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1. INTRODUCTION

The recognition of hydrogen as a ubiquitous and generally deleterious solute in metallic systems dates to the nineteenth century when Johnson (1) observed and reported most of the general phenomena of hydrogen embrittlement of steels. Since that time a great deal of research has been carried out to extend these observations to other systems, both ferrous and non-ferrous. The role of hydrogen, present as either a solute or as part of a gaseous atmosphere, has been recognized in a variety of ductile and brittle failures. Since these have often resulted in serious engineering and economic consequences, much effort has been directed towards characterizing and documenting these failures. A related body of literature directed towards stress corrosion failures has simultaneously arisen. In recent years it has been increasingly recognized that an intimate relationship exists between hydrogen and some stress-corrosion types of failure. As a result of the previous efforts, the phenomena of hydrogen related fracture are well characterized but at the present time our mechanistic understanding is somewhat faulty.

In the present paper we will review some of the major aspects of the hydrogen related failures and attempt to relate these to mechanisms of fracture. No attempt will be made to completely review the voluminous hydrogen literature (2); rather the effort will be directed towards understanding the general underlying principles which control the failures. An even more cursory review of the stress-corrosion literature will be attempted (3) as we shall only place emphasis on those aspects which are related to hydrogen failures. In carrying forth our discussion we shall take cognizance of the fact that no single failure mechanism appears to be able to account for all of the observed behavior. There appear to be a number of related mechanisms, each of which may have applicability to a class of material and to a range of conditions.

There appear to be a variety of hydrogen related failure modes. In the present paper we shall emphasize the "classical" case of hydrogen embrittlement in which there is a change from a ductile to a brittle or cleavage failure mode as a result of hydrogen present as a solute or in the environment. Only cursory mention will be made of the effects of hydrogen on ductile failure modes (4) or of elevated temperature failures caused by the interactions between hydrogen and other alloying elements such as O or C (5).

Metal-hydrogen systems exhibit a greatly disparate range of behaviors. A large number of metals form stable hydrides, i.e. compounds which are generally centered about stochiometric metal-hydrogen ratios and in which the hydrogen solutes are ordered (6, 7) (Table I). The bonding of these hydrides range from metallic to covalent to ionic and their stabilities differ greatly. All of the metals which form stable hydrides are hydrogen embrittled. The amount of hydrogen in solution which causes embrittlement is often appreciable. Hydrogen solid solubility in these systems can be very large, ranging up to values of H/Metal $\approx$ 1 and the heats of solution from the gas phase are negative (Table I). In contrast to these systems, non-hydride formers (Table I) generally have very limited ranges of solid solubilities and have positive heats of solution from the gas phase. These metals are also subject to hydrogen embrittlement, often at hydrogen concentrations as low as a

Table I. THERMODYNAMIC PROPERTIES OF SOME METAL - HYDROGEN SYSTEMS

Element	Hydrides	ΔH solution (from gas phase) (KJ/mole)	ΔH formation (of hydrides) (KJ/mole)	H solid solubility at 300K (H/Metal)	Comments
Li	LiH		-90.7	very small†	hydride has ionic bonding
Cu	CuH	+54.8		$<8 \times 10^{-7}$ *	hydride has not been reported to form from metal
Ag		+56.9	–	$<5 \times 10^{-6}$ *	
Au		+27.6	–	extremely small*	
Mg	MgH_2		-74.5	<0.02†	
Zn	ZnH_2				hydride has not been reported to form from metal
Cd	CdH_2				hydride has not been reported to form from metal
Al	AlH_3	+25.2	-46	2.4×10^{-8} *	hydride has not been reported to form from metal
Y	YH_2, YH_3		-235 (YH_2)	~ 0.2†	
Ti (α)	TiH_2 (γ)	-45.2	-123.5	0.0014†	Metastable hydrides form
Ti (β)	TiH_2 (γ)	-58.2		~ 1.0†	Solubility at $T \gtrsim 700K$
Zr (α)	$ZrH_{1.5}(\gamma)$	-51.1	-94.1	<0.01†	Metastable hydrides form
Zr (β)	$ZrH_{1.5}$ (γ)	-64.5		~ 1.0†	Solubility at $T \gtrsim 1000K$
V	$VH_{0.5}$, VH, VH_2	-31.1	-17.3 ($VH_{0.5}$)	0.05†	
Nb	NbH, NbH_2	-36.0	-29.3 (NbH)	0.05†	
Ta	TaH	-34.0	-20	0.20†	
Cr	CrH, CrH_2	+47.7		$<0.1 \times 10^{-4}$ *	
Mo		+51.5	–	$<0.1 \times 10^{-4}$ *	
W			–	extremely small*	
Mn (α)	–	-8.0	–	1×10^{-4} *	
Fe (α)	–	+28.0	–	3×10^{-8} *	
Fe (β)	–	+22.6	–		
Co (hcp)	–	+20.5	–	$<4 \times 10^{-5}$ *	
Ni	NiH	+16.7		$<7.6 \times 10^{-5}$ *	NiH has been formed by electrolytic charging and under hydrostatic pressures of about 5.7×10^{-4} Pa (10 atm.)
Pd	PdH	-9.6	20 (Pd_2H)	0.03†	
Pt		+18.8	–	$<1 \times 10^{-5}$ *	

† solubility in equilibrium with the hydride

* solubility in equilibrium with H_2 gas at 5.7 Pa (1 atm.)

few parts per million. A number of metals such as nickel exhibit an intermediate behavior, having hydrides which are stable at high hydrogen fugarities but not at the conditions under which embrittlement is observed. In view of the wide range of properties it would be fortuitous indeed if a single embrittlement mechanism could apply to all systems.

2. TYPES OF HYDROGEN RELATED FAILURES

The general classification "hydrogen embrittlement" includes a very wide range of phenomena and types of failure. In this section a brief summary of these phenomena will be presented.

Many of the earliest observations of hydrogen embrittlement were associated with the formation of high pressure hydrogen gas bubbles. These can form as a result of exposure to a high hydrogen fugacity environment such as high pressure gas, cathodic potentials in a corrosion environment or from a high supersaturation of solute hydrogen (8-15). The hydrogen fugacity in the internal bubble is less than or equal to that in the environment but can be as large as 10^5 atmospheres; particularly in an electrochemical environment. Formation of high pressure bubbles is a particularly severe problem in materials where $\Delta H_s > 0$ as high supersaturations can occur on cooling after hydrogen solution at elevated temperatures and many ingot and weld defects in steels and aluminum alloys result from these high pressure bubbles. Extension of these high pressure bubbles by a low ductility fracture mode has been observed (16-18) apparently aided by the high internal pressures. These flaws are usually observed near external surfaces and are termed "blisters: or "flakes" and have been observed in a wide range of ferrous (8, 9), aluminum (13), nickel (14), and austenitic stainless steel (15) alloys.

The presence of a high hydrogen fugacity and the possibility of forming high pressure bubbles is not necessary for failure. In high strength ferrous alloys, embrittlement has been shown to result from gaseous hydrogen environments at pressures of one atmosphere or less (19, 20). Furthermore, many systems with $\Delta H_s < 0$, in which high pressure gas bubbles cannot form as a result of supersaturation during cooling, exhibit severe hydrogen embrittlement (21).

Hydrogen affects both the plastic and fracture properties. High pressure voids in ferrous alloys generally are accompanied by very high local dislocation densities (16, 17). Severe cathodic charging produces the same effect on a more general basis and the stresses which accompany the charging has been shown to result in martensite formation in unstable stainless steels (22). These effects result in a "work hardened" structure with a resulting increased yield and flow stress. In addition, hydrides can act as precipitation strengtheners if they are present as a finely dispersed second phase. Hydrogen can interact with dislocations as a solute pinner to cause yield points and serrated flow (Portevin-LeChatalier effect) (14, 23-26). In general however, these effects are significant only at relatively low temperatures suggesting either a weak hydrogen-dislocation interaction or that the high hydrogen diffusivity (27) and concommitent drift velocity (28) allows the hydrogen to move with the dislocations except at low temperatures. In either case, solute hydrogen has relatively little effect on the macroscopic flow properties of metals in the temperature range in which major effects on the fracture behavior are noted (29-32).

