Function of Hydrogen in Embrittlement of High-strength Steels

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Various models so far proposed for the mechanism of hydrogen embrittlement (HE) of steels are critically reviewed with respect to the manifestation of hydrogen in the fracture process. Recent studies that elucidate the hydrogen states and their relevance to HE are discussed. Particular attention is paid to the role of deformation-induced defects that interact with hydrogen. A model is proposed in which increased vacancy density and agglomeration lead to the promotion of failure. The model ascribes HE to the context of ductile fracture in which vacancies play the primary role.

KEY WORDS: hydrogen embrittlement; fracture; lattice defect; fractography; thermal desorption analysis; high-strength steel.

1. Introduction

Degradation of mechanical properties or premature failure caused by hydrogen, generally in terms of hydrogen embrittlement (HE), has been a subject of extensive studies over the past several decades. Main features and proposed mechanisms have been documented in review articles,1–4) but there still exist conflicting concepts concerning the function of hydrogen in embrittlement. The dominating mechanism may differ depending on the material, hydrogen fugacity, type of loading and evaluation method, but we have to answer the following mysteries of HE: (1) why a very small amount of hydrogen induces embrittlement, (2) why susceptibility differs among materials having the same strength level, and (3) why is there a time delay to failure in delayed fracture tests.

The solid solubility of hydrogen in atomic fraction, \( C_0 \), in iron follows Sievert’s law with external hydrogen pressure \( P \) in \( \text{10}^5 \text{ Pa} \) and temperature in \( K \) as,\(^1\)

\[
C_0 = 0.00185 \sqrt{P} \exp(-3400/T) \quad (1)
\]

At room temperature under \( \text{10}^5 \text{ Pa} \), \( C_0 \) is extremely low, \( \text{ca. } 2 \times 10^{-8} \), and most of the observed hydrogen on the order of mass ppm is in trapped states in various defects.\(^1\)\(^5\) Thus, the function of hydrogen in embrittlement must be considered taking into account its trapped states. In deformed iron, the absorption of hydrogen turns from endothermic to exothermic reactions,\(^6\) implying attractive trapping at defects introduced by deformation. In order to show the scheme of the present paper, the relations between the previous models and the states of hydrogen are shown in Fig. 1, and the details are given in the following sections.

An aspect we have to keep in mind is the basic mode of fracture in HE. In general, fracture, as the process of atomic bond breakage, is governed by either tensile stress or shear strain. That being the case, it is an essential problem that the function of hydrogen has a direct effect on bond strength or an indirect one associated with the response of microstructural constituents to stress and strain states. In other words, the problem is to determine whether the brittle or ductile fracture mode is intrinsic to HE. Susceptibility to HE generally increases with the strength level. If the function of hydrogen were due to a reduction of atomic bonding strength, the stress field that pertains to the strength level might play the primary role. On the other hand, if the failure were ductile in nature, susceptibility would be controlled by the reactions of microstructural constituents, pertinent to the strengthening mechanism, to the strain field.

One difficulty in elucidating the mechanism of HE concerns the detection of hydrogen. The very low detection sensitivity, high mobility and very low concentration of hydrogen limit appropriate tools for detection. Recently, however, substantial progress has been made in Japan\(^7\)–\(^9\) in the visualization of hydrogen trapping sites and in the analysis of trapped states by means of thermal desorption analysis (TDA) of hydrogen.

With new tools for revealing the states of hydrogen, new light is being shed on the nature of HE. In this review, the mainstream of various concepts of the mechanism of HE will be followed, and recent insights into the HE mechanism will be presented.
2. Fractographic Features

The most classical model of HE was the internal pressure mechanism due to molecular hydrogen precipitated at second phase particles. Build-up of high-pressure hydrogen gas is evident in the case of high hydrogen fugacity such as cold cracking in weldments or under severe sour environments. Under favorable conditions, internal pressure can trigger brittle fracture. However, the general occurrence of crack growth under mild environments contravenes this model.

