



Approximation of Hydrogen Induced Delayed Fracture of Overlaid Cladding in Pressure Vessels Steel Structure

Ronnie H. Rusli¹ & T. Fujita²

¹Visiting Research University of Indonesia
Jl. Salemba 4, Jakarta 10430 Indonesia.

Email: ronnie@indo.net.id

²Faculty Of Engineering, Osaka University, Toyonaka, Japan.

Abstract. Distribution and electronic states of interstitial hydrogen atoms in the iron lattice are discussed in regard to their influence to the lattice bonding, and theory of hydrogen induced delayed fracture of steel based upon it is proposed. Characteristics of delayed fracture are accordingly well accounted for.

Keyword: *delayed fracture; cladding; hydrogen; steel; dislocation.*

1 Introduction

Among other interstitial type light elements to be contained purposely or unavoidably in steel and other strong metals and alloys, hydrogen is peculiar in respect to the influence to fracture and failure of these materials. It is well known that hydrogen induces embrittlement in various kinds of nonferrous metals and their alloys by forming hydrides, which are soft and brittle as compared with the matrix lattice. The hydrogen embrittlement appears in steel and iron alloys cladding frequently as the hydrogen induced delayed fracture, in which no hydride formation is observed and with a very low average concentration of hydrogen with relatively low applied normal stress a crack leading to unrecoverable fracture appears and propagates intermittently with long incubation periods. As will be mentioned later, the delayed fracture of steel has some characteristic features, which seem very difficult to be explained without deficiency of contradiction by any proposed mechanism of initiation and propagation of unrecoverable crack induced by hydrogen. It is also generally accepted that in most cases of stress corrosion cracking, hydrogen produced by chemical reactions on the surface of stainless steel cladding with acidic wet environment permeates into the material and play the main role in cracking, as well as in the case of delayed fracture in the dry condition. It is worthy of note that only hydrogen can cause embrittlement, delayed fracture, and stress corrosion cracking while other interstitial type solute elements, carbon and nitrogen, are not directly related with these fracture phenomena in steel.

In this paper, it is intended to approximate the atomic process of hydrogen induced delayed fracture, taking account of the electronic structure, bonding nature, and other related properties of the interstitial hydrogen and matrix iron atoms. By analogy with other point defects, aggregation of excess solute hydrogen atoms in the platelet shape in iron lattice under the tensile stress is considered, and a new theory of hydrogen induced delayed fracture based upon the platelet clustering of hydrogen associated with the change of bonding of the matrix iron lattice is proposed.

2 Electronic States and Distribution of Hydrogen in Iron Lattice

Hydrogen atoms absorbed interstitially in transition metal lattices are believed to be largely ionized, there is electrons being partly devoted to the conduction band and/or to the incomplete d or f shell of near neighbour metal atoms. Toya [1] treated the state of adsorption of hydrogen on metals theoretically and proposed that there are two types of adsorption: the s-type ad atoms sitting in interstices of the lattice near the surface have much the same electronic structure as the interstitial atoms in the interior except the release of lattice strain and redistribution of conduction electrons near the surface which lower the energy of the former by the order of 0.1 eV/atom. They can further lower the energy by about 0.1 eV by changing their state of adsorption to the r-type, in which the hydrogen atoms just stick out on the surface and there is electrons contribute to the resonance type bonding with nearby metal atoms on the surface due to a sort of s-p-d hybridization. This means that hydrogen atoms absorbed in excess in the transition metal lattice can lower their energy (enthalpy) by the transition from the interstitial to the s-ad- atom state, and further to the r-type state by moving to the surface. When the number of r-ad atoms is large enough, their bi-atomic association will take place to form the ad-molecules which will, then, be desorbed from the surface to the outer space becoming gas molecules which will, then, be desorbed from the surface to the outer space becoming gas molecules. Hydrogen process of desorption will require the activation enthalpy of the order of a few electron volts, but, when the hydrogen concentration in the lattice and on the surface are high enough, the chemical potential of hydrogen outside of the surface will be lower than in the interior.

Another conceivable process to lower the energy for excess interstitial hydrogen atoms is to aggregate in the lattice to form hydride of possibly small clusters. In the case of iron, carbon steel, and low alloy steels, hydride formation is not expected and therefore, their hydrogen embrittlement cannot be attributed to the hydride formation. On the other hand, from the lattice parameter change of hydrogen atom is considered to exist even though small compared with that of carbon and nitrogen, and it could drive excess hydrogen solute atoms to aggregate in platelet from in the lattice as will be discussed later. In Fig. 1 are

schematically shown the above mentioned various states of hydrogen near the surface of iron lattice. Since no exact calculations and measurements are available, their relative energy levels are tentatively indicated.