In many systems, primarily f.c.c. alloys, the effect of hydrogen is primarily to decrease the plastic strain to failure (4). Thus in austenitic stainless steels (33,34) for example, solute hydrogen decreases ductility but the mode of fracture remains a highly ductile microvoid coalescence. Thompson has suggested (33) that this may result from hydrogen segregation at second phase particle interfaces, thereby decreasing the interfacial energy and making it easier to nucleate voids during plastic deformation. In material containing a high supersaturation of hydrogen and having ΔH solution > 0, nucleation of voids also provides a "sink" for the excess solute hydrogen thereby increasing the void growth rate due to the buildup of internal pressure. Alternatively, the solution strengthening due to the solute hydrogen may limit the dislocation mobility and thereby reduce the strain to failure in the manner observed in many solution strengthened alloys. At present the relative roles of these effects are not known.

A more dramatic effect of solute hydrogen on the fracture behavior is observed in many of the b.c.c. systems such as the ferritic steels, the Group Vb metals, in zirconium and in titanium alloys as well as in many other systems (21). Over a wide range of hydrogen concentrations and tempera-

tures the ductility of these alloys are markedly decreased and the fracture mode is changed from a ductile rupture to a cleavage or intergranular brittle mode (21). The actual fracture mode depends on a variety of factors and the same system can fail in different manners depending on how it is tested. In most metal-hydrogen systems, for example, testing at high strain rates and/or low temperatures leads to a ductile failure mode whereas a brittle mode is observed at lower strain rates or higher temperatures (35-42). Thus as we will see, the effect of hydrogen on fracture appears to depend on kinetic as well as on static factors. One significant factor in controlling the fracture behavior is the flux of hydrogen to stress concentrations at which fracture can initiate. In many systems, such as Mo and W, the diffusivity of H at room temperature is low (27) and pre-charging with solute hydrogen has no effect on the ductility or fracture behavior. If however the hydrogen is produced at crack tips, as by cathodically charging during stressing, the systems are hydrogen embrittled (43, 44).

In metal systems which contain C, N or O another type of H related failure is observed at elevated temperatures; "hydrogen attack" (5). In these systems, high pressure gas bubbles are formed as a result of reactions such as $2H + O \rightarrow H_2O$ and $Fe_3C + 4H \rightarrow CH_4 + 3Fe$. The driving force for bubble formation is the high fugacity gas produced but the kinetics may be controlled by bubble nucleation or growth which generally occurs at grain boundaries and second phase interfaces. Bubble growth appears to be controlled by motion of the metal atoms away from the bubbles by diffusion or by prismatic dislocation loop punching. The consequence of this bubble formation is a catastrophic decrease in the strain to failure which rapidly occurs after prolonged anneals during which no effect is noted. The failure mode is generally due to grain boundary fissures and hence is generally intergranular ductile fracture.

3. KINETICS OF HYDROGEN TRANSPORT

In most systems which have been carefully studied, the kinetics of hydrogen related failures have characteristics which suggest that they are determined by the transport of hydrogen in the lattice or across the solid-gas interface. The details of these kinetic relationships are complicated by the fact that the hydrogen flux is affected by stress gradients, interactions with dislocations, and trapping at solutes. In the cases where the source of hydrogen is gaseous hydrogen or an electrochemical reaction, the specific state of the surface can affect the kinetics. Thus while the mechanism of failure may not change, its manifestations may be drastically altered if the mobility of hydrogen is changed.

In general, two sources of hydrogen may be available to initiate failure; internal or solute hydrogen and external (gaseous atmospheres or corrosion environments). In the former case the hydrogen must reach the point at which failure occurs by diffusion (27) and/or by dislocation sweeping (45-47). The hydrogen diffusivity has been studied in most systems of interest (27) and is generally characterized by high values of the diffusivities and low activation enthalpies. In the temperature ranges where embrittlement is observed the diffusivity generally exceeds about 10^{-6} cm^2 sec^{-1} and the random walk diffusion distance, $\bar{X} \cong 2\sqrt{Dt}$, is therefore greater than $2 \times 10^{-3} t^{1/2}$ cm in the temperature ranges where embrittlement occurs. Significant concentration enhancement can therefore be expected at the points of fracture in response to the stress concentration as will be discussed shortly. The b.c.c. metals having the highest hydrogen diffusivities (Nb, V, Ta, Fe) also exhibit sensitivity to embrittlement down to the lowest temperature ranges ($\approx 77K$) (21) while those with low diffusivities (W, Mo) generally are not embrittled by solute hydrogen (43, 44). Similar generalizations can be made on surveying the behavior of the hcp and the fcc metals. It has been pointed out (43) that hydrogen embrittlement requires the development of a critical hydrogen concentration at the stress concentration and that a uniform distribution of hydrogen solute below this critical concentration will not cause embrittlement. The return of ductility at low temperatures or high strain rates (35-42) is consistent with the necessity for diffusional transport to points of stress concentration. The increased ductility in Nb-D alloys compared to Nb-H alloys (48) also has been interpreted as reflecting the lower diffusivity for deuterium.

The flux of hydrogen in response to stress gradients at stress concentrations such as cracks has been discussed by a number of authors (49-53). As a result of the distortion field, $\in_{ij}$, around the hydrogen interstitial, the chemical potential of the hydrogen (54) will have the form

$$\mu - \mu_0 = \int \sigma_{ij} \in_{ij} dV \tag{1}$$

on applying a stress σ_{ij}. The chemical potential in the absence of a stress is μ_0 while after application of the stress it is μ and the difference is the work to introduce the hydrogen into the stress field. A stress gradient therefore results in a chemical potential gradient and hydrogen flux occurs until the concentration at all points reaches the equilibrium value,

$$C = C_0 \exp \frac{\int \sigma_{ij} \in_{ij} dV}{RT} \tag{2}$$

$$C = C_0 \exp [W/RT]$$

where C_0 is the concentration in the absence of stress. If only the volume change around the hydrogen is considered, this may be written

$$C = C_0 \exp \frac{\sigma^s \overline{V}_H}{RT} \tag{3}$$

where σ^s is the spherical stress ($\sigma^s = 1/3 (\sigma_{11} + \sigma_{22} + \sigma_{33})$) and $\overline{V}_H$ is the partial mold volume of hydrogen in solution. While the existing treatments of hydrogen flux in response to stress gradients are not complete, they do demonstrate the importance of this effect when considering the distribution of hydrogen in non-uniform stress fields.

The diffusivity of H in metals is generally characterized by a low activation energy, of the order of 0.1 eV in bcc metals (27) and therefore hydrogen remains a mobile solute down to very low temperatures. The diffusivity can be strongly decreased and the activation enthalpy increased by trapping of the hydrogen at other solutes (55-58), at dislocations (55, 59, 60), and possibly at other imperfections. Various trapping models (61-62) have been applied to hydrogen diffusion. The effect of trapping on the diffusivity is most significant at low temperatures and is of importance in the temperature range where hydrogen embrittlement is observed. These trapping effects must be considered when the kinetics of hydrogen embrittlement are studied.

In addition to transport of hydrogen by diffusion in response to stress gradients it has been suggested (45-47) that moving dislocations can transport significant quantities of hydrogen as solute atmospheres over large distances. This mechanism, based on one suggested by Cottrell (28) requires a large binding enthalpy between the hydrogen solutes and dislocation traps. Such interactions have been reported in a number of systems (63-65) with hydrogen-dislocation interaction energies of about 0.3 eV. Experimental evidence for this deformation enhanced mobility has been obtained during studies of the effects of plastic strains on hydrogen evolution (45, 66). These experimental results and theoretical estimates suggest that at low strain rates the range of dislocation transport can exceed that due to diffusion by a factor of about 10^4 (46, 47).

Thus solute hydrogen can move to the point at which fracture occurs either by diffusion or dislocation transport with appreciable mobilities. In the case of external hydrogen environments such transport may not be necessary as the hydrogen is produced at the propagating crack tip either by adsorption and dissociation of the H_2 molecule or by chemically produced H atoms. In H_2 gaseous environments the hydrogen entry into the lattice takes place at clean metal surfaces produced by the plastic deformation while in a corrosion or electrochemical environment the surface may be kept clean by chemical dissolution. The behavior at the surface during a corrosion reaction or during cathodic charging is poorly understood (67) and is discussed in greater detail elsewhere in these proceedings (3). For the purpose of the present discussion two points should be

emphasized; (a) the chemical potential of H at the surface during an electrochemical reaction can be extremely high thus producing a very large chemical potential gradient near the surface and (b) the potential at the crack tip may differ greatly from that at an adjacent flat surface (67). Under corrosion or electrochemical charging conditions hydrogen entry at points of stress concentration does not appear to be a limiting factor in the observation of hydrogen embrittlement. Indeed, because of the high hydrogen fugacity at the place where it counts, the crack tip, embrittlement is often observed under these conditions when it is not under milder hydrogen gas phase or internal hydrogen solute conditions.