A supporting fact for the brittle fracture model is crack propagation along {100} cleavage planes in 3.5% Si steels. In that case, however, fractographic features are often characterized by fine striations along slip plane traces. Slow and discontinuous crack growth in {110} directions is the origin of the striations. Recently, Terasaki et al. examined striations on the fracture surface of a hydrogen-precharged iron single crystal. Figure 2 is a reproduction of the micrograph obtained by Terasaki et al. By mating the fracture surfaces with the aid of a scanning tunneling microscope (STM), they showed that the striations are void arrays and that even the {100} fracture was associated with substantial plastic deformation, suggesting that reaction of dislocations on the {112} slip is the origin of the {100} fracture. It was also noticed that cleavage fracture initiated after the striated fracture had advanced.

Striation is a typical fractographic feature that appears in more ductile hydrogen-charged iron. In pure iron, crack growth in HE is mostly along {110} planes with striations along slip plane traces. Nagumo et al. previously showed that fine patterns of the fracture surface of a coarse-polygonal iron, subjected to an un-notched tensile test under cathodic hydrogen charging, originated in clusters of multiple slip bands as shown in Fig. 3. Observation of the cross section revealed that traces of slip planes were sensitized to attack by chemical etching as shown in Fig. 4. Correspondence between the fracture surface and the deformation structures developed within the specimen revealed that the striations were associated with the initiation and linking of voids along slip plane traces. Formation of microvoids in arrays was also observed along dislocation cell walls. This finding implies that striations on the fracture surface originate in the defects that form within the specimen prior to crack propagation.

Quasi-cleavage, another fractographic feature characteristic of HE, was shown to be crack extension along {110} martensite lath boundaries in a martensitic high-strength steel. It is to be noted that {110} lath boundaries are also coincident with the orientation of dislocation cell walls. In an experiment conducted on polycrystalline iron, quasi-cleavage-like flaky patterns as well as striated ones appeared in some grains. Apparently, the patterns depend on the grain orientation to the tensile axis due to slip configurations, and the origins of the two patterns are likely similar.

Intergranular fracture along prior austenite grain boundaries is an often-observed feature in martensitic high-strength steels. Striations approximately 1 μm in spacing were also reported on the intergranular fracture surface of hydrogen-precharged AISI 4340 steel subjected to a compact tensile test under sustained load. The spacing was close to that of martensite lath. Impurity segregation along prior austenite grain boundaries increases susceptibility to
HE, but there still is a problem that intergranular fracture is governed by either the cohesive strength of the boundary itself or deformation structures close to the boundaries. As will be described in Sec. 6, greater susceptibility to HE with intergranular fracture has been associated with increased hydrogen content upon loading. This implies that increased defect density due to straining is also an essential feature of the intergranular mode of fracture. Such observations suggest that plasticity is a common factor for both the brittle and ductile types of fracture associated with hydrogen.

### 3. Fracture Mode

Degradation of mechanical properties of steels under the presence of hydrogen appears in various ways. Enhanced shear localization at the notch root surface and subsequent promotion of the onset of ductile cracking were observed in notched bending tests of hydrogenated AISI 4340,26) spheroidized 109027) and 1520 steels.28) Nucleation and growth of cracks occurred along the characteristic slip traces, indicating mode II fracture.26,27) With respect to shear localization, Hirth examined the effect of hydrogen on the crack initiation J-integral value, J\(_T\), by means of a slant-notched compact tension test using a rotor steel.29) J\(_T\) decreased as a result of hydrogen charging, and the decrease was more pronounced for mixed-mode I–III loading than for pure mode I loading. The findings suggest that hydrogen-related failure essentially has a ductile fracture nature. Previously, Beachem observed a decrease in flow stress due to hydrogenation and proposed a hydrogen-assisted-cracking (HAC) model based on a K-decreasing test of an AISI 1020 steel.30) His model, which posits that hydrogen promotes the onset of failure, is phenomenological and does not address the intrinsic mechanism. Alteration of flow stress by introducing hydrogen into iron has been well documented,31–33) but a decrease due to hydrogenation is not the general case.

Hirth proposed an autocatalytic model of void formation at hard particles and associated promotion of shear localization.29) His model states that shear between particles in the presence of hydrogen induces particle-matrix decohesion, which leads to void formation and again subsequently to local shear band formation. The expected fractographic feature is then the dimple type with second phase particles as the void source. In actuality, however, quasi-cleavage and intergranular types are often observed as characteristics of HE. These features suggest that hydrogen is involved in the crack growth stage as well as in the initiation stage in a characteristic way different from the ordinary ductile fracture process.

