the crack tip plasticity was noticed, resulting in the absence of dislocation cell structure as formed in air in the same loading conditions. This sudden and radical change in crack tip plasticity has to be compared to the findings reported in [75], suggesting that the observed loss of ductility is not only due to a decrease in cohesion but also to a kind of extinction of the processes of local plasticity assisted by hydrogen. Regarding this issue, a noteworthy finding from the molecular dynamics simulations by Taketomi et al. [23, 76] is that the hydrogen effect on dislocation activity changes, depending on the hydrogen concentration and the stress level. Specifically, the increase in dislocation velocity (resulting in softening) occurs at lower hydrogen concentration or lower applied stress conditions. In contrast, the decrease in dislocation velocity (resulting in hardening) occurs at higher hydrogen concentration or higher applied stress conditions. This fact may provide an explanation to the transition from the intergranular fracture mode to the transgranular one as follows. When the  $\Delta K$  value is lower than the value at the onset of the transition  $\Delta K_{tr}$  (i.e. in the non-accelerated regime), as the crack tip stress intensity is low, the

solute hydrogen atoms in the vicinity of the crack tip enhance the dislocation mobility (which might be a little effect because it is not clearly confirmed in the present study). Consequently, the interaction between the enhanced dislocation activity and solute hydrogen atoms leads to the intergranular fracture process as proposed. When  $\Delta K$  reaches the  $\Delta K_{tr}$  value (i.e. at the onset of the transition regime), the crack tip stress intensity becomes sufficiently high to allow the solute hydrogen to decrease the dislocation mobility. This inhibits the crack tip blunting and induces the synergetic increases in the hydrostatic stress intensity and the hydrogen concentration ahead of the crack tip. This results in the cleavage fracture as assumed by the present model of the hydrogen-induced QC fracture.

### 3. Controlling parameters

#### 3.1. Dependencies of HAFCG on $\Delta K$ and hydrogen gas pressure

The dependency of HAFCG on the testing parameters,  $\Delta K$ , the hydrogen gas pressure  $P_{H_2}$ , and the loading frequency  $f$ , is here discussed. Since these testing parameters strongly affect the hydrogen diffusion behavior in the material, it is important to consider the hydrogen diffusion and concentration ahead of the crack tip under various testing conditions to investigate the mechanisms of the dependencies. As pointed out in [11], the concept of “critical hydrogen concentration” locally achieved is somehow fuzzy and generally does not differentiate between the total or average concentration and the local concentration. However this concentration required for the HEDE activation is assumed to be much higher than the concentration of hydrogen dissolved in the bulk [77-79]. The consideration of advanced models with the use of strain gradient plasticity [80] indeed indicates a higher local concentration of trapped and diffusible hydrogen, but does not fundamentally affect the response at the crack tip during fatigue



[81]. The objective in this section is not to propose a detailed model of the diffusion and trapping processes at the crack tip but mainly to propose a simple one-dimensional description of the competition between hydrogen penetration and crack advance.

For this purpose, in order to investigate a possible cause and effect relationship between the testing conditions and the diffused hydrogen concentration  $C_H$  ahead of the crack tip, the hydrogen diffusion from the crack tip during one loading cycle has been estimated by the following calculations. The hydrogen concentration  $C_H$  in the material was calculated by the one-dimensional Fick's diffusion law in a semi-infinite plane surface subjected to a hydrogen concentration  $C_s$  at its boundary as [82]:

$$C_H(x, t) = C_s \left\{ 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right\} \quad \text{Equation 1}$$

where  $x$  is the distance from the surface of the semi-infinite plane,  $t$  the time, and  $\operatorname{erf}$  the error function. This equation is the approximated function of Fick's diffusion law by the error function. The value of  $D$ , the diffusion coefficient, was taken as  $2.5 \times 10^{-10}$  m<sup>2</sup>/s [83]. The variation of  $C_H$  is considered for one loading cycle period, *i.e.* for  $t$  ranging from 0 to  $1/f$  [s]. The saturated hydrogen concentration at the surface  $C_s$  is obtained by the Sievert's law [84]:

$$C_s = S_0 \sqrt{P_{H_2}} \exp \left( -\frac{\Delta H}{R_g T} \right) \quad \text{Equation 2}$$

where  $S_0$  is a constant,  $\Delta H$  the dissolution enthalpy,  $R_g$  the gas constant, and  $T$  the absolute temperature. Figure 4 shows the calculated hydrogen concentration ahead of the crack tip after one loading cycle [27]. In this figure, the hydrogen concentration was indicated by a ratio of  $C_H$  to the saturated hydrogen content at  $P_{H_2} = 35$  MPa,  $C_{s, P_{H_2}=35}$ , allowing us to compare the values