Considerations in some more details on the electronic states of interstitial hydrogen iron and iron alloy lattices are obtained from the Mössbauer spectra [2]. The transition metals and their alloys are electrolytically hydrogenated, which exhibited a large positive isomer shifts, and this means either the decrease of conduction electron density against the concept of following of 1s electrons from hydrogen atoms into the conduction band of the metal, or the increase of electrons in the inner shell. The 3d band in the case of iron, which shields the probe nucleus from the outer s electrons, i.e., the conduction electrons. In addition, the amount of isomer shift is not fully accountable but only one third at most by the lattice expansion due to hydrogen absorption. More direct evidence of the change of 3d state of iron is given by the measurement of the internal magnetic field in the hydrogenated iron alloys, which shows remarkable decrease of magnetic moments of iron atoms neighbored by interstitial hydrogen atoms [3]. Therefore, it is concluded that interstitial hydrogen atoms in iron and iron alloys strongly affect the 3d state of neighbouring iron atoms, reducing the number of unpaired 3 d electrons and, consequently, the bonding nature of the iron lattice presumably inducing a bonding level below the top of 3d band by 3d-1s hybridization [4].

The Mössbauer spectroscopy also revealed inhomogeneous distribution of infused hydrogen in iron alloy lattices. For instance, the spectra from stainless steel and Fe-Ni alloys clearly indicate that hydrogen atoms occupy the interstitial sites neighbouring to nickel sites preferably and produce inhomogeneous distribution and local distortions undoubtedly because of the stronger affinity of hydrogen for nickel than iron. By further hydrogenation, vacant interstitial sites are gradually occupied to result in more homogeneous distribution in which iron atoms will be forced to have hydrogen neighbours. The inhomogeneous distribution of solute hydrogen associated with alloying elements and lattice distortions in iron alloys and steels and the change of bonding nature of iron atoms neighbouring to hydrogen atoms in the lattice are very important and must be taken into considerations when the hydrogen induced delayed fracture is to be elucidated.

3 Precipitates Associated of Point Defects

Radiation produced or thermally produced vacancies and interstitial atoms are known to cluster and form dislocation loops at the temperature where they can move in the lattice of metals. Super saturated solute carbon and nitrogen in α -iron lattice also form thin platelet like clusters and precipitates associated with

dislocation loops at their peripheries. This suggests that the platelet type aggregation of point defects in super saturation is the most stable and usual form in metals. The vacancy and interstitial type loops are not only resistive against plastic deformation due to dislocation interactions but also quite resistive against the applied stress in crack initiation because the lattice cohesion through the loop face is not disturbed at all although stacking faults sometimes appear on the loop face. Similarly, the thin plate-like clustering of carbon or nitrogen atoms in the iron lattice to form Fe_2C , Fe_4C , Fe_{16}N_2 is resistant to the crack initiation because of strong covalent bonding among the carbon or nitrogen and iron atoms in and around the cluster [5]. On the contrary, a hydrogen cluster, if exists any, could be a crack initiator under the applied normal stress, because the hydrogen atoms in the cluster have possibilities both to change the electronic state from the interstitial type to the adsorption type and to change the electronic structure of iron atoms in and neighbouring to the cluster, and accordingly, the iron lattice bonding could be loosened. The process of clustering and electronic changes will be precisely mentioned later.

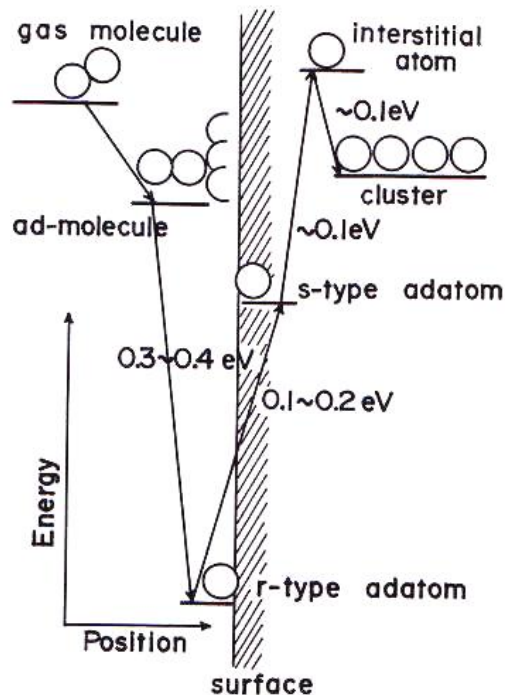


Figure 1 Various states of hydrogen near the surface of iron lattice and their estimated relative energies [8]