The problem is closely related to the nature of ductile fracture. In our previous study, on the ductile-to-brittle fracture transition in steel, ductile crack growth resistance, evaluated in terms of the R-curve, was found to be noticeably lowered when the constraint of slip extension across grain boundaries was substantial. Subsequent study using tritium thermal desorption analysis as a tracer of defects revealed that the degradation was due to the enhanced evolution of vacancy-type defects in the course of plastic straining.35) The findings suggested that the ductile fracture process is strongly affected by dynamic creation of vacancies during straining, in addition to the presence of second phase particles as the void source. Simulation of the observed R-curves by means of finite element method (FEM) analysis supported the idea that the decline in ductile crack growth resistance was associated with increased nucleation void volume fraction. The general notion of ductile fracture assumes the initiation, growth and coalescence of voids. Recently, ample evidence has shown void formation without second phase particles as the consequence of dislocation configurations and vacancy condensation, suggesting the involvement of vacancies in failure.

Using the same steels as in Ref., we have shown that hydrogen further enhanced the decline in ductile crack growth resistance as shown in Fig. 5. As the fractographic feature characterizing the effect of hydrogen, enlargement of the size and decrease in the depth/width ratio of primary dimples, occasionally associated with quasi-cleavage, were observed. The change in the dimple morphology in the hydrogen-charged steel is shown in Fig. 6. FEM showed increases in the nucleation void volume fraction and void volume localized at the crack tip in hydrogen-charged steel. Shear instability itself takes place even without the presence of hydrogen. The findings in Figs. 5 and 6...
suggest that the fracture process in the presence of hydrogen takes place in the context of ductile fracture controlled by the evolution and agglomeration of vacancy-type defects. This finding and consideration have formed the background for the vacancy agglomeration model of the HE mechanism that will be described in Sec. 6. It means that the nature of HE can be understood to be included in the scheme common to the general concept of fracture.

4. Interactions of Hydrogen with Dislocations and Vacancies

Hydrogen-induced imperfection of slip planes was formerly shown in iron single crystals as the broadening of the \{110\} Kossel lines.\(^{32}\) Direct evidence for the enhancement of dislocation mobility associated with highly localized plasticity due to hydrogen has been accumulated by means of in situ transmission electron microscopy using iron\(^{43,44}\) and fcc metals and alloys.\(^{45–48}\) Based on these findings, a hydrogen enhanced localized plasticity (HELP) model has been proposed.\(^{49,50}\) Systematic analyses showed that HELP is caused by the effect of hydrogen in solution on reducing interactions between dislocations and other elastic centers.\(^{49–51}\) The theory has been supported by observations of dislocation characteristics in AISI 310S stainless steel\(^{52}\) and aluminum.\(^{53}\) Hydrogen-enhanced shear instability is apparently consistent with the HELP model, but, as Hirth noticed,\(^{59}\) the dominance of dislocation mobility on HE may still be a matter to be examined because of the high dislocation density in complicated configurations and of various second phases in high-strength steels.

Another type of defect to be considered in connection with plastic straining is the vacancy type. As shown in Fig. 7(a),\(^{54}\) the amount of hydrogen desorbed around 100°C in TDA increased when hydrogen was charged to a low carbon steel after plastic deformation. When the deformed steel was annealed at temperatures as low as 200°C, the increase no longer appeared as shown in Fig. 7(b). It implies that defects created in the course of plastic deformation are mostly vacancy clusters. Similar results were also obtained with martensitic steels.\(^{55}\) The estimated vacancy concentration is on the order of \(10^{-3}–10^{-4}\). The vacancy concentration in metals under thermal equilibrium at room temperature is extremely small, but a substantial increase in the vacancy concentration due to straining is in accord with previous experimental\(^{56,57}\) and theoretical\(^{58,59}\) results. Excess vacancies are ready for annihilation even at sub-zero temperatures due to their high mobility, but the formation of vacancy-solute complexes, such as carbon in iron, elevates the annihilation temperature to 200°C.\(^{57,60}\)