between different hydrogen gas pressures. It has to be noted that these calculations neglect the factors influencing the hydrogen diffusion, such as the hydrostatic stress field and defects trapping hydrogen atoms as evidenced by Sofronis et al. [85, 86]. Meanwhile, Moriconi [87] confirmed that the influence of hydrostatic stress on the hydrogen diffusion is limited within only few  $\mu\text{m}$  away from the crack tip. Moreover the assumption of the a fixed concentration at the crack tip could also be questioned, in particular with respect to approaches based on generalized boundary conditions providing expressions for the crack tip hydrogen flux [88, 89]. However the main purpose of the calculations presented here is to compare different testing configurations by reliable orders of hydrogen concentration, using the same assumptions, and not to calculate precisely the hydrogen distribution in the crack-tip stress field.

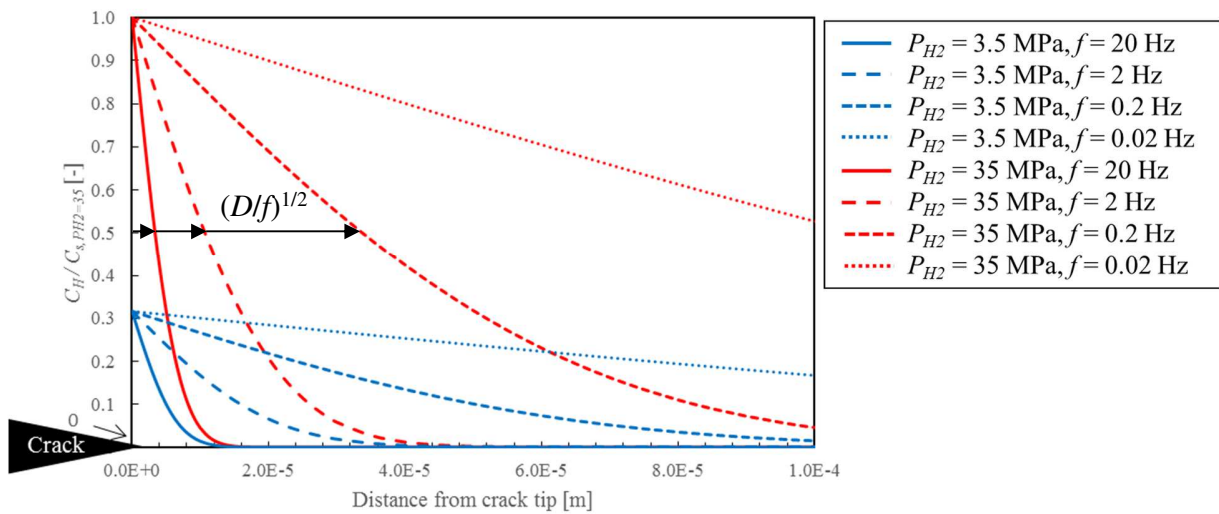


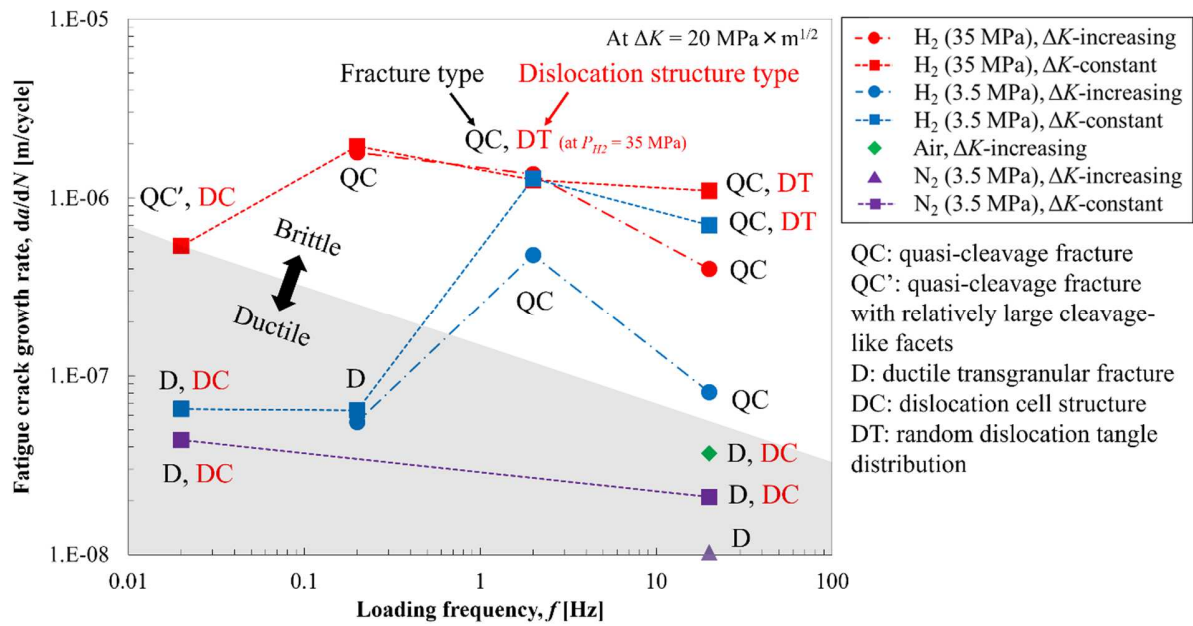
Figure 4: Comparison of the hydrogen concentration profile ahead of the crack tip after one loading cycle (from [27]).