The processes occurring during hydrogen entry from the gas phase (68) consist of (a) physisorption of H_2 (b) molecular chemisorption (c) dissociation of H_2 (d) entry of H into the lattice. All of these processes are imperfectly understood and have been studied in only a few systems. It is not generally known which of the above steps control the rate of hydrogen entry into the solid. Since some of these processes are thermally activated it is most likely that the rate limiting process will depend on temperature. In addition, many, if not all of the above steps can be expected to be material specific and structure sensitive. The physisorption step involves Van der Waal bonding of the molecule to the surface with an energy of less than 0.1 eV / molecule (69). Molecular chemisorption has been discussed theoretically and been shown to depend sensitively on the structure of the surface (70, 71). Experimentally this state has been shown (72) to have a relatively high binding enthalpy of about 0.25 eV / molecule for hydrogen on nickel. Dissociation of the molecule to atomic hydrogen is expected to be strongly site specific and therefore may require surface diffusion of the chemisorbed molecule. These heterogeneous dissociation sites may be surface steps or kinks or may be the intersections of imperfections such as grain boundaries and dislocations with the surface. Hydrogen-deuterium exchange experiments (73) suggest that surface steps play a major role in the molecular dissociation process. The importance of this dissociation step in controlling hydrogen entry is suggested by the increased hydrogen embrittlement observed (74) when dissociated molecular hydrogen is used as a gaseous environment.

In addition to structural features these surface properties are extremely sensitive to the presence of specific molecules. Very few experiments and only a rudimentary understanding of this aspect of hydrogen transport across surfaces serve to illuminate this subject. Inhibition of crack propagation in steels in a gaseous hydrogen atmosphere due to the presence of trace amounts of H_2O, O_2 or SO_2 (19, 75, 76, 77) has been observed. In contrast, crack acceleration due to trace amounts of H_2S has often been observed (77). These effects have been directly correlated with the ability of adsorbed molecules to decrease or increase the rate of hydrogen uptake (77) but the detailed mechanisms are not understood. In particular the synergistic effects of adsorbed molecular species and surface structure on hydrogen uptake and cracking have not been examined. Even relatively simple experiments on the pressure and temperature dependences of hydrogen uptake and crack propagation have not been carried out in the manner which would assist in the establishment of rate controlling mechanisms. In the surface entry steps listed above (a), (b) and (c) should exhibit a linear pressure dependence while (d) would vary as $p^{1/2}$. The few experiments on the pressure and temperature dependence of crack growth rates in steels (78, 79) will be discussed shortly.

The attainment of conditions which lead to hydrogen embrittlement will depend in a large measure on the lattice and surface transport processes discussed above. Unless hydrogen has sufficient mobility in the lattice or across the gas-solid interface or liquid-solid interface to allow the attainment of a critical hydrogen concentration, brittle fracture does not appear to occur. The exact role each process plays depends on the system and on the experimental circumstances. For example lattice transport may control the crack propagation rate in a gaseous or aqueous environment if hydrogen entry at the crack tip is blocked but can occur at places other than the crack tip. In addition, differences in hydrogen fugacities will result from different hydrogen sources and this may determine the kinetics and even the occurrence of embrittlement. All of these factors influence the cracking kinetics but probably not the cracking mechanisms. There is no evidence that the fracture mechanism depends on the hydrogen source; indeed all evidence indicates the contrary, as will be discussed.

4. REVIEW OF EXPERIMENTAL DATA

In this section we shall review some of the pertinent experimental observations associated with hydrogen related failures in a wide range of systems. Emphasis will be placed on those results which appear to be generally applicable and which bear on the failure mechanisms. Although the presentation is divided into "internal", "external" and "stress corrosion" sources of hydrogen, this is not meant to imply any differences in the basic failure mechanisms. On the contrary, we will show that the failure processes are independent of the source of the hydrogen although the failure kinetics may depend sensitively on this parameter.

4.1 INTERNAL SOLUTE HYDROGEN

The partial molal volume of solution of hydrogen in most metals is surprisingly large (about 2 cc/mole) considering its small ionic size. Consequently, hydrogen is expected to interact with dislocations. Pinning by solute hydrogen has been observed (63-65) and manifests itself in yield points and Portevin-LeChatalier effects (14, 23-26) as well as increases in the flow stresses (29-32) at low temperatures. These effects can be quite appreciable at low temperatures, as shown in Fig. 1, but in the temperature range where hydrogen embrittlement is observed, they are often small. Since hydrogen generally has a very high diffusivity compared to other solutes (27) it can move with the dislocations (28, 46, 47) and hence provides little solution strengthening except at low temperatures.

The effect of hydrogen on fracture strongly reflects this high diffusivity. As shown in Fig. 2, Nb-H alloys (38, 41, 42, 80) exhibit a ductile → brittle → ductile transition in their behavior as the tensile test temperature is decreased. At elevated temperatures a high strain to failure and a ductile fracture mode is observed and as the temperature is decreased, the macroscopic ductility decreases and the fracture mode becomes cleavage. At a sufficiently low temperature where the hydrogen diffusivity is decreased, a return of macroscopic ductility and a ductile fracture mode is observed once again. Similar behavior has been observed in a variety of systems; V (36, 38, 39, 81), Ta (39, 82), Ni (32) and ferritic steels (35, 83). The correlation between the return of ductility at low temperatures and the decreased hydrogen diffusivity can be clearly seen by the inverse strain rate effect observed in these alloys (32, 38, 39, 41, 83) (Fig. 3). Increasing the strain rate increases the ductility and at a sufficiently high strain rate the fracture mode changes from a brittle to a ductile mode, particularly at the lower temperatures. This correlation is further supported by the isotope dependence of the low temperature fracture mode in Nb-H and Nb-D alloys (48).

While results such as the above are not available for all systems, it appears that solute hydrogen affects the fracture process only under conditions where it has sufficient mobility as previously emphasized. Systems which have precipitated brittle hydrides, such as zirconium, exhibit cleavage of the hydrides on stressing and ductile failure in the solid solution between the hydrides during tension tests at room temperature (84, 85). The brittle hydride simply serves to decrease the strength and ductility as would any brittle second phase. Completely brittle fracture can however be observed in Zr-H alloys containing precipitated hydrides at very low strain rates and at temperatures where hydrogen flux to crack tips can occur (86, 87). In those systems such as Mo-H (43) and W-H (44), where the H diffusivity is relatively low at room temperature, embrittlement is observed only if the hydrogen is delivered directly to the crack tip as in simultaneous cathodic charging and tensile testing.

