13. Hydrogen Damages on Metals

Although corrosion is an electrochemical reaction between metal surface and the surrounding environment, it can cause the inside of metal to be damaged by hydrogen produced by cathodic reaction of corrosion. The hydrogen readily dissolves and diffuses in metal crystals and can have detrimental effects on mechanical strength and ductility. Mechanical damages of a metal caused by the presence of, or interaction with, hydrogen are as follows :

- Hydrogen embrittlement
- Hydrogen blistering
- Hydrogen attack
- Hydride formation

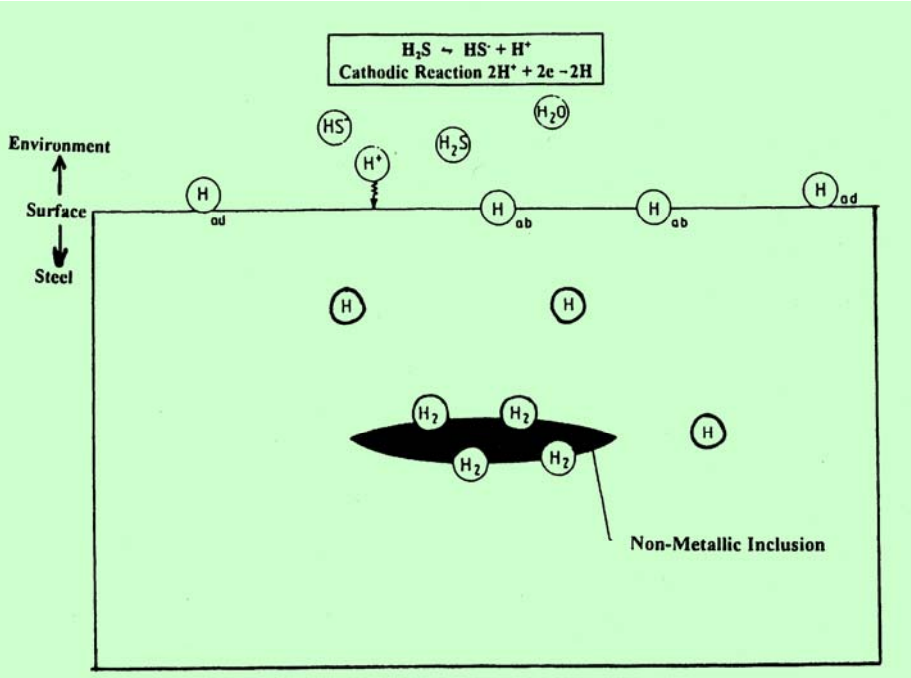


FIGURE 2. Mechanism of hydrogen entry.

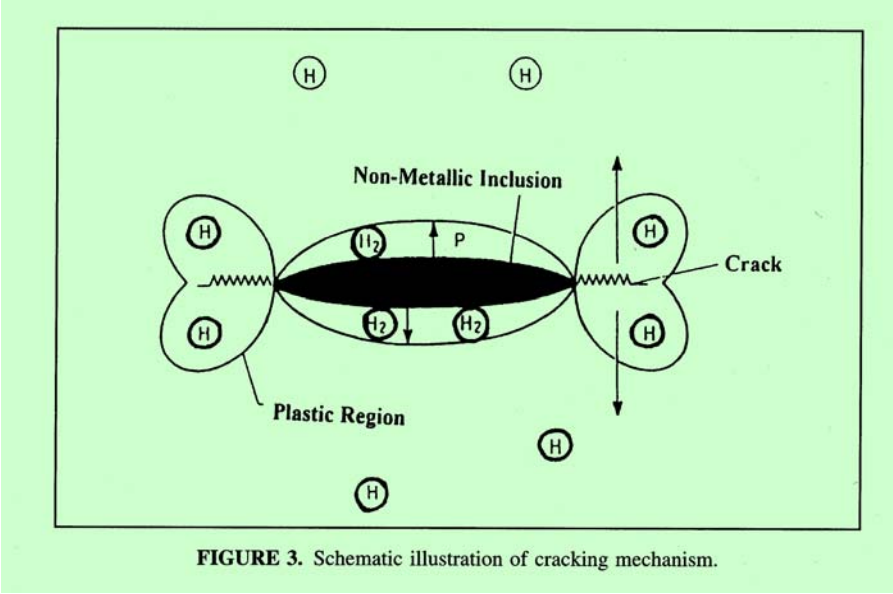


FIGURE 3. Schematic illustration of cracking mechanism.

13.1 Source of Hydrogen

1) Gas phase : H_2, H_2O, CH_4, H_2S, and NH_3.

2) Cathodic reaction in corrosion, electroplating and pickling.

$$2H^+ + 2e^- \rightarrow H_2 \text{ or } 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

3) Melting and Welding

- Hydrogen dissolved in steel during melting can lead to flakes or bursts in forging or rolling processes.
- Hydrogen pickup in welding can lead to cracks in either the weld metal or the heat affected zone.

13.2 The Hydrogen Evolution Reaction(HER) & Hydrogen Absorption Reaction(HAR) :

Electrochemical reaction of hydrogen ion on metals is divided into two components;

HER : Hydrogen is liberated as gas.

HAR : Hydrogen is dissolved into the metal lattice.

A. Reaction steps for HER

HER occurs in a number of consecutive steps ;

1) transport of a hydrated proton $(H_3O)^+$ to the double layer.

2) loss of water of hydration shield in the vicinity of the double layer,

3) adsorption of the proton to the metal surface,

4) discharge (electronation) of the proton to an adsorbed hydrogen atom,

5) a) chemical combination of two adjacent hydrogen adatoms to form a hydrogen molecule- possibility of surface migration between site of discharge and site of recombination,

$$MH_{ads} + MH_{ads} \rightarrow H_2 + 2M,$$

where M is reaction site.

b) electrodic combination of an adatom and a photon to form a hydrogen molecule,

$$MH_{ads} + H^+ + e^- \rightarrow H_2 + M$$

6) desorption of H_2

7) bubble formation as H_2 molecules coalesced, and evolution of bubbles.

- For each of the above reaction, there is an activation energy. Steps 1), 2), 3), and 7) have relatively low activation energy. Thus the overall reaction is controlled by 4), 5) and 6) steps.

- The combination and desorptions are usually combined because of the weak affinity for H_2 to chemisorb. Thus, The HER occurs in two important steps- discharge followed by chemical or electrochemical combination.

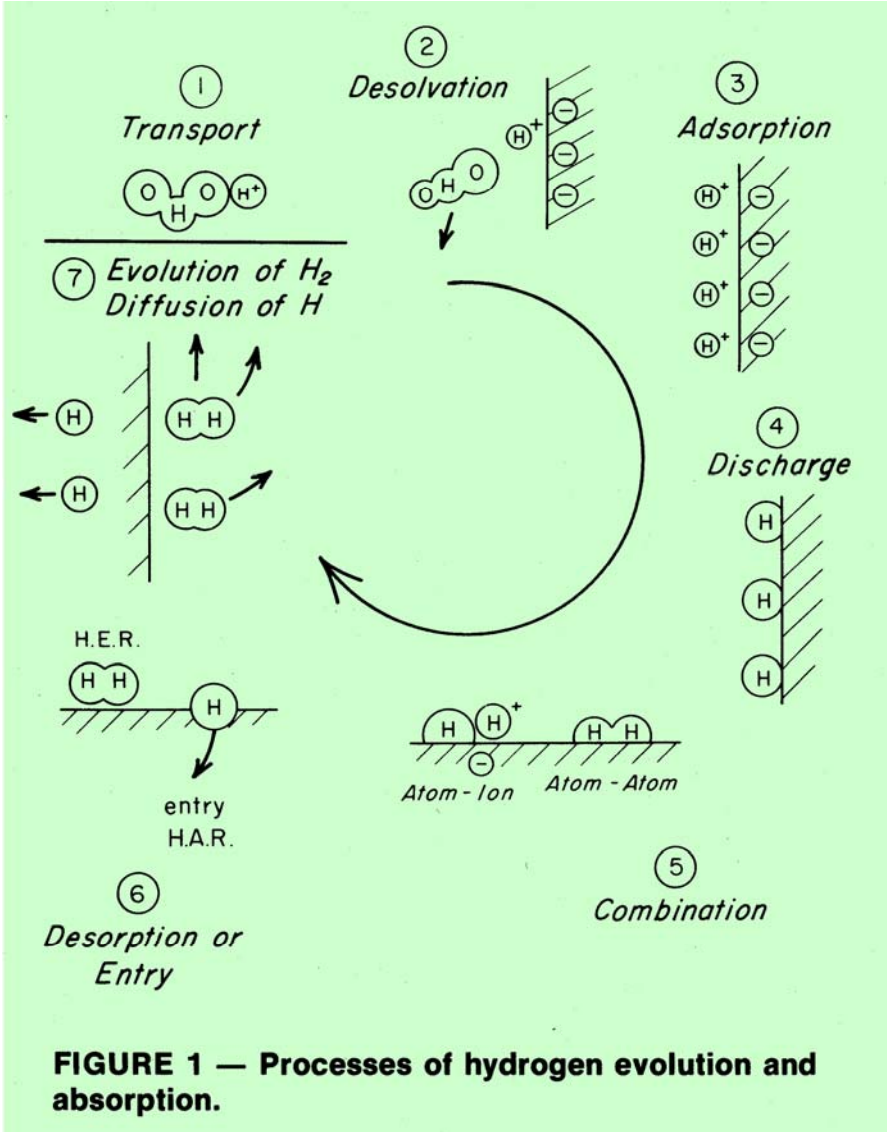


FIGURE 1 — Processes of hydrogen evolution and absorption.