In terms of the influence of hydrogen gas pressure, the value of  $\Delta K$  triggering the FCGR enhancement (i.e.  $\Delta K_{tr}$ ) decreases by increasing the hydrogen gas pressure. Equation 2 expresses

that the saturated hydrogen content  $C_s$  depends on the hydrogen gas pressure  $P_{H_2}$  (also as shown in Figure 4). Since  $\Delta K_{tr}$  depends on hydrogen gas pressure,  $C_s$  is considered as an influential factor acting on the shift of  $\Delta K_{tr}$ . This dependence of  $\Delta K_{tr}$  on the hydrogen gas pressure can be explained as follows. If hydrogen gas pressure is high, the hydrogen concentration at the crack tip ( $C_s$ ) is also elevated, hence the hydrogen-induced QC fracture can be easily activated, even with a relatively low level of stress intensification at the crack tip. On the contrary, if the hydrogen gas pressure is low, the hydrogen concentration at the crack tip ( $C_s$ ) is limited, hence a high level of stress intensity at the crack tip might be required to activate the hydrogen-induced QC fracture. A similar interpretation has also been suggested recently by Ogawa et al. [90].

### 3.2. Dependency of HAFCG on loading frequency

As regards the influence of loading frequency  $f$  on the FCGR in the highly-accelerated regime, the previous experimental study [29] clarified the relationship between the FCGR and  $f$  as presented by Figure 5 deriving the two following key points:



- Figure 5: FCGR vs.  $\Delta K$  curves of the  $\Delta K$ -constant and  $\Delta K$ -increasing tests at  $f = 0.02, 0.2, 2,$  and  $20 \text{ Hz}$  under gaseous hydrogen at  $P_{H_2} = 3.5$  and  $35 \text{ MPa}$ , as well as the tests in inert environments. This figure also presents the types of fracture mode and dislocation structure for each result of FCG test (from [29]).the magnitude of FCGR enhancement in the accelerated regime increases by decreasing  $f$  until a certain value;
- the magnitude of FCGR enhancement reaches the upper limit by decreasing  $f$  down to a certain value. If  $f$  is decreased further, the FCGR rapidly decreases as same level as in air. At the same time, the crack tip plasticity and the fracture mode also change.

If the first feature is considered from the viewpoint of hydrogen concentration ahead of the crack tip, the penetration depth  $(D/f)^{1/2}$ , which is defined as the distance from the crack tip where the value of  $C_H/C_s$  becomes  $0.5 C_s$ , increases with the decrease in loading frequency (as shown in Figure 4). This is because a longer period of one loading cycle allows hydrogen to diffuse deeper from the crack tip at lower loading frequency. According to the present model of hydrogen-

induced QC fracture, deeper hydrogen penetration ahead of the crack tip allows a longer crack advancement due to the continuous cleavage fracture, resulting in higher FCGR.

Regarding the second feature, a possible explanation is the importance of the relationship between hydrogen diffusing velocity and dislocation velocity as suggested by Takai et al. [35, 91]. They examined the hydrogen desorption behavior of pure iron during tensile deformation with various strain rates of  $d\varepsilon/dt = 4.2 \times 10^{-5} \text{ s}^{-1}$ ,  $4.2 \times 10^{-4} \text{ s}^{-1}$  and  $4.2 \times 10^{-3} \text{ s}^{-1}$ . As a result, the amount of desorbed hydrogen increased by increasing the strain rate from  $4.2 \times 10^{-5} \text{ s}^{-1}$  to  $4.2 \times 10^{-4} \text{ s}^{-1}$ , and reached the maximum amount (16% of the initial hydrogen content) at the strain rate of  $4.2 \times 10^{-4} \text{ s}^{-1}$ . And then, the amount of desorbed hydrogen decreased by increasing the strain rate from  $4.2 \times 10^{-4} \text{ s}^{-1}$  to  $4.2 \times 10^{-3} \text{ s}^{-1}$ . This result implies that, when the velocities of hydrogen and dislocation are balanced, their interaction is maximized, hence the maximum amount of hydrogen is transported by dislocations.