In hydride forming systems, the dependence of the high temperature ductile-brittle transition on the hydrogen concentration can be correlated with the solid solution-hydride solvus temperature. The fracture transition occurs at temperatures above the solvus temperature but parallels the solvus temperature as the hydrogen concentration is varied (36, 38, 39, 41, 42, 81, 88). While this correlation has been ascribed to stress induced ordering (38, 39), it has been shown (41, 42) in the Nb-H system that the fracture transition corresponds to the onset of stress induced hydride formation. This correspondence has not been directly demonstrated for other systems. In the Nb-H and V-H systems a more complex behavior has been observed at the high temperature transition (38, 41) (Fig. 2). The macroscopic strain to failure exhibits a second very narrow
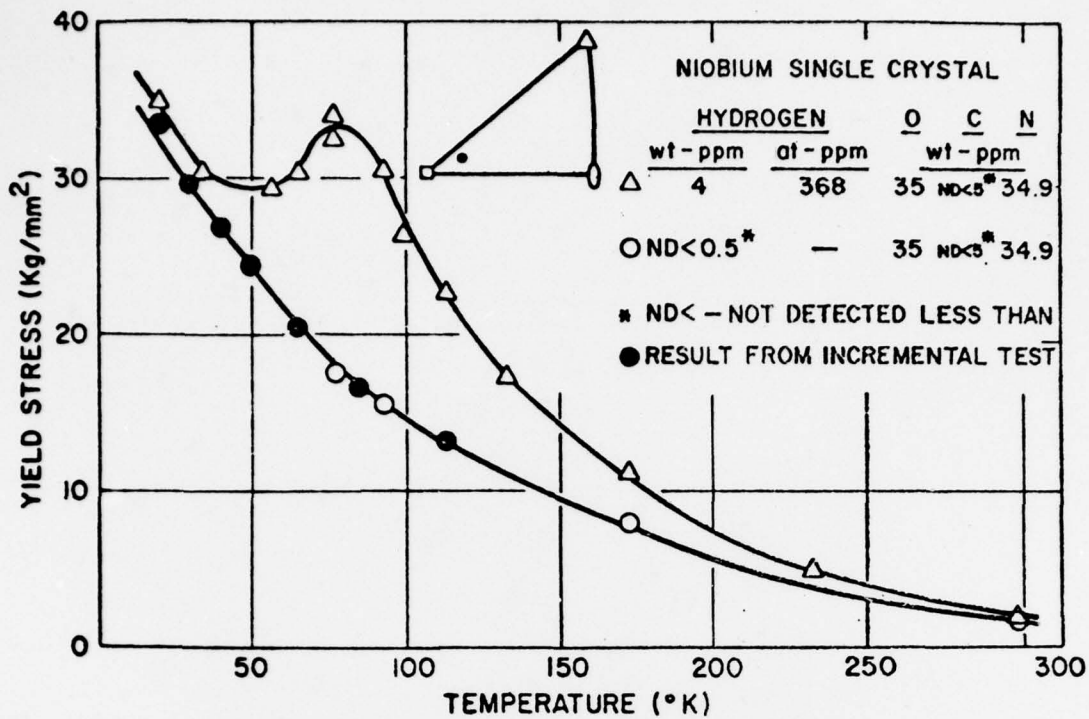
Fig. 1 Yield stress as a function of temperature for niobium single crystals; (−⊖−) hydrogen free crystals, (−△−) crystals containing 368 at.ppm H. (Ref. 29)
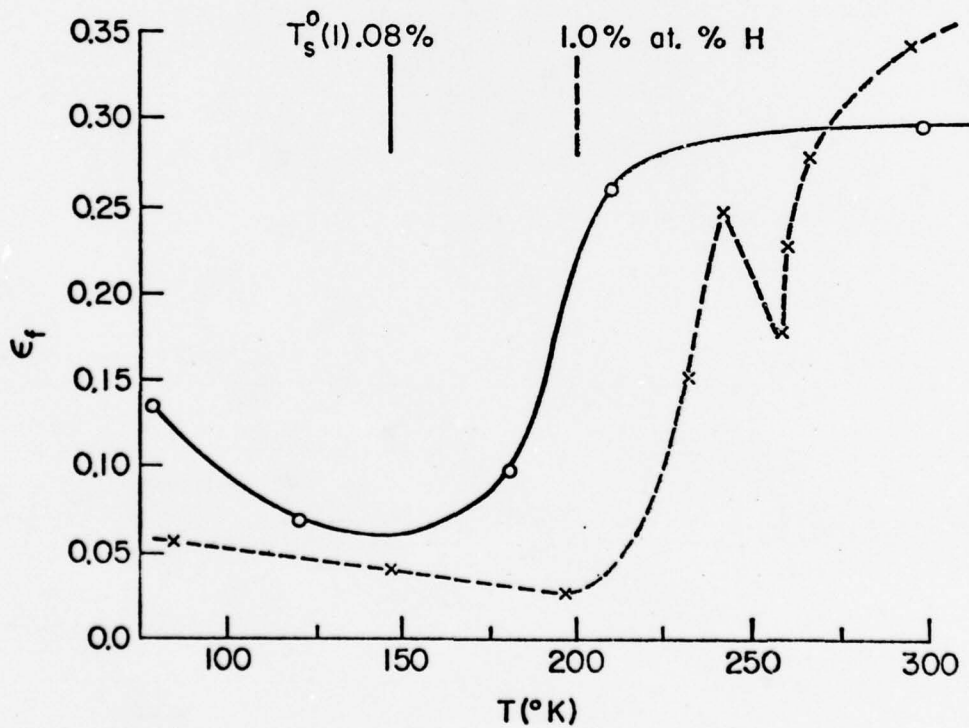

Fig. 2 Strain to failure vs. temperature for niobium-hydrogen alloys. (−o−) Nb -0.08 at.%H (−x−) Nb -1.0 at.% H alloys. The stress free hydride solvus temperature on the first cooling cycle, T_s^o is also shown. (Ref. 41)

100 µ

A

25 µ

B

Fig. 3 Effect of strain rate on the fracture of Nb -0.08 at.% H alloys at 200 K. (a) $\dot{\epsilon} \approx 2 \times 10^{-1}$ sec^{-1} (b) $\dot{\epsilon} \approx$ 2×10^{-4} sec.$^{-1}$ (Ref. 41)

FRACTURE 100 µ

a

10 µ

b

100 µ

c

100 µ

d

Fig. 4 Fracture surfaces of Nb -0.08 at.%H alloys tested at (a) 210 K (b) 180 K (c) 120 K (d) 77 K. (Ref. 41)

ductility minimum at temperatures just above the main ductile-brittle transition. As shown in Fig. 4, there does not appear to be any significant change in fracture morphology throughout this temperature range.

In the non-hydride forming systems, such as the ferritic steels and nickel, correlation of the high temperature fracture transition temperature with hydrogen concentration has not been carried out. In marked contrast to the hydride forming systems, which can exhibit ductile fracture at room temperature even at hydrogen concentrations of the order of 1 at .%, non-hydride forming systems are generally embrittled by very low concentrations of hydrogen, often of the order of a few parts per million. As the strength of these alloys is increased, the C_H at which embrittlement occurs is decreased (9, 19, 26). A large number of studies have examined the effect of different microstructures on the hydrogen embrittlement (34, 89, 90). In general, the high strength martensitic steels exhibit brittle fracture along the prior austenitic boundaries at very low C_H. Pearlitic structures require much higher values of C_H for embrittlement and the austenitic steels are relatively insensitive to solute hydrogen in their fracture behavior. The austenitic stainless steels containing hydrogen exhibit a reduced strain to failure but the fracture mode remains predominantly ductile in tensile tests.

The behavior of stainless steels containing hydrogen or tested in hydrogen gas suggest that γ phase stability may be of great significance in determining the mode of fracture (91, 92). Sustained load testing at stresses close to the ultimate strength has produced cleavage fracture in the "unstable" type 304 stainless steels while the "stable" type 310 steels do not exhibit any embrittlement. The lack of significant hydrogen embrittlement in macroscopic tensile specimens of type 304 stainless steels tested at typical tensile strain rates may reflect the low diffusivity of hydrogen, as surface cracking has been seen (93, 94) and thin specimens are severely embrittled (35).

Systems containing solute hydrogen are susceptible to the phenomena of static fatigue (95) which is illustrated in Fig. 5. This phenomenon, which has primarily been studied in ferrous systems, corresponds to the nucleation and slow growth of a brittle fracture at stresses well below the macroscopic yield stress. It has been shown that the nucleation stage is reversible, i.e., removal of the stress at early times allows complete recovery of the material without any permanent damage (96). The time for static fatigue failure at any stress and the stress below which no fracture is observed increases as the hydrogen concentration decreases. The kinetics of the static fatigue reflect the hydrogen diffusivity. Static fatigue failure i.e. slow crack propagation at constant stress intensity has also been reported in Zr-H alloys (86, 87), and in a number of Ti alloys particularly those containing the hcp α phase (97, 98).