B. HAR reaction

the absorption reaction rate, $r = \nu\theta M_s \exp(-\Delta H^*/RT)$,

where

• M_s is the number of metal sites available for adsorption, θ is the fraction of these covered.

ΔH^* is the activation energy for the absorption step.

• The HAR is often studied by permeating a thin metal specimen. The following equation obtains at steady state :

$$\text{Permeation rate, } P = D(C_s - C_L)/L,$$

where C_s is the subsurface conc. at the entry side, C_L is the conc. at a depth L. D is the diffusivity of hydrogen.

• Models of Hydrogen Entry

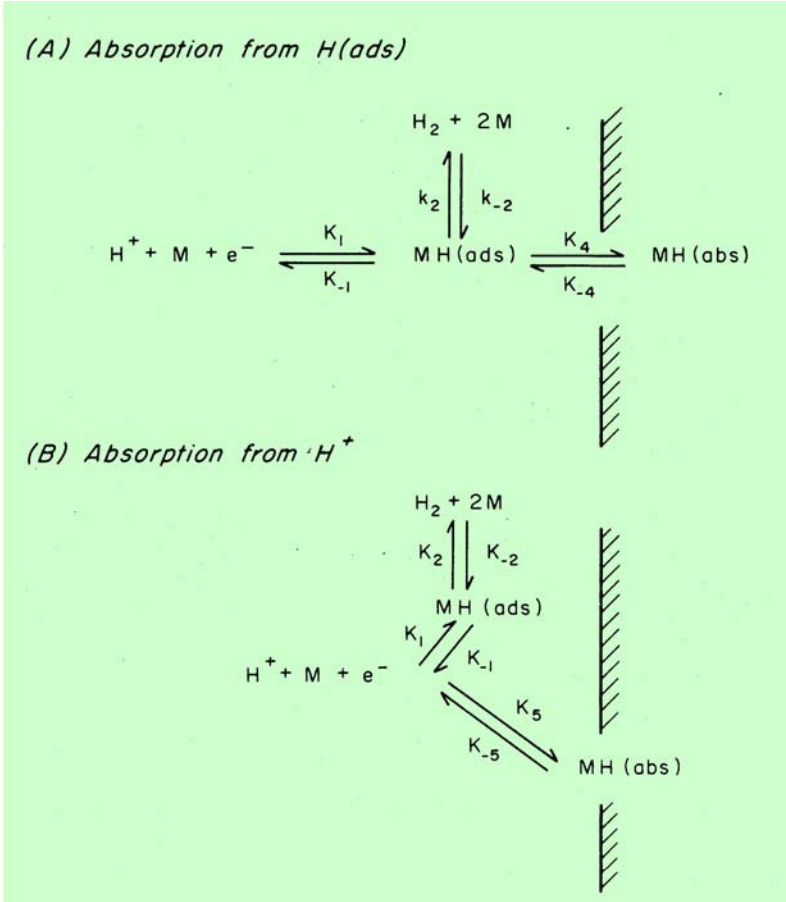


FIGURE 2 — Models for hydrogen entry into metals. (A) Absorption from atomic hydrogen, and (B) absorption from protons.

C. Effects of environmental variables on the HAR

1) Electrochemical potential

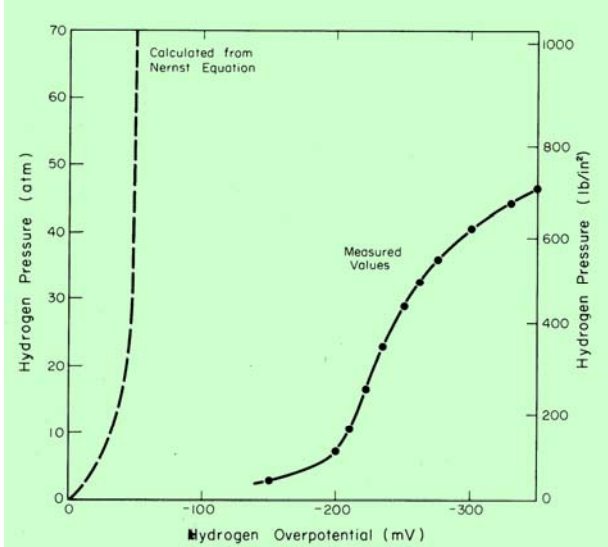


FIGURE 4 — Relationship between theoretical and measured hydrogen gas pressures and overpotential of an iron cathode polarized in 0.1N H_2SO_4. (From the work of de Luccia *et al.*, reported by Enyo.)[13]

2) Solution composition

- pH : At the corrosion potential, the hydrogen entry kinetics increase with the acidity of solution. At the same applied potential or current, the absorption rate is much higher in the acid solution. Thus, the lower the pH is, the higher the entry rate will be.

- Type of anion : Halides such as Cl^-, Br^- and I^- are very effective in increasing the hydrogen uptake due to the increase the surface coverage. Very little hydrogen is absorbed during pickling in nitric acid despite a high a corrosion rate. This is because the nitrate ion is easily reduced by freshly-discharged nascent hydrogen to NO_2, NO, N_2 or NH_3 depending on the circumstances.

3) Hydrogen Promoters

The very small additions of As, P, S, Sb etc. in solution (or alloy) bring about a substantial increase of the hydrogen entry kinetics by inhibiting the hydrogen recombination reaction. These promoter species form stable hydrides such as H_2S, H_2Te, H_2Se, PH_3, AsH_3 and SbH_3. Elemental form of promoters have very low exchange current densities of the HER.

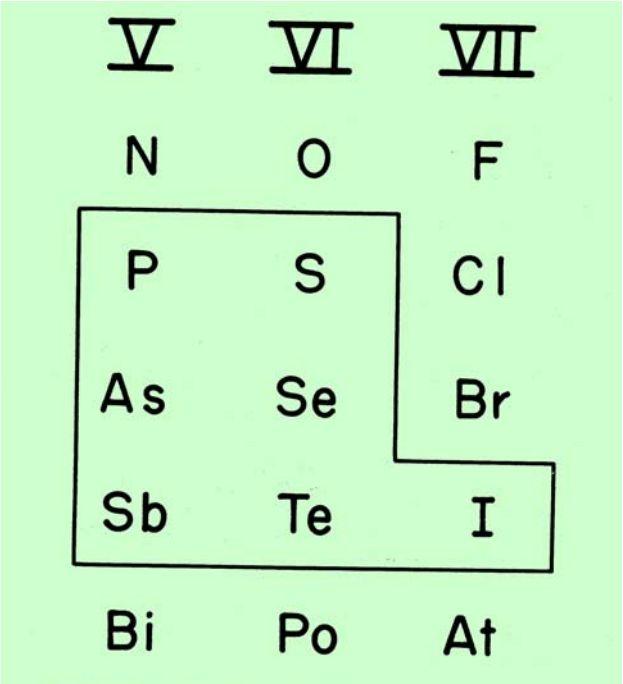


FIGURE 6 — Portion of the Periodic Table showing location of promoter elements.

4) Hydrogen entry inhibiting species

The organic nitriles such as benzonitrile C_6H_5CN and naphthonitrile $C_{10}H_7CN$ decrease decrease hydrogen absorption when they are added to solution. These molecules probably adsorb vertically thereby restricting the access of hydrogen ions to the surface.