Aggregation of excess hydrogen in a platelet form in iron and steel has actually been observed by Kamachi et al. [6]. By electron microscopy of hydrogenated stainless steel and structural steel, they found that thin plate like aggregates accompanied with tangled dislocations appear and grow as the hydrogenation proceeded, finally leading to severe lattice distortion and spontaneous crack initiation. This fact strongly supports the before mentioned presumption that planer clustering of interstitial hydrogen atoms in iron and steel lattice may take place associated with the strain energy release and the lattice binding could be weakened.

4 Characteristic Features of Delayed Fracture and Proposed Theories

The hydrogen induced delayed fracture of steel has various characteristic features, which are summarized in the following:

- (1) The delayed fracture takes place in steels, which have very small solubility's for hydrogen and have no tendency to form hydrides. It is worthy of note that Fe-30%Ni alloy can contain a large amount of hydrogen and thereby produces hydride, which accordingly causes the hydrogen embrittlement, and yet exhibits characteristic behaviour of hydrogen induced delayed fracture [7].
- (2) A certain level of applied stress exclusively in tension is necessary to induce the delayed fracture. Stress concentration around large size imperfections and high internal stresses in the complicated structure of high tensile strength steels seem to assist the applied stress in crack initiation and propagation.
- (3) The temperature range, in which delayed fracture appears, is confined between about -50°C and $+100^{\circ}\text{C}$, and the crack needs the incubation periods for initiation and intermittent propagation. These facts clearly show that the process is controlled by the trapped diffusion of hydrogen in the material [13].
- (4) The influence of lattice defects, especially dislocations, to the delayed fracture is noticeable.
- (5) The average concentration of hydrogen in steel efficient to induce delayed fracture is as low as the order of p.p.m. but local concentrations are considerably high at the large size imperfections, such as sulphide, phosphide and other inclusions, and the propagating crack usually start from them.

The theories so far proposed by many investigators are not always success to explain all of the above characteristics nor in agreement with each other. For instance, Zapffe [8] and Kazinczy [9] proposed that the internal hydrogen gas

pressure in a pre-existing void would assist the applied stress to initiate a crack and to continue its propagation. Nevertheless, the estimated gas pressure does not always look sufficient, and the idea is not applicable to the open crack, which cannot maintain the gas pressure. Petch [10] argued that hydrogen is adsorbed on the inner surface of a void or Mott-Stroh type crack [11,12] and makes the crack formation and propagation easier by lowering the surface energy which is balanced with the elastic strain energy. Johnson, Morlet and Troiano [13], on the other hand, interpreted their own experiment of low temperature deformation and successive annealing of hydrogenated steel by assuming that high concentration of hydrogen in the triaxial region just ahead of the crack tip can weaken the lattice binding and will control the brittleness. Oriani [14] also considered the lattice embrittlement by interstitial solute hydrogen. However, the experiment by Johnson et al. could be explained by either the gas pressure theory or the surface energy reduction theory if the effect of collection and transfer of hydrogen by tangled dislocations around the void is taken into consideration [15]. The lattice weakening by interstitial hydrogen atoms with certain level of concentration is difficult to estimate and not conclusive unless the hydride formation is expected. While, the gas adsorption theory does not seem favourable for explaining the incubation periods and the effect of dislocations.

5 Clustering Model of Hydrogen Induced Delayed Fracture of Steel

Consider a number of excess interstitial hydrogen atoms in the lattice in steel. Since the solubility of hydrogen in iron lattice is extremely small, in order to reduce the chemical potential they will diffuse to large size lattice imperfections such as non-metallic inclusions, pre-existing voids or micro-fissures, plastically deformed zones with a large number of dislocations, etc., which will accordingly absorb them and become powerful hydrogen reservoirs, especially when hydrogen is generated at the surface of the material. The reduction of enthalpy will rise partly from lattice strain energy release of the order of 0.1 eV and partly from the change of electronic state from the isolated interstitial type to the adsorbed type with a reduction of energy of the same order. Various types of state of hydrogen atoms shown in Fig. 1 are expected in and around the lattice imperfections.