As may be seen from the above review, primary experimental attention has been focused on the behavior of the B.C.C. metals as these appear to be most susceptible to solute hydrogen embrittlement. With the exception of Ni (14), Pd (99), and Al (100), and austenitic stainless steel (34, 101) alloys, the f.c.c. structure metals have not been shown to be significantly embrittled by solute hydrogen. Nickel alloys exhibit intergranular embrittlement after thermal or electrolytic charging with hydrogen; both processes leading to high hydrogen supersaturations. At still higher hydrogen chemical potentials, an extremely brittle nickel hydride is formed and leads to severe embrittlement. Palladium alloys having a high enough hydrogen concentration to be in the β phase (H/Pd $\gtrsim$ 0.6) are quite brittle. High strength aluminum alloys do not exhibit hydrogen embrittlement in gaseous H_2 (102, 103) or in the presence of atomic H (104) but are embrittled by the presence of a small partial pressure of H_2O (105). Intergranular fracture of high strength Al-Zn-Mg alloys also results from solute hydrogen (13, 106, 107) at slow strain rates and this effect is reversible on removal of the hydrogen by a vacuum annealing treatment. Under cathodic precharging conditions aluminum alloys (13) exhibit reduced ductility and both intergranular and transgranular cracking.

A number of the hcp metals such as Ti (108) and Zr (109) alloys are severely embrittled by solute hydrogen. These systems exhibit precipitation of hydrides on cooling the solid solution with the structure and morphology of the hydrides depending on the cooling rate and on the hydrogen concentration. Deformation of these two phase structures (hydride and solid solution) in tension tests results in ductile failure of the solid solution matrix between cleavage of the hydrides (84, 85, 110, 111). Under sustained loading a slowly propagating cleavage fracture mode has been observed (86, 87, 97, 98). In Zr alloys the slow strain rate fractures appear to result from stress induced

trations such as calculated with Eqn. 3. The effects of extremely high concentrations on individual
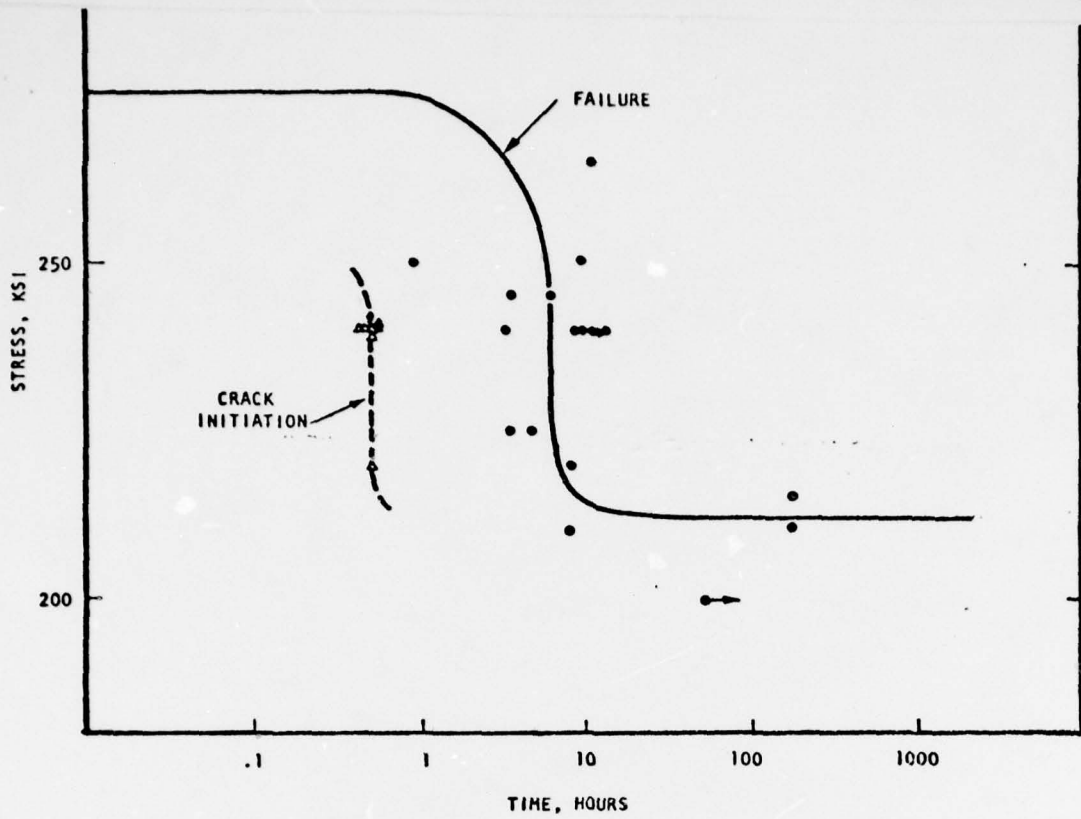
Fig. 5 Static fatigue behavior of 4340 steels at 77 K. The times for crack initiation and for crack propagation are shown as a function of stress. (Ref. 96)
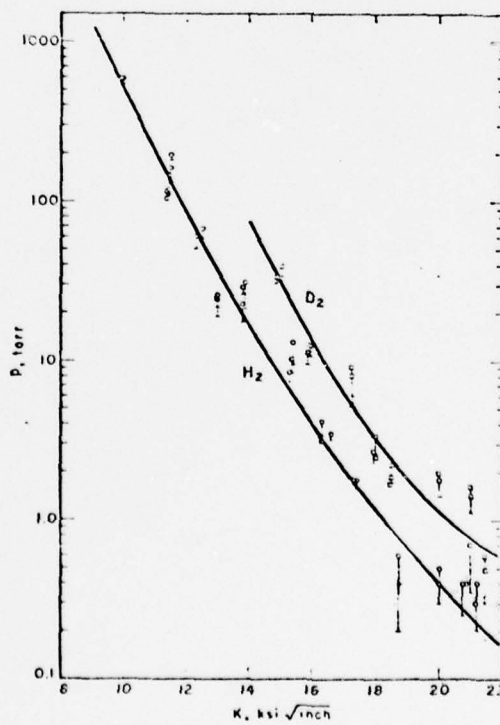

Fig. 6 Relation between the hydrogen gas pressure and the stress intensity required for crack propagation in 4340 steel. (Ref. 115)

hydrides at the crack tips. The b.c.c. β Ti phase has a high solubility for hydrogen and no significant embrittlement of this structure has been reported. The hcp α phase having a much lower H solubility is severely embrittled; failing by a cleavage mode. In α - β alloys the fracture appears to occur along the α - β interfaces (112). Although titanium hydride is stable and forms in the α phase, its role in the fracture process has not been definitively established.

4.2 EXTERNAL GASEOUS HYDROGEN

As previously discussed, the mechanisms of hydrogen embrittlement appear to be independent of the hydrogen source, in contrast with earlier viewpoints. The kinetics may be markedly affected by various transport processes and it is this which distinguishes "internal" from "external" hydrogen induced fractures. Indeed the very occurrence of embrittlement may reflect these kinetic factors as previously discussed. High strength nickel base alloys for example are not particularly embrittled by solute hydrogen but are susceptible to hydrogen induced fracture in high pressure hydrogen gas (113). This difference in behavior may reflect the low mobility of solute hydrogen due to trapping in the first case and the high hydrogen fugacity present at the crack tip in the second. In considering the behavior of metals in gaseous environments, two primary factors must be discussed: the kinetics of transfer of hydrogen across the solid-gaseous interface and the hydrogen fugacity which determines the hydrogen concentration. In this section we shall review the literature only from the viewpoint of crack propagation kinetics.

Hydrogen embrittlement in high pressure gaseous hydrogen atmospheres has been observed in many alloy systems. Since the hydrogen solubility obeys Sieverts' law, the hydrogen solute concentration increases with the (hydrogen fugacity)$^{\frac{1}{2}}$ and under equilibrium conditions the fugacity of hydrogen in internal voids will equal that of the external atmosphere. The formation of high pressure internal gas bubbles can lead to embrittlement and has given rise to suggested hydrogen embrittlement mechanisms based on the formation of high pressure gas bubbles (114). Embrittlement due to such high pressure bubbles is only a subset of the failures associated with hydrogen.

Hydrogen embrittlement of high strength steels has been shown to occur at pressures much below one atmosphere of H_2 (19, 115). Since the fugacity of any internal gas bubble can not then exceed the external pressure, fracture occurs as a result of hydrogen at the surface or as a solute in equilibrium with the gas phase. Oriani and Josephic (115) demonstrated the existence of an "equilibrium" relationship between the stress intensity, K_I, and the H_2 pressure shown in Fig. 6. At a constant K_I the crack could be stopped or started by changing the gas pressure. This relationship was isotope dependent with higher pressures being required for crack propagation in D_2.