It is to be noted that straining in the presence of hydrogen further increased the vacancy concentration. From thermodynamic considerations, a substantial increase in the thermal equilibrium concentration of vacancies was predicted when complexes with impurities are formed.\(^{61–63}\) In a simple form, the concentration of the solute–vacancy complex \(C_{\text{VS}}\) is given by the solute concentration \(C_{\text{S}}\) under the assumption of a thermal equilibrium between monovacancies and complexes, as

\[
C_{\text{VS}} = C_{\text{S}}C_{\text{V}}Z \exp \left( \frac{E_{\text{b}}}{RT} \right) \quad \text{......(2)}
\]

where \(C_{\text{V}}\) is the thermal equilibrium monovacancy concentration, \(Z\) is the coordination number and \(E_{\text{b}}\) is the binding energy of the solute with vacancies. Provided that \(E_{\text{b}}\) is much larger than \(RT\), as in the case of hydrogen–vacancy binding, the exponential factor overwhelms a small value of \(C_{\text{V}}\), resulting in a substantial amount of \(C_{\text{VS}}\). For \(C_{\text{V}}\), the value associated with plastic deformation can be employed instead of the thermal equilibrium value. The increase in the vacancy concentration in the presence of hydrogen has been revealed experimentally in many fcc and bcc metals and alloys.\(^{64–68}\) With regard to embrittlement, an increase in the vacancy concentration due to hydrogen well explains the decrease in the R-curve shown previously.\(^{51}\)

5. Fracture Criteria

5.1. Hydrogen in Solution

For the brittle fracture model, the Griffith equation acts as the governing principle. When failure takes place under applied stress or internal pressure not high enough to trigger failure, the effect of hydrogen has been ascribed to a decrease in crack surface energy\(^{69,70}\) or cohesive strength between atoms.\(^{71,72}\) The latter is the lattice decohesion theory that presumes a decline in cohesive strength \(F_{\text{m}}\) with increasing hydrogen concentration, \(C_{\text{H}}\), in the form,\(^{24}\)

\[
F_{\text{m}} = F_{\text{m0}} \exp \left( -\frac{Q}{RT} \right) \quad \text{......(3)}
\]
where $F_m$ is the stress intensity factor for a crack of length $m$. This concept has been extended to fracture mechanics terminology taking into account the effect of dislocations near the crack tip.\textsuperscript{73,74} There is still the assumption that the local critical stress intensity factor $k_{cr}$ decreases in proportion to increasing $C_{m}$.

$$K_{cr} = \frac{1}{\beta'} \exp \left( \frac{(k_{cr} - \alpha C_{m})^2}{\alpha' \sigma_{ys}} \right)$$ ..........................(4)

A factor that gives rise to the increase in the solute hydrogen concentration is the elastic interaction between hydrogen and the stress field. The solute hydrogen concentration under hydrostatic stress $\sigma$ is given as,\textsuperscript{75,76}

$$\ln \left[ \frac{C_{H}}{C_{0}} \right] = \frac{\sigma V}{3RT}$$ ..........................(5)

where $C_{0}$ is the concentration under no stress and $V$ is the molar volume of hydrogen. A site where high stress builds up is the crack or notch front. Gerberich \textit{et al.}\textsuperscript{73} estimated the magnitude of the stress field and hydrogen concentration in front of the crack tip taking into account dislocation shielding of the crack tip. The result strongly depended on the models employed, and a very high stress field and associated solute hydrogen concentration could be expected. Experimentally, accumulation of hydrogen at stress concentrations is evident, but so far there have been no direct observations that support very high local concentration of hydrogen.

The HELP model, as well as the lattice decohesion model, concerns hydrogen in solution. Recent calculation by Ferreira \textit{et al.}\textsuperscript{53} for the elastic interaction between hydrogen atoms and dislocations showed that the formation of a solute hydrogen atmosphere at edge and screw dislocations stabilizes the edge component, decreasing cross slip. However, in order to be effective, substantial, say, 10$^{-3}$, solute hydrogen concentration was required.