Another possibility to reduce the energy for excess hydrogen atoms in the lattice is to cluster in the thin platelet form along a certain kind of lattice plane, as mentioned before, by which the lattice strain energy associated with each interstitial will be released to a large extent. Since the diameter of hydrogen interstitial is as small as 1 Å, the density of hydrogen atoms in the cluster could be very high, possibly higher than that of carbon in the carbon clusters or the

first form of precipitation with the compositions of Fe_4C and Fe_2C respectively. The energy difference between the octahedral and tetrahedral interstitial site for hydrogen in the iron lattice must be very small and occupancy of both of them could result in a very dense structure of the clusters. Applied tensile stress normal to the platelet face of the cluster will accelerate the hydrogen clustering because it can lower the strain energy of the system, as will be mentioned later.

Change of the total lattice energy associated with platelet clustering of hydrogen can be roughly calculated as a function of the cluster size and applied normal stress [16]. The energy decrease due to aggregation of hydrogen in a platelet with the effective thickness, b , and the radius, r , is $-\pi r^2 b \epsilon / \Omega$, where ϵ is the binding energy of a solute hydrogen atom to the cluster and Ω the atomic volume of hydrogen in the cluster. ϵ contains the energy release by strain energy interaction of hydrogen interstitial and the electronic energy change in the cluster, which will also be mentioned later. When a normal stress, σ , is applied perpendicular to the platelet as indicated in Fig. 2, a further release of the lattice strain energy of $-\pi r^2 b \sigma$ will occur since the two lattice planes above and below the platelet are displaced outward by $b/2$ each by the clustering under the stress σ . More precisely, the interaction between the applied tensile stress and randomly distributed single interstitials, which may have a uniaxial anisotropic stress configuration around each and yet produce a uniform isotropic volume expansion of the lattice as a whole, should be taken into consideration as a basis of the above calculation of strain energy release. However, in order to avoid the complication in calculation $-\pi r^2 b \sigma$ is tentatively multiplied by a numerical constant, k , which may be smaller than but not very far from 1. On the other hand, the clustering produces a dislocation loop with the radius, r , and the Burgers Vector, b , which increases the energy of the system by $G b^2 / 2 (1-\nu) r \ln (r/r_0)$ where G is the modulus of rigidity, ν the Poisson's ratio and r_0 the dislocation core radius. Therefore, the total energy of the system will be changed by the formation of a cluster by

$$\Delta E = \pi r^2 b \epsilon / \Omega - k \pi r^2 b \sigma + G b^2 / 2 (1-\nu) r \ln (r/r_0). \quad (1)$$

At present the value of ϵ is not known, but we may tentatively take it as 0.05 eV, one order of magnitude smaller than that of carbon and nitrogen, about 0.3 eV. Then, taking the other values as $\Omega = 10^{-24} \text{cm}^3$, $b = 2.5 \times 10^{-8} \text{cm}$, $G = 4 \times 10^{12} \text{dynes/cm}^2$, $r_0 = 5 \times 10^{-8} \text{cm}$, $K = 1$, and $\nu = 0.34$, ΔE is calculated by varying b and r as in Fig. 3. When σ is larger than 200 kg/mm^2 , no activation would be required for the formation of platelet cluster of hydrogen except for migration of interstitial hydrogen atoms. Even when σ is lowered to 100 kg/mm^2 , the cluster will still grow up nearly continuously by surmounting critical size, r^* , of about $7.8 \times 10^{-8} \text{cm}$ and the critical activation energy, F^* , of about 0.8 eV. The process

in this condition will readily proceed at around room temperature, as actually observed as before mentioned. When no normal stress exists, the critical size and energy increase to about $15 \times 10^{-8} \text{cm}$ and 4.3 eV respectively, as the rightist curve in the figure shows. This means that without a large normal stress the excess hydrogen atoms will not collect together to form a growing cluster before they are trapped by other effective lattice defects or diffuse away because of the very small binding energy among themselves and a long incubation time to reach the above-mentioned large critical size and energy. A tensile stress of the order maximum of up to 100 kg/mm^2 can easily be achieved at the tip of either a pre-existing crack or a propagating crack, and it will effectively raise the binding energy between the hydrogen atoms in the cluster and make the process of clustering proceed.