This mechanism may explain the dependency of HAFCG on loading frequency as follows. When the loading frequency is high (e.g. 20 Hz in the case of  $P_{H_2} = 35 \text{ MPa}$ ), since the crack tip straining rate is high, the dislocation velocity emitted from the crack may be much higher than hydrogen diffusing velocity. Thus, the interaction between hydrogen and dislocation is still weak. When the loading frequency decreases (e.g. 2 Hz), the dislocation velocity decreases and approaches the hydrogen diffusing velocity. As the hydrogen and dislocation velocities are getting close to each other, their interaction becomes strong, reducing the dislocation activity. This effect leads to the crack growth enhancement by the proposed cleavage fracture model. Finally, when the hydrogen and dislocation velocities are balanced by decreasing  $f$  down to a certain level (e.g. 0.2 Hz), their interaction is maximized, exhibiting the maximum FCGR enhancement. When  $f$  is decreased further (e.g. 0.02 Hz), the dislocation velocity becomes lower

than the hydrogen velocity, the connection between hydrogen and dislocation becomes weak again. Consequently, the influence of hydrogen on dislocation disappears. As mentioned above, this theory explains well the second feature of the  $f$ -dependency of HAFCG (the presence of the upper limit of enhanced FCGR and the attenuation of hydrogen effects of the FCGR enhancement, the crack tip plasticity, and the fracture mechanism), in fact, as well as the first feature (the increase in FCGR by decreasing  $f$ ). Therefore, the two possible explanations exist for the first feature.

However, the dislocation and hydrogen velocities in the vicinity of the crack tip in the present case of FCG tests have not been quantitatively examined yet, since it is difficult to precisely estimate them due to the complexity of the crack tip stress field under cyclic loading. The quantitative investigation on this issue is necessary in the prospective work in order to verify the above assumption and to clarify the interaction between hydrogen and dislocation.

In addition to the above qualitative interpretation for the second feature based on the relationship between hydrogen and dislocation velocities, another important quantitative finding for the attenuation of the hydrogen effects has been made by Yoshikawa et al. [92, 93] based on their experimental results of FCG tests in low carbon steel with a wide range of hydrogen gas pressure and loading frequency. In this research, the FCGRs at relatively low hydrogen gas pressures exhibit a reversal effect of loading frequency similar the one observed in this study. Yoshikawa et al. [92, 93] have estimated the hydrogen distribution ahead of the crack tip by means of the same method as explained in the previous section, and calculated the gradient of hydrogen concentration in the vicinity of the crack tip expressed by:

$$\text{Hydrogen gradient: } \left( \frac{P_{H_2} \times f}{2D} \right)^{1/2} \propto (P_{H_2} \times f)^{1/2} \quad \text{Equation 3}$$

The definition of this term is a gradient of hydrogen concentration between the crack tip ( $x = 0$ ) and the position in which  $C_H$  becomes  $0.5C_s$  (the penetration depth  $(D/f)^{1/2}$ ). Yoshikawa et al. have found out that, by rearranging the FCGR data by  $(P_{H_2} \times f)^{1/2}$ , it can be seen that the attenuation of FCGR enhancement at  $\Delta K = 30 \text{ MPa}\times\text{m}^{1/2}$  occurs when  $(P_{H_2} \times f)^{1/2}$  is lower than  $0.2 \text{ (MPa}\times\text{s}^{-1})^{1/2}$ , regardless of the hydrogen gas pressure.

To investigate the validity of the criterion  $(P_{H_2} \times f)^{1/2}$  for the present results, the relationship between the FCGRs in hydrogen and  $(P_{H_2} \times f)^{1/2}$  is shown in Figure 5 [27, 29]. This diagram clearly demonstrates that the onsets of FCGR enhancement by increasing loading frequency at both hydrogen gas pressures occur at the same value of  $(P_{H_2} \times f)^{1/2} \sim 2 \text{ (MPa}\times\text{s}^{-1})^{1/2}$ . This result indicates that the hydrogen gradient  $(P_{H_2} \times f)^{1/2}$  is likely a valid criterion for the onset of HAFCGR enhancement of the present case in Armco iron.