5) Temperature

6) The presence or absence of stress

D. HAR from the gas phase

$$H_2 \rightarrow 2H_{abs}$$
$$k = C_{H_{abs}}{}^2/PH_2$$

$$\therefore\ C_{H_{abs}} = kPH_2{}^{1/2}$$

$$\begin{array}{ccc} H_2 & \rightarrow & H_2 \\ & \downarrow\uparrow & \\ H_{ads} & \rightarrow & H_{abs} \end{array}$$

13.3 Hydrogen Permeation

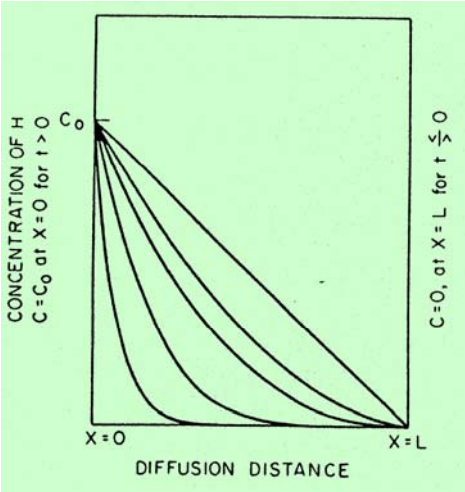
The permeation rate for hydrogen in a metal is a function of both diffusivity(D) and solubility(S):

$$P = f(D)(S)$$

A. Factors affecting solubility of hydrogen

- Type of lattice structure
- Alloy content
- Hydrogen pressure
- Cold work

B. Electrochemical method on hydrogen permeation through thin membrane

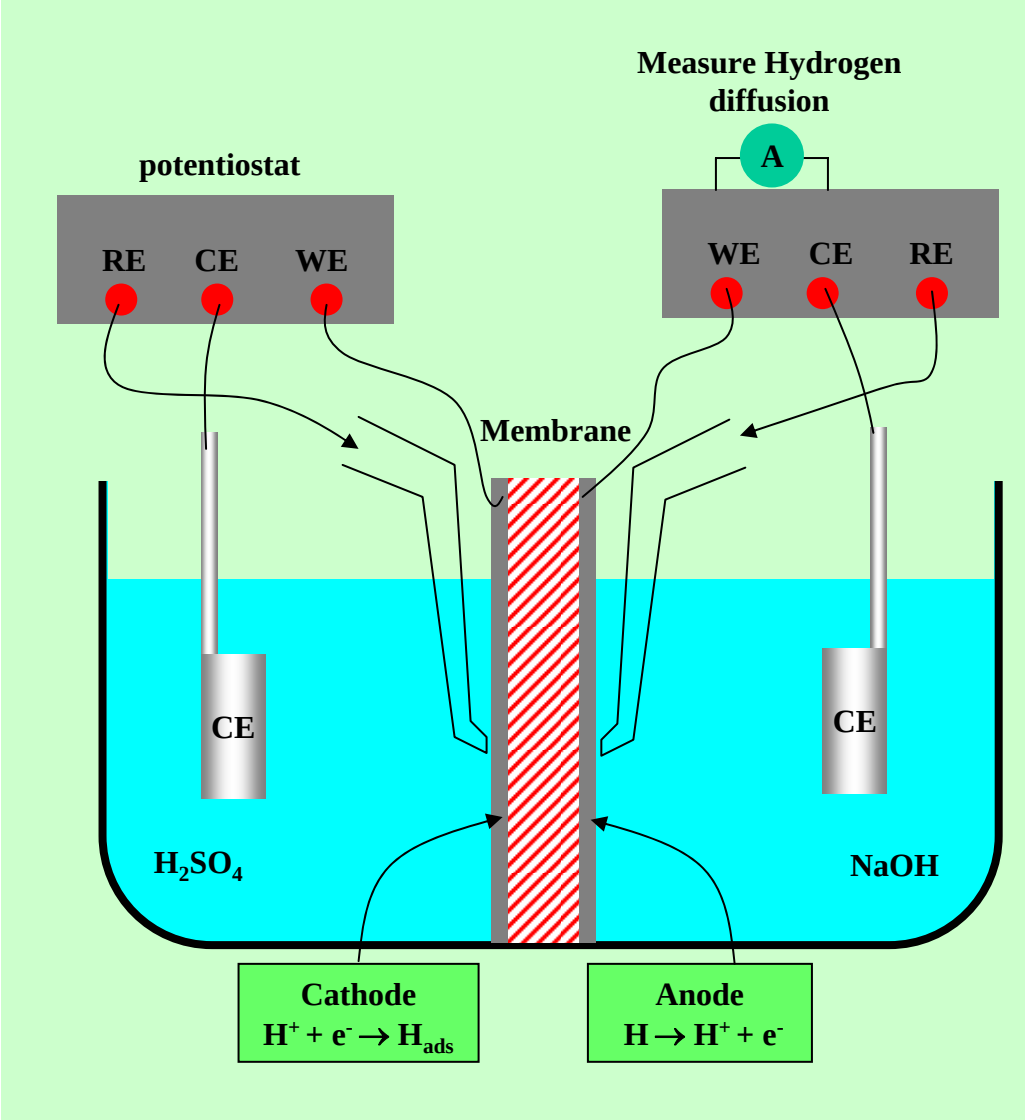


$$\frac{\partial C_H}{\partial t} = D\frac{\partial^2 C_H}{\partial x^2}$$

$$-D\frac{\partial C_H}{\partial x} = \frac{J}{zF}$$

The steady-state de-electronation current density i_d is related by the condition of flux equality to the flux J of hydrogen permeating through the membrane :

$$i_d/F = J$$



Using Fick's law for the steady state permeation flux,

$$i_d/F = J = -D_H (C_{entry} - C_{exit})/L = -D_H (C_o - 0)/L = -D_H C_o/L,$$

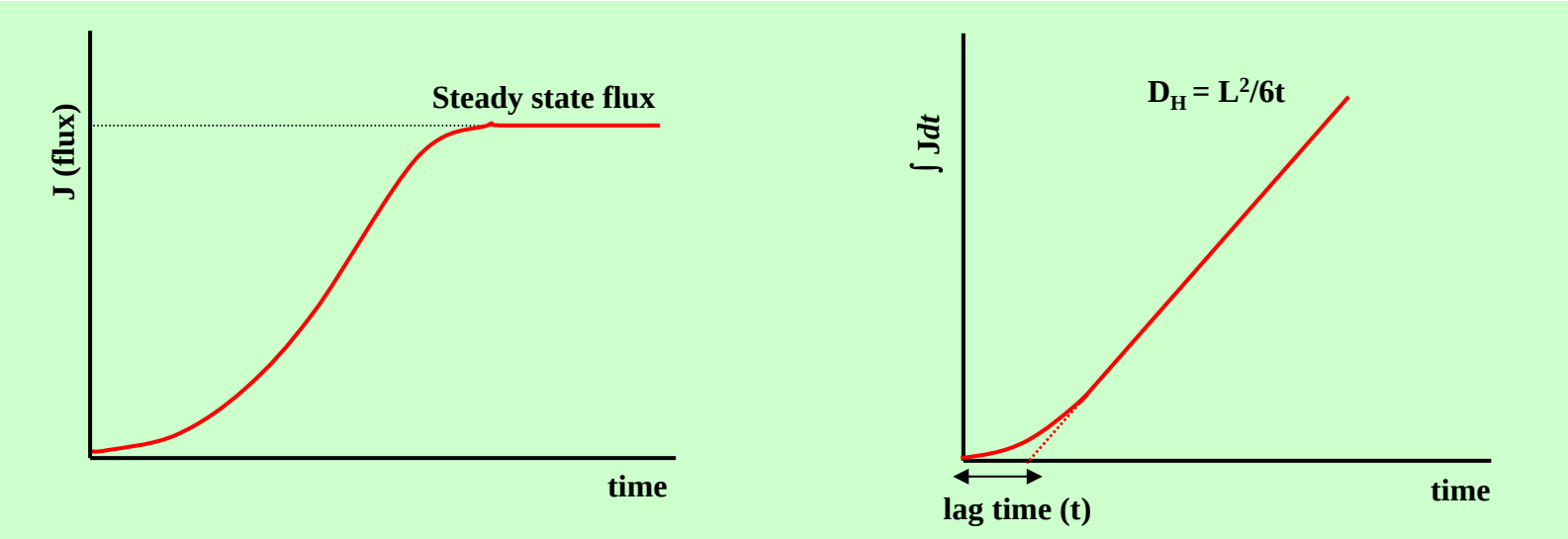
where C_o is the solubility of hydrogen on the entry side of membrane of thickness L.