Under less controlled conditions, the kinetics of crack propagation in hydrogen atmosphere are somewhat more complex and have been studied by measuring the subcritical crack propagation rate, da/dt as a function of stress intensity, K_I, hydrogen pressure and temperature. The crack kinetics usually exhibit a three stage behavior (Fig. 7) for steels (78, 116) and titanium alloys (79). The stress intensity at which fracture initiates, K_{th} is relatively independent of the H_2 pressure once a critical pressure is exceeded and the crack velocity is initially very strongly dependent on K_I (Stage I). At higher K_I (Stage II) da/dt has less dependence on the stress intensity and at still higher stress intensities (Stage III) the K_{IC} of the steel is approached and unstable crack propagation which is independent of the presence of hydrogen occurs. Gangloff and Wei (78) have reported that da/dt is independent of K_I over a very wide range of values in contrast to previous results (117).

Crack growth rates in Stage II show a very complex temperature dependence (78, 79). For maraging steels at $T \lesssim 273$ K, da/dt increased with temperature according to an Arrhenius relation with an activation enthalphy of ≈ 18 KJ/mole. The activation enthalphy was independent of the H_2 pressure but the values of da/dt were proportional to $P_{H_2}^{\frac{1}{2}}$. A maximum da/dt was achieved at temperatures which increased with K_I. At $T \gtrsim 300$ K, da/dt exhibited a negative dependence on temperature and the hydrogen pressure dependence increased from a $P_{H_2}^{\frac{1}{2}}$ dependence to a $\approx P_{H_2}^{1.5}$ dependence. The mechanistic understanding of these relationships is not presently available. It has been suggested (74, 118) that the increase of da/dt with temperature and the p$^{\frac{1}{2}}$ dependence was

indicative of kinetics controlled by lattice diffusion while the higher order pressure dependence and the decrease of da/dt with temperature resulted from surface process kinetics. This interpretation has recently been challenged (78). The importance of the surface reactions is emphasized by the sensitivity of da/dt to trace impurities in the H_2 gas (19, 77).

Subcritical cracking kinetics have generally been studied for a gaseous hydrogen atmosphere. In the few cases (86, 87, 119, 120) where solute hydrogen was used the curves exhibited mainly Stage I. In Nb-H alloys (120) a linear relation was observed between ln (da/dt) and K_I which extended over the range $10^{-8} \lesssim da/dt \lesssim 10^{-3}$ m/sec. and which did not indicate the existence of a threshold K_I. The temperature dependence of da/dt at constant K_I was an Arrhenius relation whose activation enthalpy agreed very well with that for H diffusion. In Zr-H alloys two stage crack growth kinetics were observed (85, 87) and were accounted for by a theory based on stress induced hydride formation.

Many alloy systems other than the steels are susceptible to hydrogen embrittlement from a H_2 gaseous atmosphere. Titanium alloys, particularly those having an acicular α - β microstructure are embrittled on testing in H_2 gas over a wide range of pressures (121). The fracture morphology is cracking along the α - β interfaces as it is for "solute" hydrogen embrittlement (74, 97). Nickel alloys such as Inconel 718 are severely embrittled when tested in hydrogen gaseous atmospheres under conditions where significant plastic deformation is occurring, i.e., in a slow strain rate tensile test (122). Under stress rupture tests (where little deformation occurs) however, no significant effects of hydrogen atmospheres have been noted. This suggests that the embrittlement is controlled by hydrogen transfer across the surface, a process which is aided by the formation of slip steps. The Group Vb refractory metals would be expected to be severely embrittled on testing in gaseous H_2 if sufficient disruption of the surface oxide permeation barrier by plastic deformation occurs. Similarly, other hydride forming metals such as Mg alloys and Al alloys should be severely embrittled under conditions where the hydrogen fugacity in the gas is large enough to form the hydride and where the transfer across the metal surface is aided by plastic deformation. The fact that such embrittlement is not generally observed probably reflects the efficacy of the oxides in preventing hydrogen entry from the gaseous phase.

4.3 FRACTURE MORPHOLOGY

An understanding of hydrogen embrittlement requires a recognition of the various types of fracture morphologies and paths which result from the embrittlement. The systems affected by hydrogen group themselves into three classes based on the fracture morphology: (a) ductile fracture (b) cleavage and (c) intergranular brittle failure.

In systems which exhibit ductile failure (34) the fracture morphology is unaffected by hydrogen except to a secondary degree such as changes in the sizes of "dimples" or microvoids which characterize the fracture surface (33, 123). In most commercial alloys these microvoids are formed at second phase particles. If the second phase particles are coherent or semicoherent hydrogen appears to affect the nucleation of microvoids at the particle-matrix interface and the microvoid density is increased and the average size decreased (33). The contrasting case is for incoherent particles where hydrogen assists microvoid growth thereby increasing the average size and decreasing the density (123). In these cases we must understand the effects of hydrogen on microvoid nucleation and growth.

In systems which form stable hydrides the failure mode in the absence of hydrogen is ductile whereas when hydrogen is added as a solute a cleavage failure mode occurs as shown in Fig. 4. The fracture mode is true crystallographic cleavage and in the Nb-H system has been shown to be accompanied by little local deformation (41, 42). This is true despite the fact that extensive deformation may occur prior to failure (Fig. 8). Thus the fracture is somewhat anomalous as it is a "brittle" failure mode in a "ductile" alloy. This point will be discussed subsequently. In the Nb-H system the cleavage plane is the {110} (referred to b.c.c. axes) (41, 124) and has been shown to correspond to cleavage in stress induced hydride (41, 42, 124). Single crystals of NbH hydride exhibit {110} cleavage identical to that observed in hydrogen embrittled Nb (124).
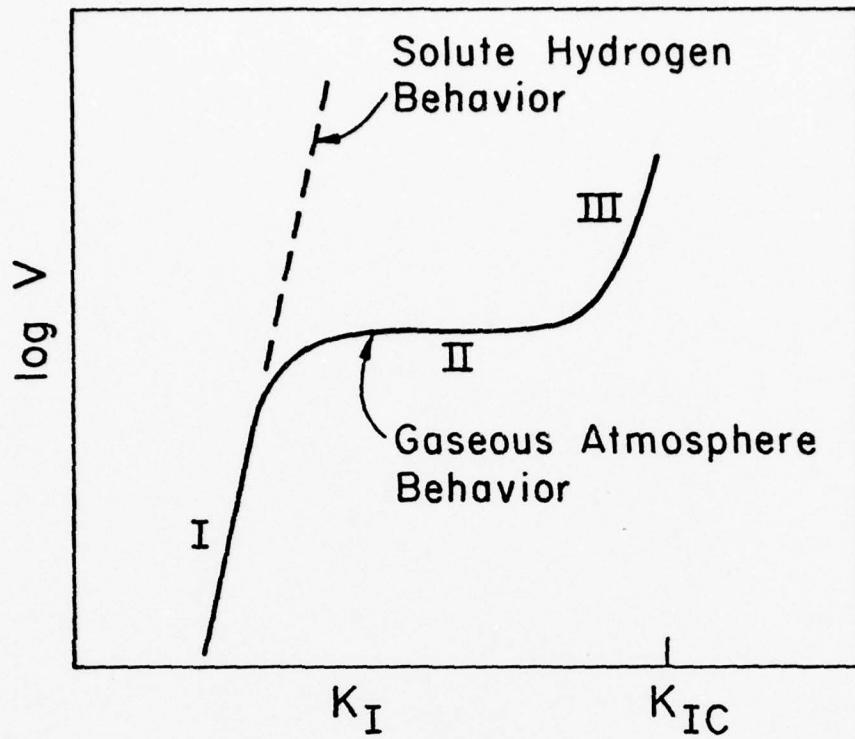
Fig. 7 Schematic showing the dependence of the crack velocity on the stress intensity.
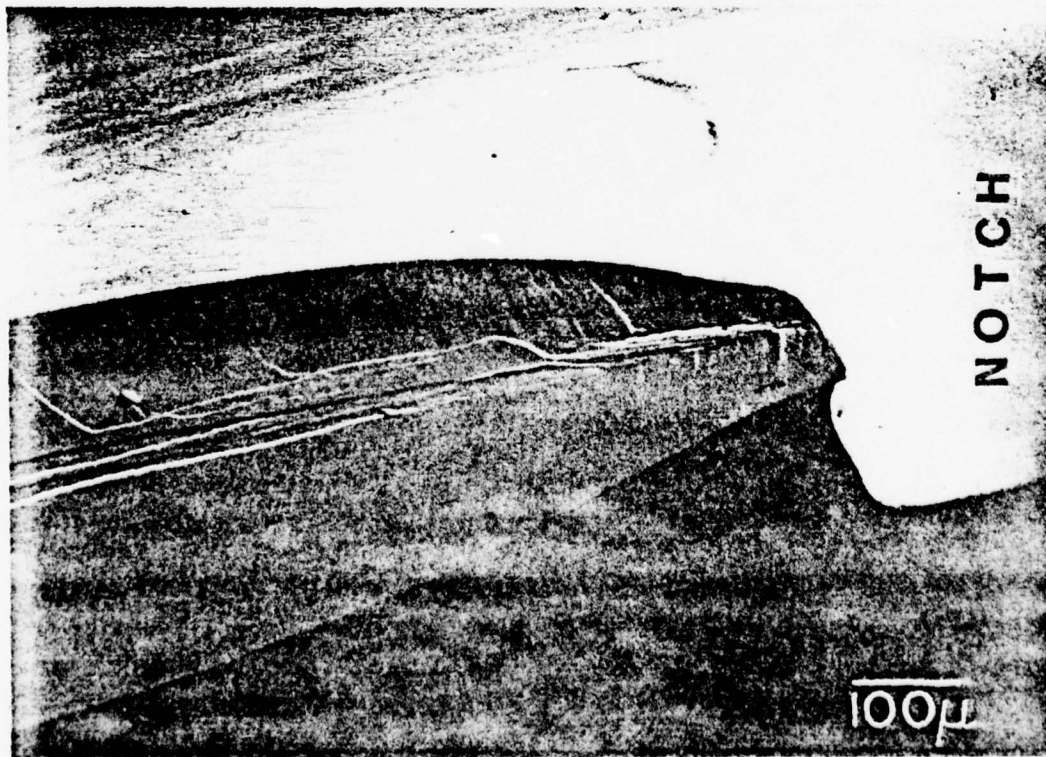