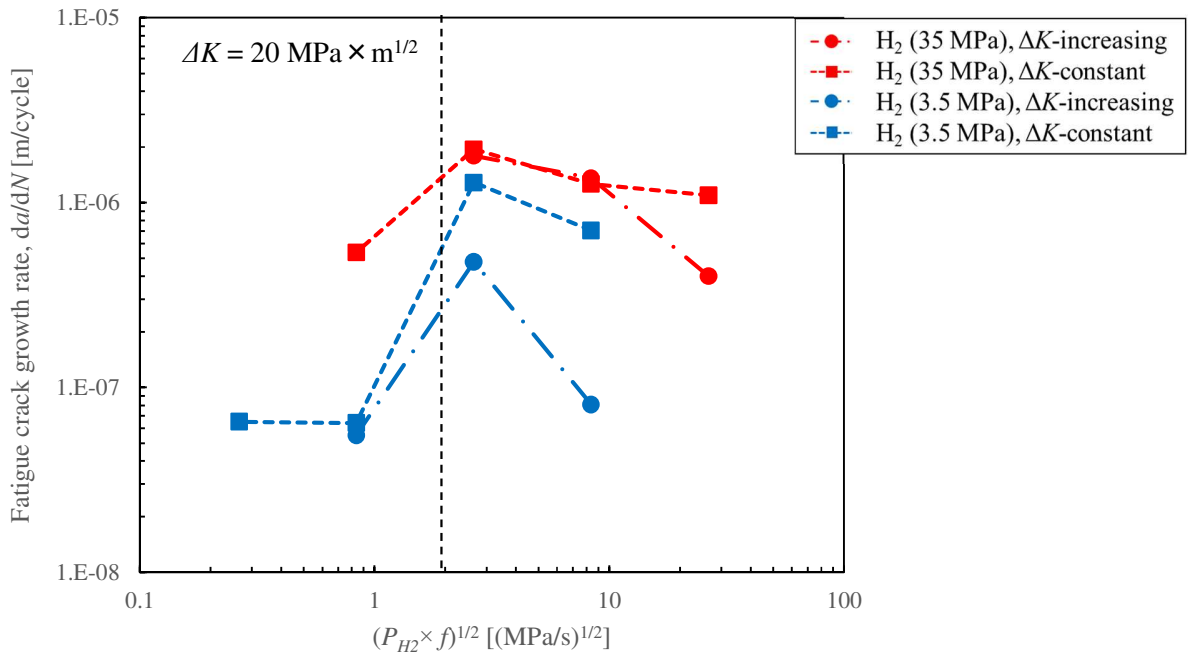


Figure 6: Relationship between HAFCGR and hydrogen gradient  $(P_{H_2} \times f)^{1/2}$  at  $\Delta K = 20 \text{ MPa}\times\text{m}^{1/2}$  (from [27, 29]).

Yoshikawa et al. [92, 93] also observed that a clear reduction of the extent of plastic deformation near the crack tip occurred during the enhanced FCG with a high level of hydrogen gradient. On the other hand, at low level of hydrogen gradient without the FCG enhancement, the extent of crack tip plasticity was the same level as in air, which is consistent with the present results. However, they did not provide any clear explanation why the hydrogen gradient is so important for the activation of hydrogen effects in their literature.

The reason why the hydrogen gradient controls the HAFCG enhancement may be understood by the framework of the above-mentioned theory of the balance between hydrogen and dislocation velocities. Theoretically, the hydrogen flux  $J$  is a function of the hydrogen concentration gradient  $\nabla C_H$ . Therefore, a higher hydrogen concentration gradient induces a higher hydrogen flux ahead of the crack tip, namely a higher number of hydrogen atoms diffusing. As described above, the mobile dislocations and the diffusing hydrogen atoms interact when their velocities are similar. Therefore, it is considered that a movement of many hydrogen atoms driven by a large hydrogen concentration gradient is a necessary condition for the interaction between hydrogen and dislocation. If the hydrogen concentration gradient is small (i.e. a hydrogen-saturated state), the diffusion of hydrogen atoms does not occur, and as a result, the interaction between hydrogen and dislocation does not occur. This assumption may explain well the importance of hydrogen gradient as one of the essential factors to activate the HAFCG enhancement. This assumption is in a good agreement with the results of tensile tests [94]: indeed it was concluded that the hydrogen embrittlement effect under saturating hydrogen conditions is less severe than the one obtained in conditions where the hydrogen concentration is less but presents a higher gradient. Furthermore, another conclusion, that hydrogen does not influence uniform deformation while it does influence crack growth with stress gradient, can also be interpreted as follows: hydrogen



intensively diffuses to the crack tip due to stress concentration (stress gradient) at the crack tip. As a result, a hydrogen concentration gradient is generated, and it may activate the crack growth enhancement effect by hydrogen.