The D_H is calculated by measuring the lag time, t, from the following relationship :

$$D_H = L^2/6t$$

By measuring the permeation current, it is possible to obtain the D_H and solubility of hydrogen(C_o) :

$$J = - D_H C_o/L \rightarrow C_o = - JL/D_H$$



C. Effect of stress on the permeation of hydrogen

When a hydrogen atom occupies an interstitial site, there is a certain displacement of the atoms around the interstitial atom. Hence, one may consider that there is a certain change in volume due to the entry of hydrogen atom into the lattice. The net change in volume so resulting, due to one gram of hydrogen, is the partial molar volume V_H, of hydrogen in the metal.

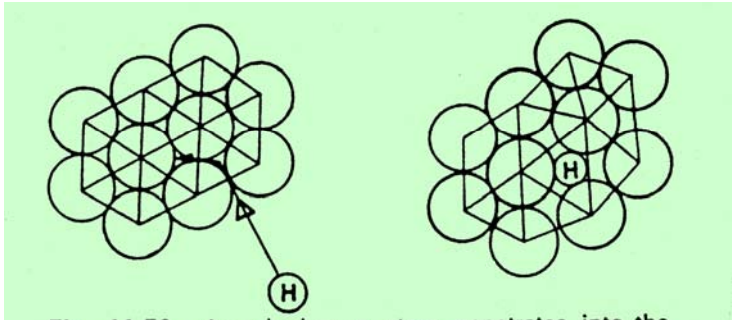


Fig. 11.50. As a hydrogen atom penetrates into the lattice, slight distortion takes place to accommodate it.

From the thermodynamic relations ;

$\mu_H = \mu_o + RT\, ln\, C_H$, $(d\mu_H/d\sigma) = V_H = RT\, ln\, C_H/d\sigma$

$P = 1/3\,(\sigma_x + \sigma_y + \sigma_z) = \sigma_h$, where σ_h is the hydrostatic stress.

$$\int_{C_{O.H}}^{C_H} \partial \ln C = \int_{\sigma_{h=0}}^{\sigma_h} \frac{\overline{V}_H}{RT} \partial\sigma \quad \Rightarrow \quad \ln \frac{C_H}{C_{H.O}} = \frac{\overline{V}_H \sigma_h}{RT}$$

$$\therefore C_H = C_{o.H} \exp(V_H \sigma_n / RT)$$

where C_H and $C_{o.H}$ is the hydrogen solubility in the presence and absence of stress.

- Applied stress does not significantly change the D_H since the lag time(t) remains nearly the same. Thus, the applied stress changes the solubility and permeation for hydrogen. The larger the lattice strain or distortion, the larger the concentration of hydrogen. All imperfections in crystals are regions of distortion or strain. Hence, absorbed hydrogen finds its way of experimentally to, and concentrates at, such imperfections.

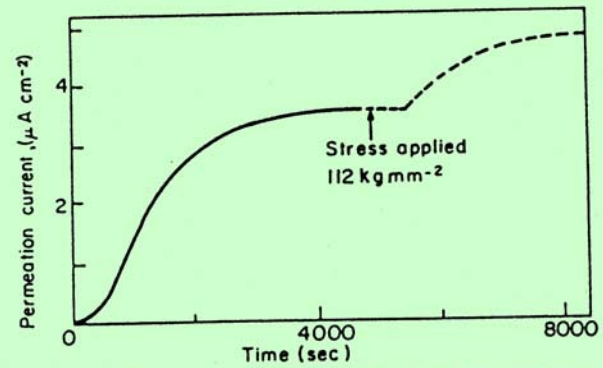
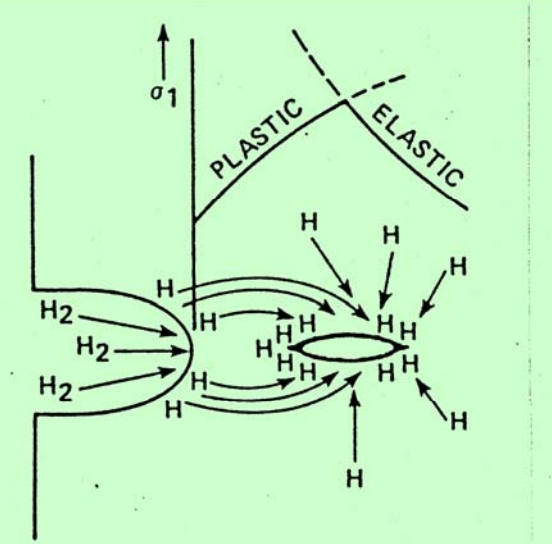


Fig. 11.53. As the metal membrane is strained, the hydrogen-permeation current increases.

- Due to the triaxial stress state near the notch or cracks, the higher solubility of hydrogen exists in those regions. Thus, the hydrogen absorbed or dissolved in the lattice will diffuse to the region of triaxial stress from adjacent region, which is called a <u>stress induced diffusion of hydrogen.</u>



D. Hydrogen Traps

Hydrogen diffusing through a metal lattice accumulates at metallurgical defects such as grain boundary, inclusions, interfaces, voids, dislocations, solute atoms and vacancy. An interaction between hydrogen and defects is called hydrogen trap. The hydrogen accumulation by traps cause a lag in the hydrogen flux through a thin sheet of the metal. The rate of steady-state hydrogen diffusion is reduced by the presence of traps indicating that filled traps have an attraction for the passing hydrogen flux.

a. Reversible traps : hydrogen trapped with a low binding energy can be released from trap ; interaction with mobile dislocations.
b. Irreversible traps : hydrogen trapped with a high binding energy is tightly bound, completely immobile; interaction with stationary solute atoms, interfaces, and grain boundary.

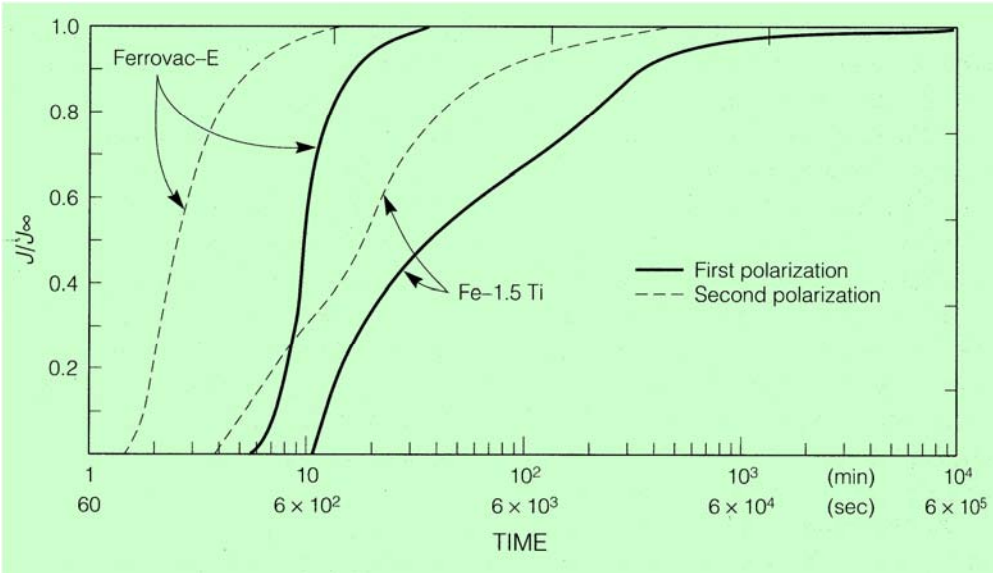


Table 1. Selected Values of Trapping Parameters for Hydrogen-Trap Interactions in α-Iron

Trap	E_B, kJ/mol	N_T, m^{-3}
Interstitial solutes (N, C)	~3-15	10^{25}
Si atom	>20	10^{27}
Ti atom	26	10^{27}
Vacancy	46	$<10^{23}$
Y-vacancy	126	$\sim 10^{23}$
⊥ Elastic stress field	20	10^{19}-10^{26}
⊥ Core (screw)	20-30	10^{19}-10^{26}
⊥ Core (mixed)	59	10^{19}-10^{26}
$\frac{1}{2}H_2$ (vapor/void)	29	–
Grain boundary	~59	10^{19}-10^{23}
Free surface	70-95	10^{21}
AlN interface	65	10^{24}-10^{25}
Fe_3C interface	84	10^{24}-10^{25}
TiC interface	96	10^{24}-10^{25}

E. Temperature Effect on the Hydrogen Permeation

A deviation of hydrogen diffusion from the relationship of

$$D_H = D_{o.H} \exp(-Q/RT)$$

occurs due to the trapping of hydrogen.