Fig. 8 Fracture surface of Nb -1.0 at%H specimen deformed at a temperature below the stress free solvus temperature. The fracture was by cleavage along the {110} after very extensive plastic deformation and necking.

Cleavage is also observed in the other Group VB metals containing hydrogen as well as in Ti alloys and Mg-Al alloys. In many cases the fracture morphology has not been carefully studied and in others the cleavage plane does not correspond to the expected cleavage plane of the matrix. An example of the latter is Mg -7.5% Al tested under stress corrosion conditions where it exhibits cleavage on the $\{31\overline{4}0\}$ rather than the expected hcp cleavage plane $\{0001\}$ (125). Since systems which form hydrides may fail by cleavage through the stress induced hydrides (see Section 5.5) the fracture plane would correspond to the hydride cleavage plane rather than the matrix cleavage plane. In a Ti-8Al-1Mo-IV alloy having a Widmanstatten structure slow crack growth in a hydrogen atmosphere occurs along the $\alpha - \beta$ interfaces and titanium hydride is observed at the fracture surface (112). A transgranular fracture which appears to be cleavage occurs in α phase Ti-8Al-IMo-IV alloys under stress corrosion conditions along a plane which is 15° from the expected (0001) h.c.p. cleavage plane (98, 126). While the role of hydrogen in stress corrosion of Ti alloys is somewhat controversial (3) it is worth pointing out that the difference in fracture morphology may reflect a difference in hydrogen transport kinetics rather than a difference in fracture mechanism. In $\alpha - \beta$ alloys the β phase may provide a high diffusivity "conduit" for solute hydrogen transport to the $\alpha - \beta$ interface where formation of a hydride in the α phase (which has a low H solid solubility) can occur. The fracture by hydride cleavage would then follow the $\alpha - \beta$ interface. In a stress corrosion test of α phase alloys, the high hydrogen fugacity may cause the formation of massive hydride at the crack tip which would then fail by cleavage along the hydride cleavage plane.

In non-hydride forming systems such as Ni and Fe alloys the hydrogen induced brittle fracture generally occurs intergranularly. In the case of steels embrittled by solute or gaseous hydrogen the fracture occurs along prior austenitic boundaries with a decreasing amount of local plasticity as the strength level or hydrogen concentration increases. Transgranular cracking has been observed in Fe-Si (17) and in Fe (18) as a result of the high H fugacity which resulted from cathodic charging. High strength iron single crystal whiskers (about 25μ in diameter) have been tensile tested in H_2 and H_2S gaseous atmospheres (127). Despite the high strength of these whiskers they exhibited ductile failure in all cases.

Hydrogen embrittlement of nickel alloys by solute or gaseous hydrogen also occurs by intergranular cracking (14). Single crystals exhibit ductile fracture when tested under conditions which cause hydrogen embrittlement in polycrystalline specimens (128). The provision of a stress concentration by notching the Ni crystals has been recently reported to lead to transgranular cleavage (129).

Recent results have suggested possible synergistic effects between H and other solutes which segregate at crystalline boundaries in steels and nickel alloys. Latanison and Opperhauser (130) have suggested that segregation of hydrogen recombination poisons, such as Sb and Sn, at grain boundaries leads to preferential H entry at such points during cathodic charging and hence to intergranular cracking. In steels, Banerji et al (131) have drawn attention to the interactions between those solutes responsible for temper embrittlement and hydrogen embrittlement. Intergranular hydrogen induced cracking at prior austenitic grain boundaries at low stress intensities was observed in a commercial 4340 steel and in a "high purity" steel having low P but significant Mn and Si levels. Both of these steels exhibited P segregation at the prior austenitic grain boundaries and were susceptible to temper embrittlement. In a high purity steel having low P, Mn and Si levels, P segregation at the prior austenitic boundaries did not occur and H induced crack propagation only occurred at high K_I values. In this case the fracture was transgranular and was described by the authors as "rupture and cleavage". (The published micrographs suggest a primarily ductile rupture mode.) The implication of these recent results is that the form of hydrogen embrittlement generally observed in high strength steels, i.e. low ductility intergranular fracture at low K_I, reflects the combined effects of hydrogen and other solutes segregated at prior austenitic boundaries. This suggestion is supported by the iron whisker embrittlement studies (127).

5. MECHANISMS OF FAILURE

In the years since the role of hydrogen in reducing the ductility and/or the fracture strength of materials has been recognized, myriad mechanisms have been proposed to account for the observations. These can be grouped into a few general classes as listed below:

(a) high pressure bubble formation
(b) surface adsorption effects
(c) plastic deformation effects
(d) decohesion
(e) hydride precipitation

Since factors such as hydrogen solubility, hydride stability, hydrogen diffusivity, etc. differ so widely among systems which are embrittled by hydrogen, it would be fortuitous indeed if a single mechanism were responsible for embrittlement in all systems. No attempt will be made to identify such a uniform failure mechanism; rather certain mechanisms will be shown to be inapplicable, others will be shown to apply in certain limited situations and others to have a more general albeit as yet undefined applicability.

As discussed earlier, it is important to distinguish kinetic factors from embrittlement mechanisms. The manifestations and kinetics of embrittlement may be quite different when hydrogen is present as solute or when it is supplied externally from a gaseous atmosphere or from a corrosion reaction. These differences arise from the vastly different hydrogen fugacities as well as from the spatial relationships between the hydrogen sources and the propagating crack and from the variety of hydrogen transport mechanisms. The different manifestations of hydrogen embrittlement do not necessarily suggest differences in the fracture mechanisms.

5.1 HIGH PRESSURE BUBBLE FORMATION

High pressure hydrogen filled bubbles have been observed to form in a variety of metals having endothermic heats of hydrogen solution under conditions of high hydrogen fugacity. The bubbles which form can often attain internal pressures of the order of 10^5 atmospheres. Propagation of brittle fracture from these high pressure bubbles has been observed (17, 18) and appears to serve as a mechanism which reduces the internal pressure.