Calculations of the electronic structure of iron have shown the possibilities of the function of hydrogen to reduce cohesive strength and the shear modulus.\textsuperscript{76,77} The hydrogen concerned is in solid solution. An essential problem is whether high concentrations of hydrogen sufficient to cause decohesion or softening can be realized or not, and the failure criteria must consider the various distinct states of hydrogen.

5.2. Trapped Hydrogen

Microstructural heterogeneities such as precipitates, grain boundaries and dislocations act as traps of hydrogen. The function of a trap is related to the diffusivity of hydrogen that controls the kinetics of entry or accumulation at stress concentration. The equilibrium partition between lattice and trap sites is given as,\textsuperscript{78}

$$F_{eq}(H)=F_{m}^{eq} + \alpha C_{H}$$ ..........................(3)

where $F_{eq}$ is the trap binding energy in negative value. Under the condition of a local equilibrium between hydrogen in lattice and trap sites, the diffusion constant has been given by Oriani\textsuperscript{79} as

$$D=D_{0} \left[ 1+K_{D} \exp \left( \frac{E_{b}}{RT} \right) \right]^{-1}$$ ..........................(7)

where $D_{0}$ is the normal diffusion constant of hydrogen and $K_{D}=N_{t}/N_{l}$, where $N_{t}$ and $N_{l}$ are the numbers of the trapping and normal lattice sites, respectively, per unit volume. $R$ is the gas constant and $T$ is the absolute temperature.

As for the involvement of trapped hydrogen in HE, hydrogen accumulation kinetics at various traps was calculated and compared with the observed intergranular cracking in Fe–Ti–C alloys,\textsuperscript{80} resulting in the critical hydrogen concentration in grain boundaries to induce cracking. Pound introduced an intrinsic susceptibility factor $k$ defined as

$$k=2\pi d^{2}N_{t}D_{t}/a$$ ..........................(8)

which is the rate constant for irreversible trapping, and was determined by an electro-chemical potentiostatic pulse technique.\textsuperscript{81} In Eq. (8), $d$ and $a$ are the radii of trap defects and metal atoms, respectively, $N_{t}$ is the defect density and $D_{t}$ is the lattice diffusivity. $d^{2}N_{t}$ represents the trapping capacity of particles. The $k$ values differ depending on the type of precipitate, with large values seen for MnS or coarse M$_{2}$C particles, and an inversely parallel relationship between $k$ and $K_{SCC}$ was obtained with high-strength steels.\textsuperscript{82} Homogeneously distributed fine ($\approx 1 \mu m$) traps such as solute Ti and fine TiC particles appeared rather to decrease or be immune to susceptibility.\textsuperscript{83} Similarly, Yamazaki and Takahashi observed low susceptibility to delayed fracture by fine precipitates in properly heat-treated V-containing steels.\textsuperscript{83} The basic concept is compatible with the concept of the critical local hydrogen concentration, because the accumulation of hydrogen to the critical concentration at available sites was assumed to govern crack initiation.

It is a very important issue from both theoretical and practical alloy design viewpoints to determine the optimum precipitates or traps. In this respect, TDA is a powerful tool for analyzing the trapped state of hydrogen. In most cases, a desorption rate peak appears around 100°C upon linear heating, and the peak profile gives information about the density and hydrogen binding energy of defects. For desorption from strong, irreversible traps, two competing processes upon heating, i.e., an increasing thermal detrapping rate and associated decrease in the hydrogen occupation of traps, give rise to the desorption-rate peak.\textsuperscript{84,85} The peak temperature $T_{c}$ is given as,\textsuperscript{84}

$$E_{a} \phi \exp \left( \frac{E_{a}}{RT} \right)$$ ..........................(9)

where $E_{a}$ is the activation energy of detrapping, $\phi$ is the linear heating rate, $A$ is a constant and $R$ is the gas constant. When two types of traps are present, the release of hydrogen from the respective traps will appear at two temperatures. In Eq. (9), the trap density is not included and $T_{c}$ is
It has been well recognized that hydrogen desorption substantially increases when the sample was deformed as shown in Fig. 7, being desorbed from vacancy-type defects created upon straining. The relevance of the increased desorption to HE susceptibility was demonstrated with martensitic steels containing three levels of Mn, each tempered to give the similar tensile strength. The increased hydrogen weakly trapped and reversible to solid solution. It is to be noted, however, that the TDA peak of hydrogen released from multiple traps with various binding energies with hydrogen. In high-strength steels, a part of the desorption peak remains after the sample is kept for a substantial period at room temperature. The total desorbed hydrogen, i.e., the integrated intensity of the desorption peak, has been correlated with the delayed fracture characteristics of high-strength steels with respect to the strength level, alloying elements, and microstructures. The threshold stress for inducing failure in a delayed fracture test of hydrogen-precharged steel is reduced by the increase in the total desorbed hydrogen.