- A given steel can exhibit high susceptibility to hydrogen embrittlement if stressed at temperatures enough for adequate diffusion of hydrogen to occur (T_A), but low enough for hydrogen trap binding energies E_B to dictate a significant population of hydrogen in trap sites that lead to embrittlement (T_B).

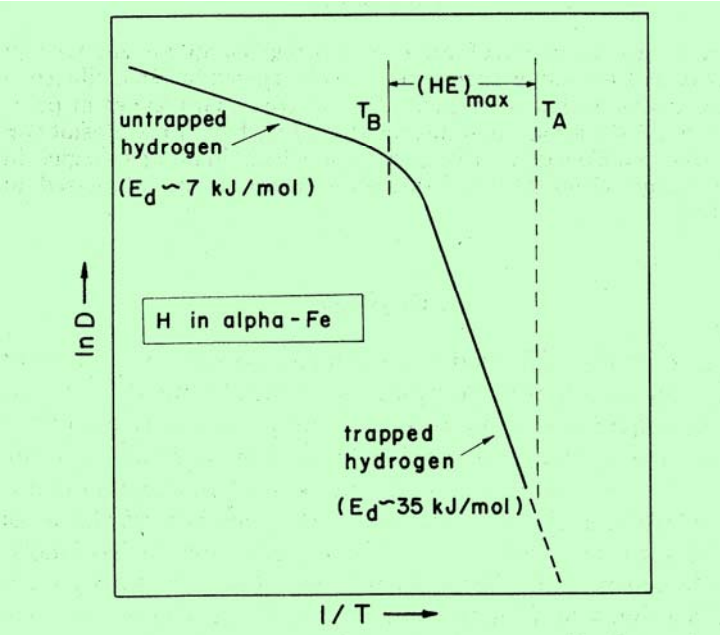


Fig. 1. Schematic illustration of the diffusivity of hydrogen in α-iron. Room temperature typically falls in the range between T_A and T_B where the apparent migrational energy E_d is high.

F. Effect of microstructure of on hydrogen migration

Because traps are associated with various microstructural features, alloying and metallurgical treatments to modify trapping properties offer a promising means to the development of alloys with max. resistance to hydrogen damage. Very fine microstructure such as tempered martensite have a lower permeation rate than coarse structure such as pearlite or spheroidite) because of an increase in the interfacial area between ferrite and cementite.

13.4 Effect of Hydrogen on Iron Base Alloys

1) Hydrogen embrittlement (HE)

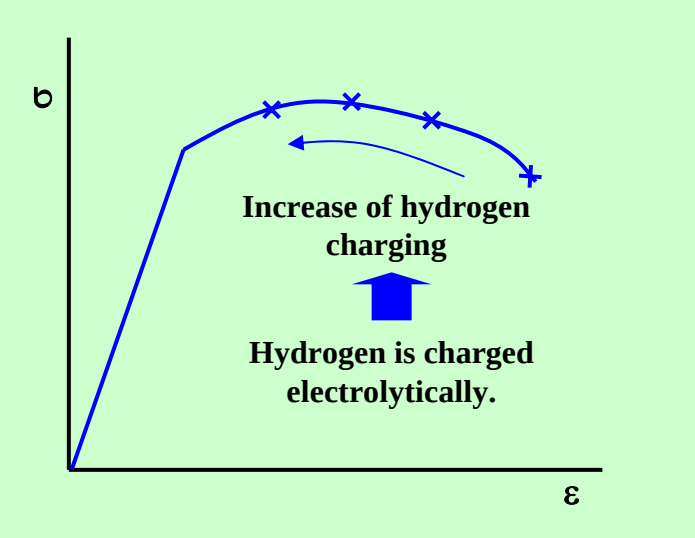
- HE occurs at temperatures between -100 and 300 °F at which hydrogen moves at the same rate as that of dislocation motion.
- At temp. above 300 °F, hydrogen diffusion is too fast to affect metals.
- At temp. below -100 °F, hydrogen diffusion is too slow to affect metal.

2) Effects of strength on HE

The susceptibility to HE depends on the strength level of alloys.

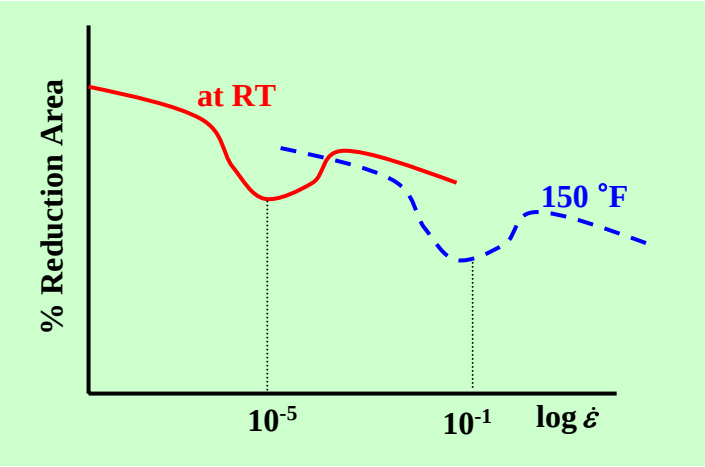
A. Low strength steels

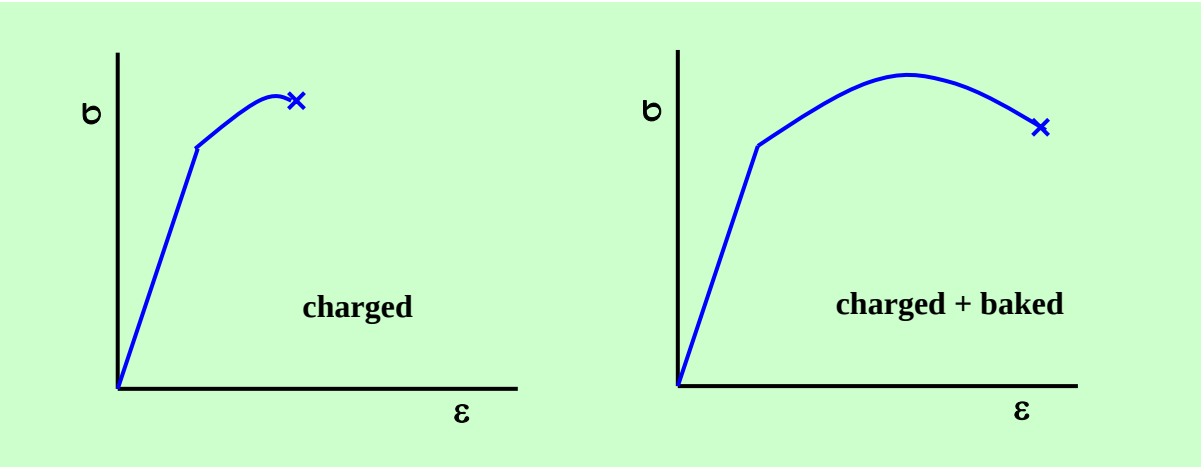
- HE of low strength steel(yield strength<100ksi) is manifested by reduction in ductility. Hydrogen absorbed into a low strength steel does not influence the yield strength and elastic limit but cut off the stress-strain curve drastically.
- The reduction of area (%R. A) is influenced by both the temperature at which tensile test is conducted and the strain rate employed. The total loss of ductility is controlled by the diffusion of hydrogen in a metal.



- The above result is consistent with hydrogen diffusion being related with embrittlement. At a given temp., there will be a strain rate such that hydrogen is just dragged along dislocation.

- HE is reversible under outgassing treatment, or annealing in vacuum.