In contrast, Somerday et al. [35] suggested that the attenuation of the hydrogen effect at very low loading frequency might be caused by an oxidation of crack surface near the crack tip impeding an hydrogen absorption on crack tip surfaces. The amount of oxygen, even very small (10 ppm) in the hydrogen gas, may therefore be a controlling factor of  $f$ -dependency. Thus, it is possible that the influence of impurities such as oxygen contained in the hydrogen atmosphere exists in the present case. However, Matsunaga et al. [36] have denied this explanation by referring their experimental results of the FCG tests in hydrogen-charged 304 stainless steel which have demonstrated the attenuation of the hydrogen effect at very low loading frequency without any influence of the impurities.

The dependency of HAFCG on hydrogen gas pressure and loading frequency elucidated from this study is sketched in Figure 6. If the hydrogen concentration gradient ahead of the crack tip is below a critical level due to a low hydrogen gas pressure and/or a low loading frequency, the fracture mode becomes more ductile, comparable with that produced in air, and no FCGR enhancement occurs. On the other hand, once the hydrogen gradient exceeds the critical level by increasing the hydrogen gas pressure or increasing the loading frequency, the hydrogen effect is activated, inducing a crack growth by QC fracture and a FCGR enhancement. At the same time, the FCGR depends on the hydrogen gas pressure and the loading frequency. If the loading frequency is decreased, the crack advancement per cycle increases by the two possible mechanisms: (i) the hydrogen atoms may penetrate deeper from the crack tip, which allows the cleavage fracture to continue over a longer distance; and/or (ii) the dislocation velocity decreases

and becomes closer to hydrogen diffusing velocity, which induces their stronger interaction. This enhances the cleavage crack growth. On the other hand, when the hydrogen gas pressure is increased, as the hydrogen concentration at the crack tip increases, the critical stress intensity at the transition ( $\Delta K_{tr}$ ) triggering the QC fracture decreases and as a consequence, the FCGR enhancement may occur from lower  $\Delta K$  values.

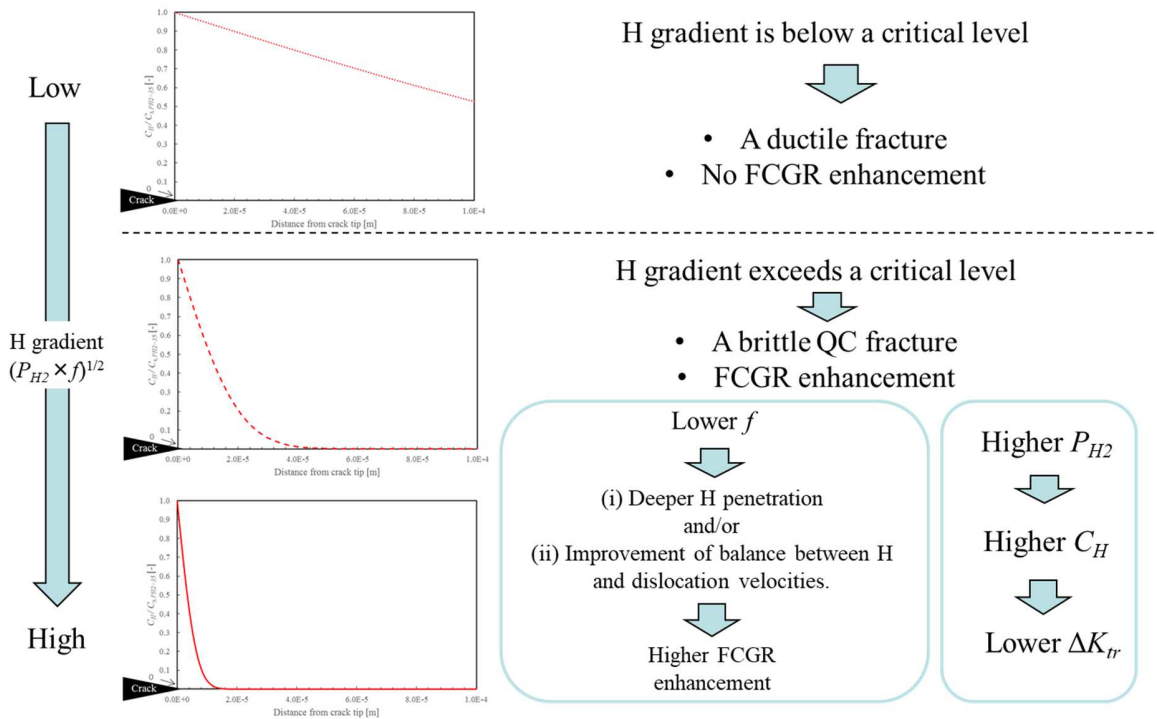


Figure 7: Summary of dependencies of HAFCG on hydrogen gradient  $(P_{H_2} \times f)^{1/2}$ , hydrogen gas pressure, and loading frequency.