The critical hydrogen content is an intuitive, but no more than a phenomenological or hypothetical quantity that causes failure upon accumulation of hydrogen. The quantity has been specified not only for steel as a whole, but also locally for grain boundaries, precipitates and for various fracture modes. For practical application, the allowance for the critical concentration of hydrogen introduced from the environment has been proposed as the safety criterion for use. However, the critical hydrogen concentration may differ depending on the actual usage conditions. More essentially, as will be shown in Sec. 7, the occurrence of failure is not always associated with an increase in hydrogen content. This implies that the defects acting as the traps of diffusive hydrogen, rather than hydrogen itself, must be more carefully examined as the essential factor of HE. The issues involved in the concept of the critical hydrogen concentration, if indeed it is valid, are why it differs from material to material and how it operates in the fracture process.

6. Defects Induced by Plastic Deformation

Degradation of mechanical properties is a phenomenon that takes place under stressing. In the lattice decohesion theory, accumulation of hydrogen in stress concentrated areas was considered. Stress concentration at the crack or notch front generally accompanies strain concentration that creates defects acting as the hydrogen traps. Sofonis et al. calculated the hydrogen distribution ahead of a blunted crack tip, taking into account the partition of hydrogen to interstitial lattice sites and trapping sites. In the case of high plastic strain near general yield, the trapped hydrogen rather than the hydrogen in solution predominates in the total amount of hydrogen. It has been suggested that a combined effect of hydrogen and other factors might determine the critical state for fracture.

It has been well recognized that hydrogen desorption substantially increases when the sample was deformed as shown in Fig. 7, being desorbed from vacancy-type defects created upon straining. The relevance of the increased desorption to HE susceptibility was demonstrated with martensitic steels containing three levels of Mn, each tempered to give the similar tensile strength. Mn increases susceptibility to HE associated with intergranular fracture, and a slow strain rate test under hydrogen charging confirmed the decrease in fracture stress, elongation to fracture and reduc-
tion of area.

A factor concerning hydrogen behavior is shown in Fig. 9,99 which shows the total amount of desorbed hydrogen determined by TDA. Interestingly, the amount was the same between the three steels in non-stressed states. However, when straining was given, desorption increased with the Mn content. It implies that the incremental hydrogen associated with plastic strain is closely related to susceptibility to HE.

As for material differences in susceptibility, an experiment was conducted with tempered martensitic steels to determine the defects involved by means of TDA.100) Susceptibility to HE was evaluated in terms of the time to fracture in a delayed fracture test. Hydrogen was charged to samples under three conditions: (1) non-loading, (2) pre-loading and (3) loading concurrent with charging. In the TDA results, a desorption peak appeared around 50–200°C and the amount of desorbed hydrogen was increased by pre-loading and more markedly by loading in the presence of hydrogen. The associated peak profile change was distinguished from that of the non-loading sample by the increment of desorption, $\Delta H$.

In the early stage of hydrogen entry, the increment appeared in the low temperature region in the original peak, and then, as hydrogen entry proceeded, it appeared in the higher temperature region, while the initial increment in the low temperature region was reduced. It should be noted that the change occurred earlier in steels tempered at a lower temperature, i.e., with higher embrittlement susceptibility, as shown in Fig. 10.100) A similar correlation between delayed fracture susceptibility and hydrogen TDA profile change was also observed with pretatigue-treated steels that showed higher susceptibility to delayed fracture.101)

The change in incremental desorption was attributed to the formation of large vacancy clusters having high hydrogen binding energies. Accordingly, deformation-induced vacancies and their clusters, being enhanced and stabilized by hydrogen, were considered to play the primary role in HE of high-strength steel. Consistent with the decrease in ductile crack growth resistance due to hydrogen (Fig. 5), the primary function of hydrogen and the mechanism of HE have been ascribed to the stabilization and promotion of vacancy agglomeration.100) The effect of microstructures on susceptibility to HE is likely to depend on their stability in creating vacancies under stress.