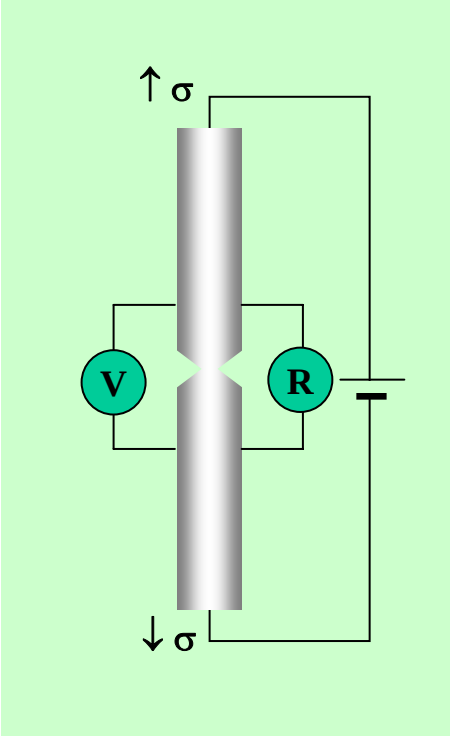




B. HE of high strength steels - Brittle Delayed Failure

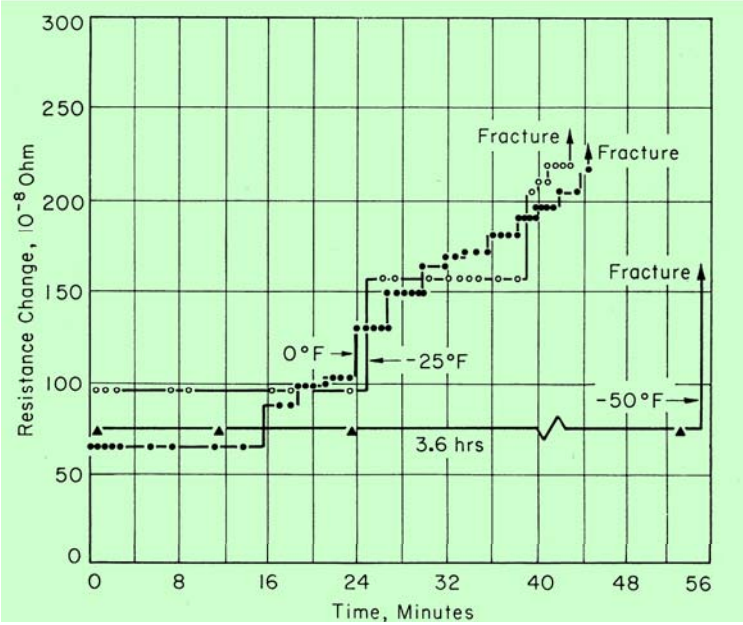
Brittle failure occurs without warning !

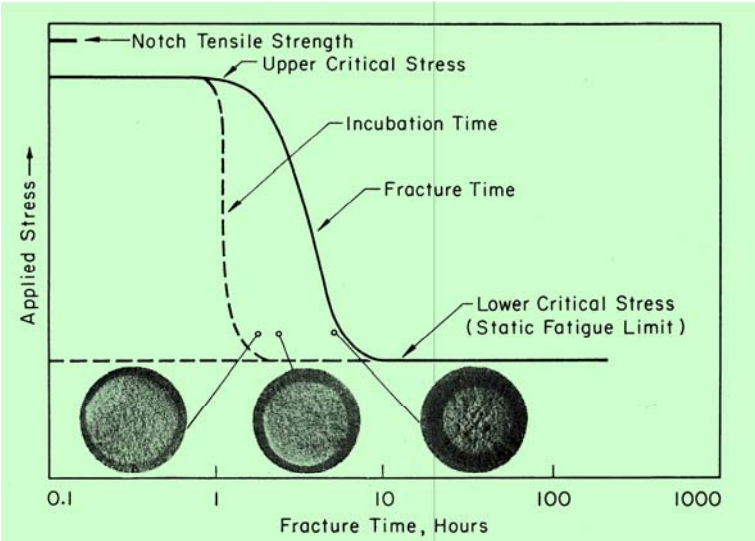
- Hydrogen is electrochemically charged to notched tensile specimens of high strength steel(4340), then cadmium electroplated to preserve hydrogen in the alloy.
- Load statically a series of notched specimens at different stress levels.
- Detect the change in electrical resistance or potential induced by the initiation and propagation of cracks. The decrease in cross sectional area by the initiation and propagation of cracks should cause a measurable change in potential drop or electrical resistance across the crack.
- Measure failure time of the notched tensile specimen at different nominal stresses ;
  nominal stress : load/ area of notched region.

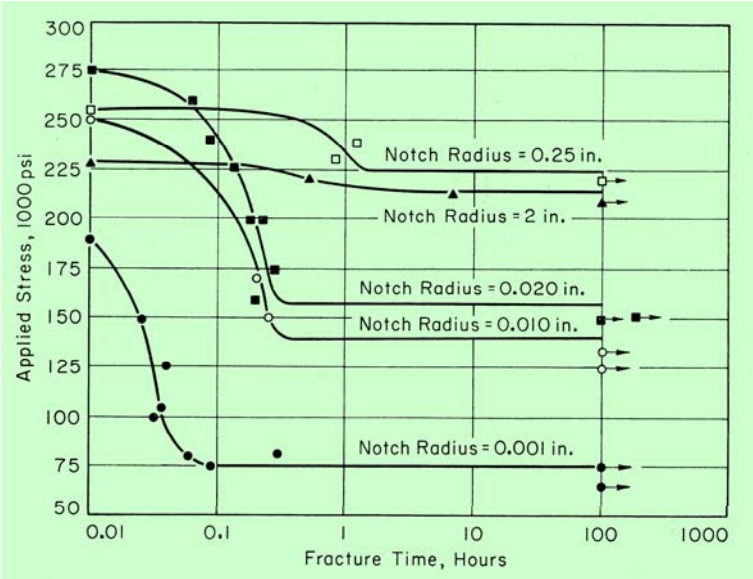


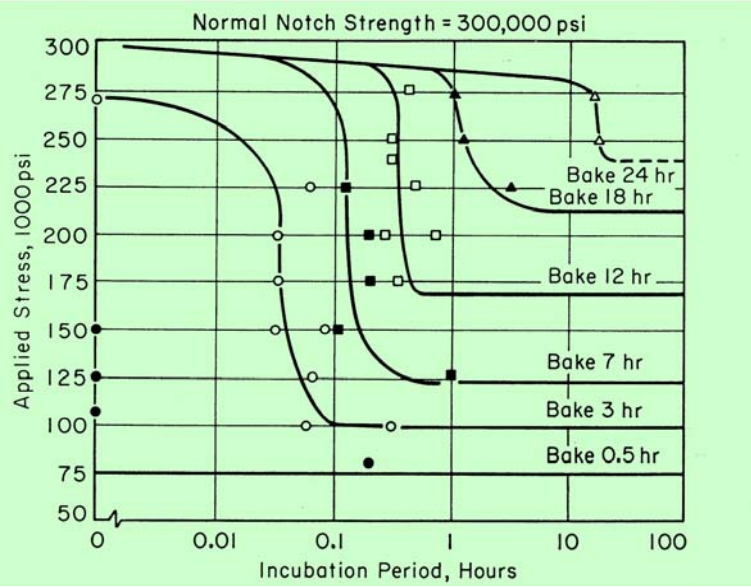
Results

- Crack initiated after an incubation time and then propagated discontinuously.
- Hydrogen induced delayed failure may occur over a wide range of applied stress.
- There is a minimum critical stress below which failure does not occur. i.e., lower critical stress = static fatigue limit.
- Notch strength, failure time, and static fatigue limit increase with decreasing hydrogen concentration.
- Lower critical stress increases with decreasing yield strength of steel. Lower critical stress may equal to the yield strength if the yield strength of steel is 100 ksi or lower.
- The lower critical stress varies with notch severity; it rises as the notch severity (radius) decreases.