#### 4. Criteria for HAFCG enhancement

From the discussions so far, one of the important findings is the presence of the three criteria for the HAFCGR enhancement: the upper limit of HAFCGR;  $\Delta K_{tr}$ ; and  $(P_{H_2} \times f)^{1/2}$  as indicated in Figure 7 [29].

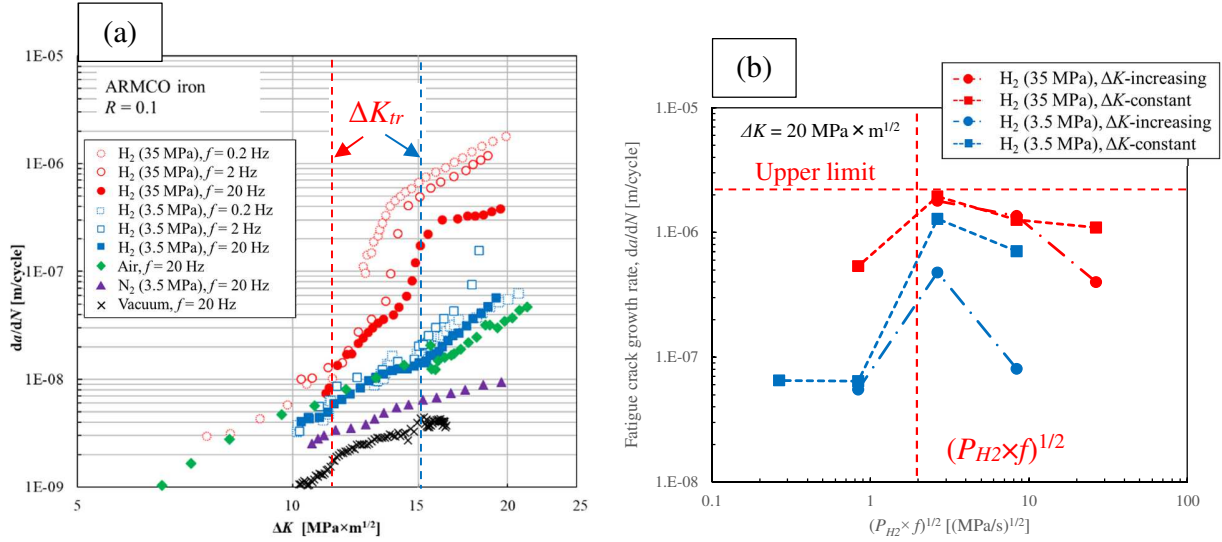


Figure 8: Three criteria for hydrogen-induced FCGR enhancement:  $\Delta K_{tr}$  indicated in the diagram of FCGR vs.  $\Delta K$  (a); the upper limit of FCGR enhancement; and hydrogen gradient  $(P_{H_2} \times f)^{1/2}$  indicated in the diagram of FCGR vs. hydrogen gradient (b) (from [29]).

The physical meanings of the criteria interpreted by the above discussions are:

- i.  $\Delta K_{tr}$ : a necessary crack tip stress intensity to occur a hydrogen-induced cleavage fracture. It depends on  $P_{H_2}$  (i.e.  $C_s$ ) because a combination of both parameters must satisfy a critical condition to activate a hydrogen effect reducing dislocation activity, which results in crack tip plasticity reduction and cleavage fracture.
- ii.  $(P_{H_2} \times f)^{1/2}$ : a hydrogen concentration gradient ahead of a crack tip required to trigger a hydrogen-induced cleavage fracture. Under a certain level of hydrogen gradient,

diffusing hydrogen atoms may interact with mobile dislocations. Their interaction induces a hydrogen effect, which results in limited crack tip plasticity and cleavage fracture.

- iii. Upper limit of FCGR: a possible maximum FCGR enhanced by hydrogen which is roughly 50 times higher than the one in air in the present case. This value is determined by a crack advancement per cycle when hydrogen and dislocation velocities are balanced, and the interaction between hydrogen and dislocation is maximized.