Consequently, our new insight is that the role of hydrogen in embrittlement is indirect and rather subsidiary. The precise process of vacancy creation and agglomeration is not definite yet, but it may originate in dynamic interactions between dislocations at sites like slip bands where dislocation density is high, in keeping with fractographic features.

7. Effect of Environmental Alterations

Accelerated crack growth and failure by cyclic stressing under corrosive environments have been documented in terms of corrosion fatigue102,103) and degradation in delayed fracture characteristics.104,105) One proposed mechanism is the combined effect of cyclic stressing and hydrogen introduced from the surrounding environment.106,107) The increased uptake of hydrogen may result from the failure of a protective film or the slip steps on the specimen surface.108) In a delayed fracture test of high-strength steels, cyclic alteration of applied stress at very low frequencies of tens of cycles per minute, cpm, reduced the time to fracture in a short period of less than $10^5$ cycles.109) In that case, earlier failure was not associated with the increased entry of hydrogen compared with the test under constant stress.

With the aim of proving the assumption that cyclic de-trapping and retrapping of hydrogen at vacancies increase their density, the effect of cyclic alteration of the external hydrogen potential on HE was investigated.110) Cyclic alteration of the hydrogen-charging current density reduced the time to fracture in the delayed fracture test of a high-strength steel as shown in Fig. 11.110) Since the amount of hydrogen introduced into the samples was uniquely determined by the supplied electric charge irrespective of current alternation, accelerated failure in the case of the cyclic current condition took place with less hydrogen than that in the constant current condition. The TDA peak profile

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changed with the progress of hydrogen entry. Under the cyclic current conditions, the evolution of incremental desorption, due to loading, in the high temperature region of the original peak took place earlier than in the constant current case. The correspondence of current alternation to the delayed fracture characteristics was similar to the behavior in the martensitic steels tempered at different temperatures.

Substantial variation of the solute hydrogen concentration was estimated as the result of current alternation. Thus, if the alternating current increased the vacancy density by promoting the chance to form vacancy/hydrogen complexes, the observed result is consistent with the model which posits that earlier failure is a consequence of promoted vacancy agglomeration, the function of hydrogen being to stabilize and increase the vacancy density.

In a practical case, Yamakawa et al. found cyclic variation of the permeation current in SCM 440 steel exposed in a natural environment. It was also reported that hydrogen content did not show a unique increase in a dry/humid cycle test, but decreased after reaching a peak value. Although that might be caused by some changes in the rust layer on the surface, failure ultimately takes place at a lower hydrogen content. While further studies are necessary, it is suggested that environmental fluctuation both of applied stress and the external hydrogen potential is a factor that controls the time to fracture in practical situations.

8. Conclusions

Elucidating the mechanism of HE is a difficult task because HE appears in various forms and there is a lack of tools for direct observation of hydrogen in the fracture process. In the present paper, conflicting models so far proposed have been critically reviewed in the context of the manifestation of hydrogen in the fracture process, focusing mostly on high-strength steels under relatively mild hydrogen conditions. The dominating mechanism may differ from case to case, but there may be a consensus that plasticity is strongly involved in HE. Though various difficulties still exist, recent advances in discriminating hydrogen states show a good prospect for revealing the role of defects that act as hydrogen traps.

When we look at HE as a fracture phenomenon, defects rather than hydrogen itself might play an essential role. TDA results have revealed that the hydrogen concentration is not a decisive factor in HE, and that deformation-induced defects, probably vacancy clusters, are related to HE susceptibility, which differs depending on the microstructure. The role of hydrogen has been ascribed to the stabilization of and increase in vacancy density. A model has been proposed that posits the increased vacancy density and agglomeration lead to the promotion of failure. This model places HE in the context of ductile fracture in general in which vacancies play the primary role.

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