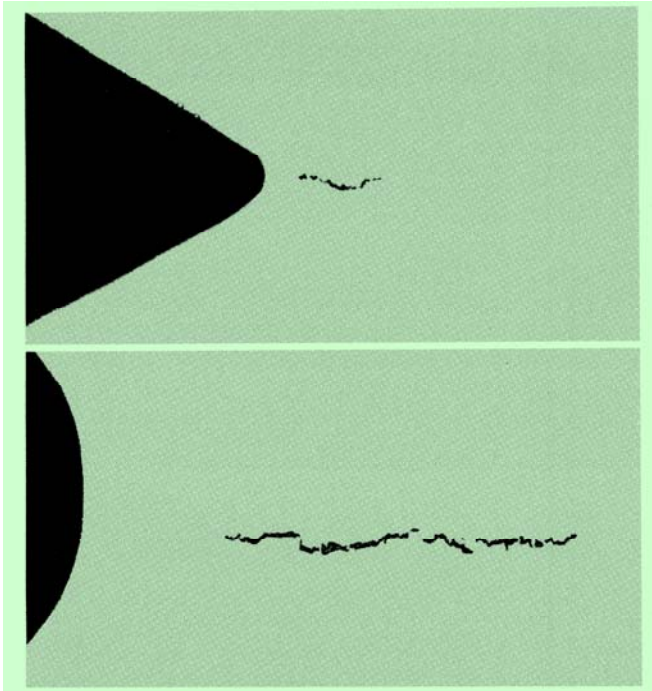
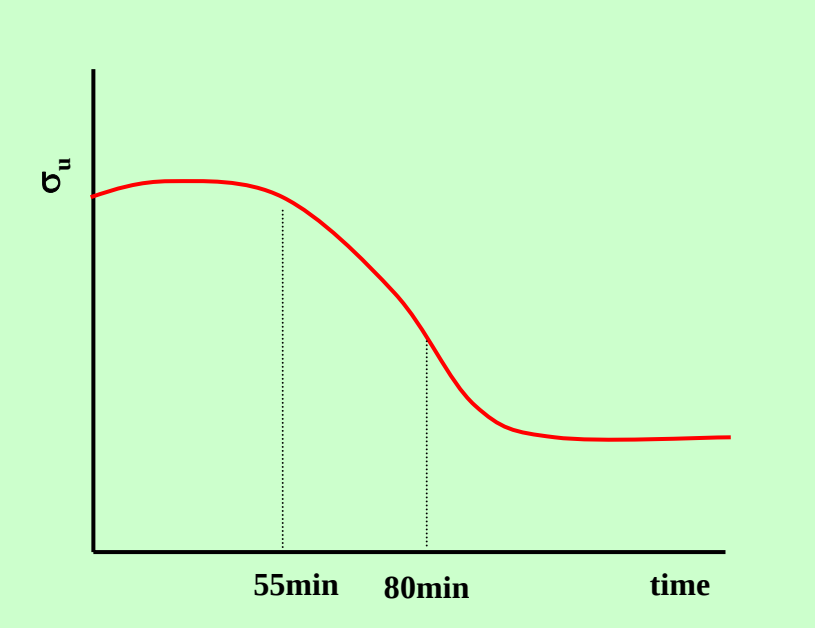


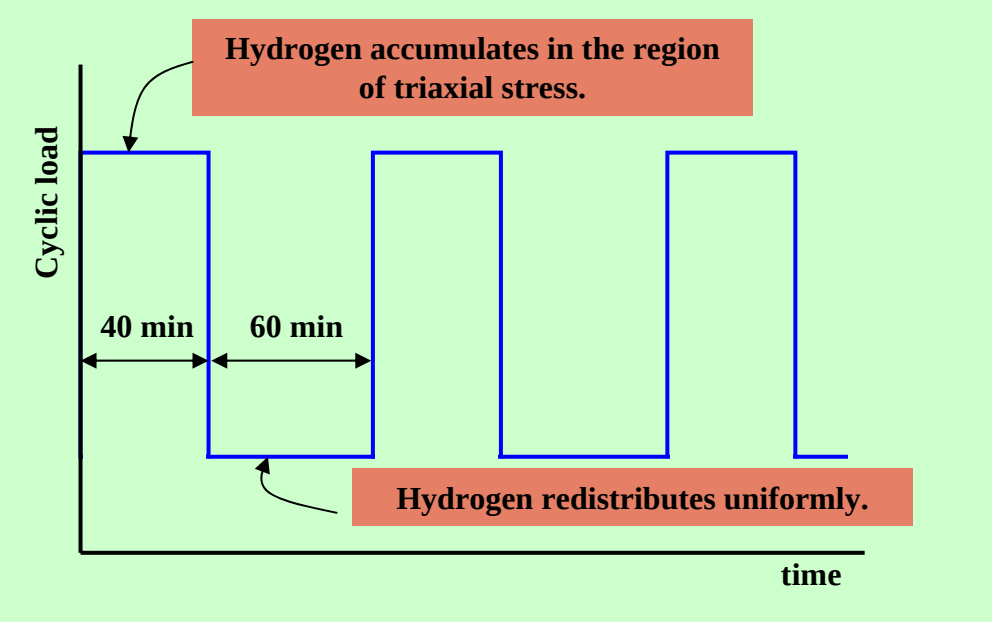
Fig. 4—Cracks Observed in Hydrogenated Notched Specimens Sectioned After Static Loading. Longitudinal section at × 100. Top specimen has 0.001-inch notch radius and bottom specimen has 0.010-inch notch radius. (14)

- The incubation time must be the time necessary for the hydrogen to concentrate in triaxial tensile stress region ahead of notch by stress induced diffusion. A critical concentration of hydrogen is required for crack initiation.

Reversibility of hydrogen induced brittle delayed failure

The 40 min.-stress application and 60 min. unloading has been repeated 15 times without failure.

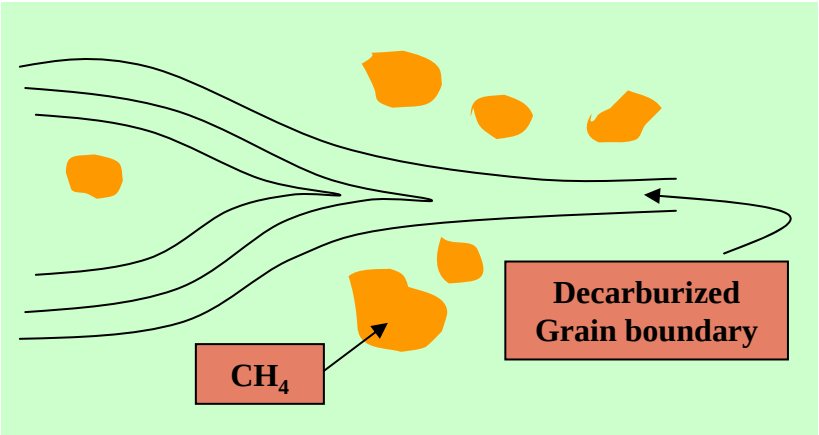




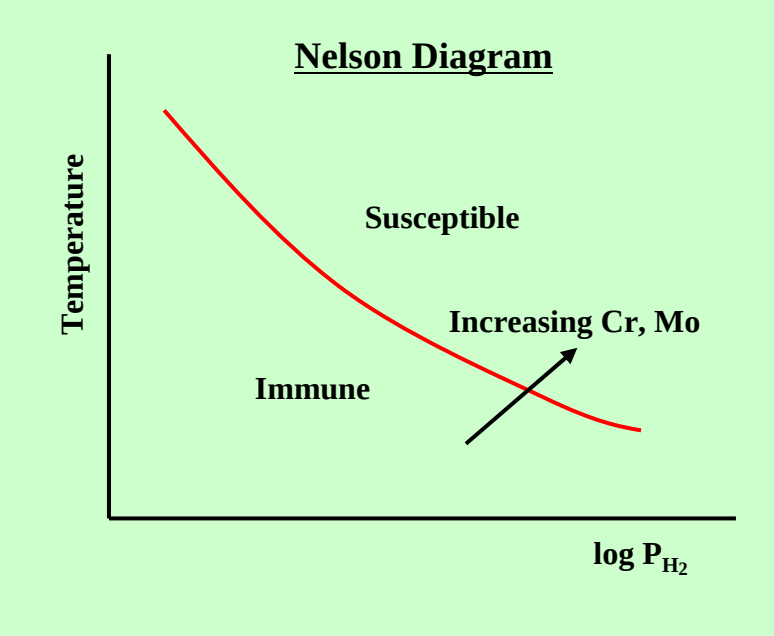
13.5 High Temperature Attack

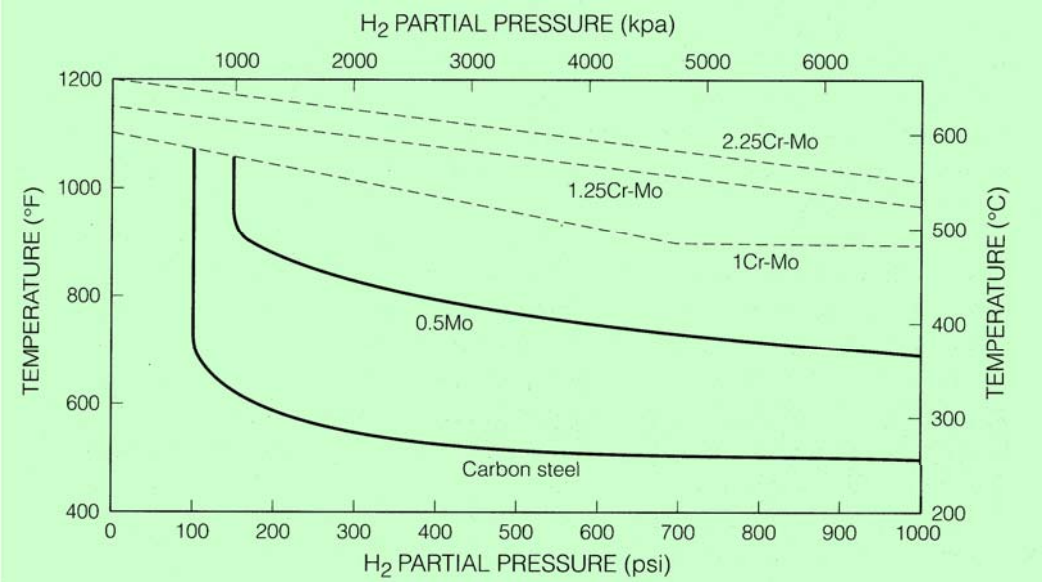
Hydrogen in steels at elevated temperatures (1000-1200 °F) can react with carbides to form decaburized structures and methane gas.