When a cluster is formed in the lattice with the aid of applied tensile stress, conduction electrons must be repelled more or less from the cluster region because of the lattice expansion and bonding level formation, as before mentioned, and the hydrogen atoms in it would closely resemble the s- type ad atoms in respect to the strain energy release and the conduction electron redistribution. Repulsion of conduction electrons from the cluster region will diminish the iron lattice bonding to a considerable extent. In addition, a more severe change to loosen the lattice cohesion could be expected by the conversion of the s-type like hydrogen atoms in the cluster to the r-type like atoms. The resonance type local bonding of the strain energy release and the conduction electron redistribution. Repulsion of conduction electrons from the cluster region will diminish the iron lattice cohesion could be expected by the conversion of the s-type like hydrogen atoms in the cluster to the r-type like atoms. The resonance type local bonding of the r-like atoms with nearest iron atoms above and below the platelet cluster.

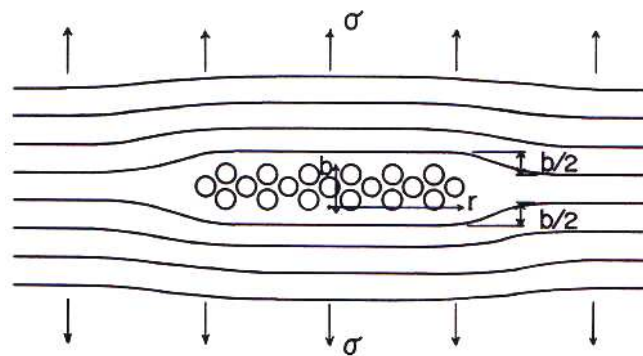


Figure 2 A platelet hydrogen cluster with the radius, r , and thickness, b , under the applied normal stress, σ .

On the other hand, conversion from the s-type to the r-type ad atoms must increase the overall lattice bending around the cluster, since the r-type ad atoms need more room than the s-type ad atoms in the iron lattice.

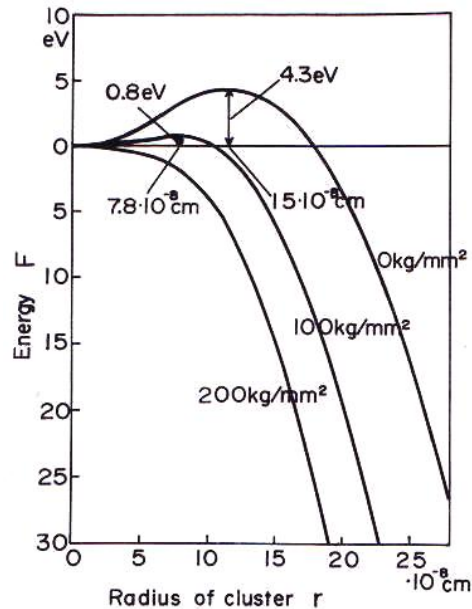


Figure 3 The calculated energy change associated with the hydrogen cluster formation under various applied stresses.

The necessary lattice relaxation may be achieved, if some dislocations are created so as to yield the room for the r-type atoms, as Fig. 4 indicates. When the above processes from the excess isolated hydrogen interstitials to the platelet cluster, s-ad atom like aggregation, conversion from s-like to r-like adsorption state and finally a slight opening of the lattice by dislocation motion are allowed successively, they will further proceed until the r-type ad atoms are partly desorbed to produce gas molecules inside the opening. These processes are illustrated in sequence by Fig. 2 and Fig. 4. if supply of hydrogen from outside is very high and unexhausted, the aggregate will continuously grow up and ultimately cause the spontaneous crack formation. This seems to be what Kamachi et al. [16] observed by X-ray diffraction and electron microscopy. In their case, no tensile stress was applied during the electrolytic hydrogenation and, therefore, according to the above calculation the clustering of hydrogen is not always expected. However, the nickel content and the defects of large size in their specimens presumably attracted the infused hydrogen atoms, and without the nucleation process continuous aggregation and spontaneous cracking took place.

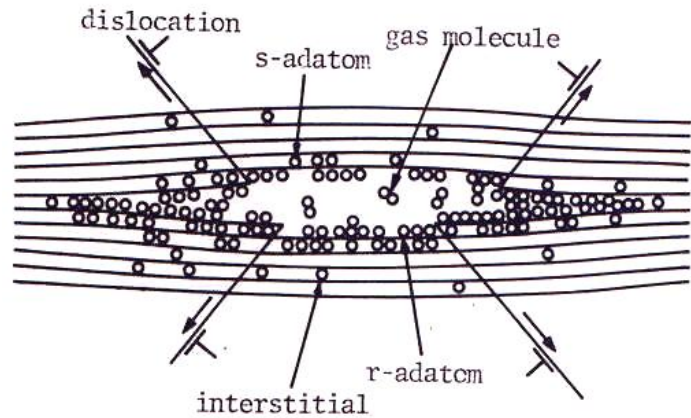


Figure 4 Schematically representation of the process of platelet aggregation of hydrogen atoms and spontaneous of hydrogen atoms and spontaneous crack formation in the iron lattice.