Even though both parameters,  $\Delta K_{tr}$  and  $(P_{H_2} \times f)^{1/2}$ , are the criteria controlling the onset of HAFCG enhancement, the phenomena represented by these parameters are different. This can be confirmed by two experimental evidences. The first evidence is that the fracture mode in the condition not satisfying the criterion is different between  $\Delta K_{tr}$  and  $(P_{H_2} \times f)^{1/2}$ . Indeed the fracture mode in the non-accelerated regime ( $\Delta K < \Delta K_{tr}$ ) is intergranular, while the one in low hydrogen gradient ( $(P_{H_2} \times f)^{1/2} < 2$ ) is ductile transgranular (and QC). The second evidence is the shift of  $\Delta K_{tr}$  as a function of pressure or frequency cannot be accounted for by the  $(P_{H_2} \times f)^{1/2}$  parameter. For example, the two testing conditions  $P_{H_2} = 35$  MPa,  $f = 0.2$  Hz and  $P_{H_2} = 3.5$  MPa,  $f = 2$  Hz are characterized by the same value of this parameter  $(P_{H_2} \times f)^{1/2}$ , namely  $2 \text{ (MPa}\times\text{s}^{-1})^{1/2}$ , but the values of  $\Delta K_{tr}$  are different, as shown in Figure 7. These values of  $\Delta K_{tr}$  should be consistent if  $\Delta K_{tr}$  was also controlled by  $(P_{H_2} \times f)^{1/2}$ . Therefore, the physical phenomena triggering the hydrogen-induced QC fracture accompanied by FCGR enhancement by satisfying  $\Delta K_{tr}$  and  $(P_{H_2} \times f)^{1/2}$  are different.

The three criteria are expected to be useful for a fatigue design and a fatigue life prediction of hydrogen-related equipment. The upper limit of HAFCG rate can be considered as a maximum possible FCGR at any loading frequency under hydrogen environment. This value would enable

to estimate a minimum fatigue life of products and to determine the periods of usage and replacement of products. Besides, the value of  $\Delta K$  at the transition  $\Delta K_{tr}$  and the exposure parameter  $(P_{H_2} \times f)^{1/2}$  could be considered as criteria for degradation of fatigue crack resistance. These criteria are useful to determine the usage condition of materials under hydrogen environment avoiding a critical degradation of fatigue life. Identification and application of the criteria is expected to greatly contribute to the improvement of reliability of hydrogen-related equipment.

## 5. Conclusions

In this paper, the mechanisms of influence of hydrogen on fatigue crack growth have been discussed based on previously published experimental results. A scenario has been proposed to account for the different regimes noticed in the crack growth behavior.

1. A model of hydrogen-induced intergranular fracture mechanism has been proposed as follows. Under cyclic loading, hydrogen atoms diffuse and are swept-in by mobile dislocations ahead of the crack tip. The mobile dislocations carrying hydrogen atoms stop and pile-up at the intersections of the dislocation walls and the grain boundary, accompanied by hydrogen concentration. The highly accumulated dislocations and hydrogen atoms induce the nucleation of microvoids at the grain boundary. Finally, the highly accumulated microvoids and hydrogen atoms at the grain boundaries weaken the bonding energy of the grain boundary, triggering a separation of grain boundary by decohesion and microvoid coalescence along lines. This scenario can be considered as a HEDE-dominated process,

mediated by the intragranular plasticity but without any evidence of a significant HELP contribution

2. A model of hydrogen-induced cyclic cleavage fracture mechanism has been proposed as follows. Solute hydrogen atoms locally concentrated in highly stressed region at the crack tip modifies the plastic deformation at the crack tip by the hydrogen effects suppressing dislocation emission and mobility. The stress intensification ahead of the crack tip is further enhanced by the sharpened crack tip due to the limited crack tip blunting, inducing higher hydrogen concentration as a synergy effect. When both stress intensity and hydrogen concentration reach a critical level, cleavage fracture occurs either by the HEDE mechanism or by a AIDE-type process.
3. The dependency of  $\Delta K_{tr}$  on hydrogen gas pressure can be interpreted by the proposed cleavage fracture model assuming that a combination of high hydrogen concentration and high crack tip stress intensity is required to trigger the cleavage fracture.
4. The dependency of HAFCG on loading frequency can be interpreted by referring the hydrogen penetration depth and/or the balance between hydrogen diffusing velocity and mobile dislocation velocity which is likely important for their interaction inducing the crack tip plasticity reduction by hydrogen.
5. The upper limit of HAFCG rate is likely achieved when hydrogen diffusing velocity and mobile dislocation velocity are balanced.
6. The attenuation of HAFCG enhancement at very low loading frequency can be explained as a result of the weak interaction between hydrogen and dislocation when dislocation velocity becomes smaller than hydrogen velocity by decreasing the loading frequency.

7. Three criteria for HAFCG ( $\Delta K_{tr}$ ,  $(P_{H2} \times f)^{1/2}$ , and Upper limit of HAFCG rate) have been identified. These criteria are expected to be useful for improving a reliability of hydrogen-related equipment.

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