$$C \text{ (in Fe)} + 4H \text{ (in Fe)} \rightarrow CH_4$$



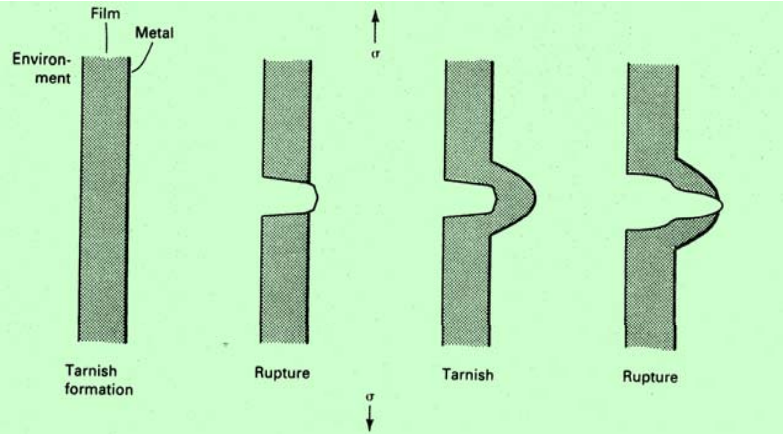
- Decaburization along with grain boundary produces sudden reduction in strength and ductility. To prevent forming CH_4, alloying of strong carbide forming elements is needed in melting ; Zr, Ti, V, Nb, Mo, W, and Cr.
- Cr and Mo is commonly used to increase resistance to susceptibility to hydrogen attack.
- Nelson diagram defines the limits of temp. and hydrogen partial pressure for resistance to hydrogen attack for various alloys.





13.6 Hydride Embrittlement

- The degradation of Group Vb metals (Nb, V, Ta) and Ti, Zr, Hf (group IV) in hydrogen environments by the formation of a brittle metal hydride at the crack tip. When sufficient hydrogen is available in the alloy, a metal hydride precipitates.
- Crack growth by the rupture of brittle hydrides at crack tip → crack arrest by the ductile matrix → reprecipitation of hydride at crack tip under triaxial stress (stress induced hydride formation) →cracks propagate again when a certain value of hydrides is exceeded →show a discontinuous crack propagation.



13.7 Mechanism of Hydrogen Embrittlement

1. Hydrogen gas pressure theory : assumed that HE is caused by a substantial buildup of pressure arising from the formation of molecular hydrogen in internal voids or pores. Such high pressure can undoubtedly be generated under certain conditions, e.g. cathodic charging and may assist the externally applied stress. However, the model does not address the basic question of how the normally ductile metal undergoes brittle failure rather than deforming plastically. Also, the model does not explain the brittle failure of high strength steels exposed to low partial pressure of hydrogen, but it is relevant to blistering in low strength steels.

2. Adsorption theory : Based on the principle that hydrogen adsorbed on the surface of a crack lowers its surface energy required to propagate the crack → Griffith theory

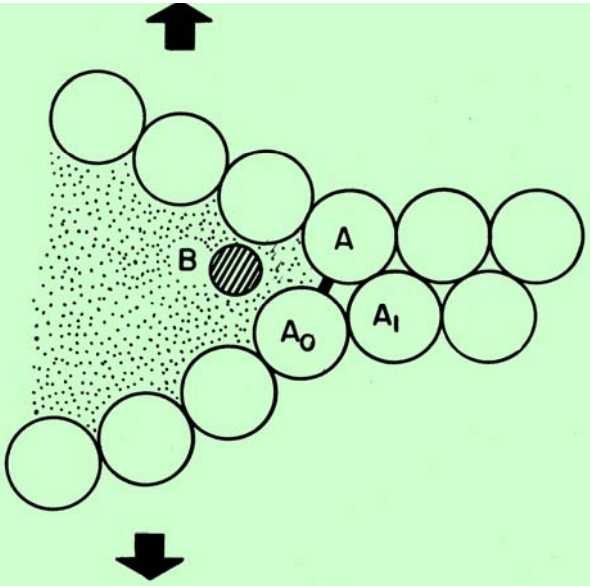
$$\sigma = k\sqrt{E\gamma / a}$$

By lowering $\gamma \rightarrow \downarrow \sigma$: true for brittle material

$$\sigma = k\sqrt{E(\gamma + \gamma_{pe} / a)}$$

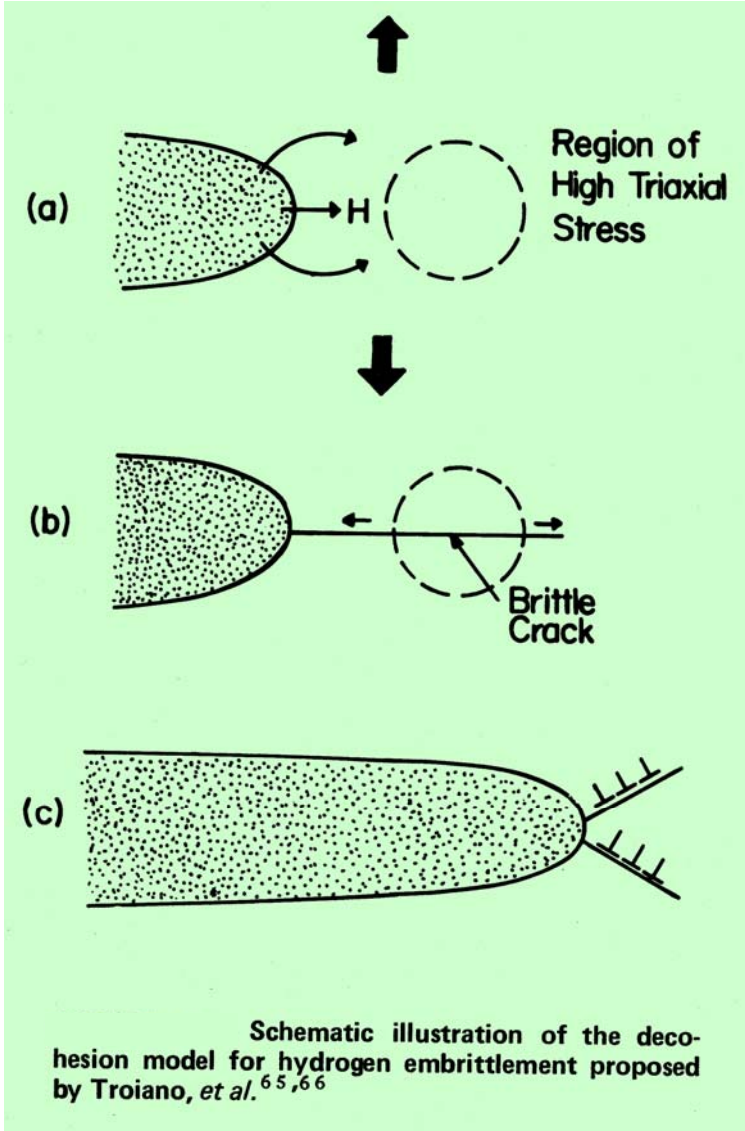
$\gamma_{pe} << \gamma$ for metal

The model does not account for the discontinuous crack growth.



Schematic illustration of the adsorption model.[35] The model requires that a specific ion from the environment, B, interacts and reduces the cohesive strength of strained bond A-A_O at the tip of a brittle crack.

3. Decohesion Theory ; assumed that hydrogen absorbed into the metal lowers the cohesive energy between atom-atom bonds in the metal lattice. Proposed originally by Troiano and his coworkers. They proposed that hydrogen diffuses to regions of triaxial stress ahead of the crack, thus producing large local concentrations. Reduction of cohesive strength was considered to result in crack nucleation when the local hydrogen concentration attains a critical value, the resulting crack rejoining the main front of crack and also advancing out of the region of hydrogen accumulation, where it becomes arrested by plastic deformation; the process was thought to repeat, leading to discontinuous propagation.



Schematic illustration of the decohesion model for hydrogen embrittlement proposed by Troiano, *et al.*[65,66]