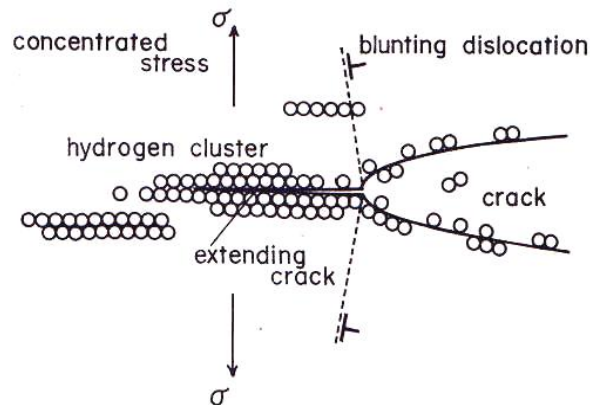


Figure 5 A possible mechanism of extension of crack in the delayed fracture of iron and steel.

In order to explain the usual delayed fracture in steel, let us consider the before mentioned pre-existing cracks. Due to the reactions during the process of production of steel or due to the following environmental effect, they will attract and absorb a certain amount of hydrogen. The multiplied tensile stress in the vicinity of the crack tip tends to start a propagating crack and, at the same time and the same place, to induce the platelet clustering of hydrogen as before mentioned. In the absence of hydrogen, the concentrated stress will give rise to plastic deformation which will then conversely relax the stress concentration by blunting the crack tip before the propagating crack unless the applied stress exceeds a certain critical the crack tip by emitting dislocation is suppressed, as calculated by Rise and Thomson [18]. By taking account of the shear interaction

force, image force, and ledge formation force on the blunting dislocation from the crack tip, for instance in the case of iron lattice, to be of the order of 2 eV. This means that the iron lattice can be either ductile or brittle according to the change of testing temperature or some other slight changes in mechanical or physical conditions around the crack in problem.

In the presence of hydrogen, the clusters would be formed ahead of the crack tip by the stress assisted thermal process with an activation energy of the order of 1 eV, which is probably lower than that for emitting the blunting dislocations, as already mentioned, and the above crack propagation conditions would be largely changed: For instance, since the lattice relaxation perpendicular to the cluster face, that is taken into account by the second term of the energy expression of Eq. (1), takes place at the very tip of the crack, the concentrated stress to initiate dislocations from the crack tip will be dispersed and weakened. Consequently, the Rice Thomson condition will become more favourable for brittleness. In addition, another origin of brittleness will be induced by the change of bonding nature in the cluster too loosen the lattice cohesion, as mentioned before. Thus, the hydrogen cluster will become an effective path for crack extension as shown in Fig. 5. Then extending crack will be arrested after passing through the region of cluster formation, and will not proceed further until the hydrogen atoms come to the new site ahead of it to form new clusters. This process of the stress-induced diffusion of hydrogen to form clusters ahead of the crack and the crack extension will be repeated intermittently. In fact, Takano and Suzuki [19] have observed under the electron microscope that in hydrogenated vanadium thin platelets of hydride were formed at the tip of a propagating crack repeatedly and allowed the intermittent crack propagation. In the case of the delayed fracture in ordinary steels, the platelet hydrogen clusters may fill the role of embrittlement instead of the hydride in vanadium.

6 Summary

Dislocations seems to be closely related with the above mechanism of hydrogen induced delayed fracture in many respects. Not only acting as the stress reliever or the crack-blunting medium, dislocations produced in the plastic zone ahead of the crack tip will be a powerful collector and transferred of solute hydrogen as Bastian and Azou [20] have considered.

Kikuta et al. [21-22] calculated the diffusion process of hydrogen toward the plastic zone with a high density of dislocations, and interpreted my experimental results of delayed fracture by using the calculation. Occurrence of delayed with either the brittle or ductile appearance could be well explained by such correlations between hydrogen clustering and dislocations as above.

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