Hydrogen embrittlement mechanisms based on the formation of high pressure bubbles have been proposed (114, 132, 133). In these mechanisms the driving force for crack propagation is the internal pressure of the bubble or the sum of the external stress and the internal pressure. In general these theories do not adequately address the question of how the fracture mode is changed from a ductile to a brittle one by the presence of the high pressure bubbles. While the internal pressure in the bubble provides an initial driving force for crack propagation, this would decrease rapidly in the absence of a continuous source of high fugacity hydrogen. The observation that fracture often occurs under conditions where such a decrease in bubble pressure must occur as the crack propagates, such as embrittlement by solute hydrogen, suggests that the pressurized bubble theory is not sufficient to account for the embrittlement. The observation of severe hydrogen embrittlement by low pressure hydrogen gas where high pressure bubbles can not form (19, 115) supports this point.

It has been suggested by Tien et al (134) that significantly enhanced local hydrogen fugacities may occur by dislocation annihilation at other dislocations or at voids or inclusions under conditions where the primary hydrogen transport mechanism is dislocation atmosphere dragging. If such enhanced fugacity occurs it could affect the stability of micro-cracks formed by the dislocation interactions as discussed by Bilby and Hewitt (135). The occurrence of such enhancement in the presence of realistic hydrogen diffusivity values has however been questioned by Johnson and Hirth (136). We may conclude that the formation of high pressure hydrogen bubbles, which may occur only in systems having endothermic heats of hydrogen solution, can provide sites for crack nucleation. The internal pressure can provide a driving force for crack propagation. The question of why the material in front of the crack is embrittled is not addressed by the high pressure bubble theories and it is this point which is pertinent to fractures which occur at low hydrogen fugacities.

5.2 SURFACE ADSORPTION EFFECTS

As will be the case for a number of suggested mechanisms, it is difficult to draw a sharp distinction between decreases in fracture stress due to adsorption of hydrogen at surfaces (and the attendant decreases in surface energy) and to decreases in the "cohesive energy" (or atomic bond fracture stress) at the crack tip. As discussed by Oriani (137), the two concepts are closely linked. In the Petch-Stables adsorption mechanism (138, 139) attention is focussed on the effects of hydrogen on the surface energy of surfaces produced by an advancing crack while the "decohesion model" discusses the effects on the atomic bond energy at the crack tip. We shall consider surface adsorption effects in the classic case of the Griffith criteria for crack propagation as first suggested by Petch. A development of this fracture criteria which includes the effects of plastic strain at the crack tip (140) results in similar conclusions to those based on the concept of a completely brittle crack. In this formulation a necessary condition for crack propagation may be derived from the energy balance during crack extension and may be written for plane strain as:

$$\sigma_f = [2\gamma E/\pi c (1-\upsilon^2)]^{\frac{1}{2}} \tag{4}$$

where σ_f is the fracture stress, γ is the effective surface energy, 2c is the crack length, E is Young's modulus, and υ is Poisson's ratio. In this proposed fracture mechanism, the principal effect of hydrogen is to reduce the effective surface energy γ as a result of adsorption on the surface produced as the crack propagates. The fracture criteria of Eqn. 4 can be combined (140) with adsorption data for H on Fe (141) to yield a relation of the form

$$\ln P_{H_2} = \alpha + \beta \sigma_f \tag{5}$$

where α and β are constants which are known from the material properties and from the hydrogen adsorption measurements and P_{H_2} is the hydrogen gas pressure. This relation has been tested (140) against data for P_{H_2} vs K_I (stress intensity) for crack propagation and shown to be in poor agreement.

A number of objections may be raised to the surface adsorption embrittlement mechanism. The effective surface energy, γ which characterizes the fracture is generally very much greater than the thermodynamic surface energy γ_s and includes the energy of plastic deformation, γ_p which accompanies fracture. Hydrogen adsorption can reduce γ_s but since γ_p is usually much greater than γ_s the fracture stress will not be markedly affected. As shown in Table II hydrogen does strongly adsorb on clean metal surfaces; but so does H_2O, O_2, N_2, etc. Indeed, these other species have higher heats of adsorption and therefore reduce γ_s to a greater extent than does H_2. Nonetheless it is known (19) that H_2O and O_2 in trace amounts arrest hydrogen embrittlement rather than enhancing it.

Additional inconsistencies of this mechanism with experimental observations can be found. In gaseous H_2 crack propagation velocities measured at constant stress intensity at $T \lesssim 273K$ exhibit an increase with test temperature rather than the decrease expected from an adsorption mechanism (78, 79). While few detailed observations of in-situ crack propagation have been carried out, Johnson et al (95) reported that cracking occurs in the solid in front of the main crack at regions corresponding to maximum stress triaxiality in steels containing solute hydrogen; an observation not in accord with surface energy reduction by adsorption. The discontinuous nature of crack propagation has been noted in many systems. There is no a-priori reason why the surface adsorption mechanism should result in anything but a continuous crack propagation. The "incubation time" prior to crack propagation in a static fatigue test of specimens containing solute hydrogen has been reported to be reversible upon stress removal in a number of systems (96). Hydrogen adsorption on surfaces is not expected to be stress reversible.

All the above evidence weighs against the applicability of a surface adsorption mechanism. It should also be pointed out that the Griffith fracture criterion (or variations of it which account for crack tip plasticity) is a necessary thermodynamic condition and may not be a sufficient condition for fracture. Surface adsorption theories can not account for the observed phenomena.

Table II. ENTHALPY* OF CHEMISORPTION (142)

metal\molecule	H	O	N
Ta	188		586
W	188	649	398
Cr	188		
Ni	130	544	
Fe	134	314	167
Rh	117		
Pt	126		

*Units of KJ/mole

5.3 PLASTIC DEFORMATION EFFECTS

Plastic deformation at stress concentrations and crack tips can affect fracture in many ways and a number of mechanisms for hydrogen affected fracture have been based on the influence of hydrogen on the plastic properties of solids. In addition to these mechanisms discussed below, it should be recalled that deformation can affect the kinetics of fracture by dislocation transport mechanisms (which increase the effective hydrogen "diffusivity") and by trapping effects (which decrease the effective "diffusivity"). Furthermore, the stress field at the crack tip will depend on the extent and distribution of the plastic zone and therefore the stress dependent chemical potentials of solutes and hydrides will be affected.

Solute hydrogen has been shown to have appreciable binding enthalpies to dislocations in a number of systems (63-65) and therefore can be expected to have an appreciable effect on plastic deformation. Hydrogen-dislocation interaction effects are however mitigated by the high mobility of solute hydrogen in many systems. In Nb for example hydrogen atmospheres can drift with dislocations at velocities up to 2 meters sec. $^{-1}$ at 300K and therefore do not exert appreciable drag forces on dislocations at normal strain rates. The hydrogen solute strengthening effects have been shown to be significant primarily at low temperatures where hydrogen can act as a relatively immobile pinning point (29-32). The temperature range over which hydrogen can act as an effective dislocation pinning point will depend on the hydrogen concentration and diffusivity and hence will vary between systems. Some of these dislocation pinning effects have been discussed in Sections 2 and 4.1.

In the case of the ferrous systems the reported effects of hydrogen on the plastic properties are conflicting. Wilcox and Huggins (143) reported an increased Hall-Petch slope and a decreased friction stress in polycrystalline iron after hydrogen charging while Adair (144) reported the opposite result. In Fe-0.15 Ti alloys Bernstein (145) has reported that solute hydrogen reduces the lattice friction stress and increases grain boundary hardening. Beachem (146) has reported a decreased yield and flow stress on hydrogen charging 1020 steel while Asano and Otsuka (147) report increases in flow stresses in a variety of steels. Matsui et al (148) have reported extremely large flow stress decreases in high purity iron and small decreases in less pure iron.

The most remarkable feature of these experiments is the diversity of the results from seemingly similar experiments. One possible cause for this may be seen in the paper by Asano and Otsuka (147) who show that stress relaxation occurs as a result of cathodic charging. This behavior is indicative of dislocation generation or rearrangement and suggests that the introduction of hydrogen, particularly by cathodic charging, may cause irreversible changes in the dislocation structure and therefore affect the flow curve in ways which reflect the detailed experimental procedure.

Several hydrogen related fracture mechanisms have been proposed based on changes in the plastic properties caused by hydrogen. These too are rather divergent in their approaches. Stroh (149) originally suggested that hydrogen embrittlement in steels could be accounted for by solution strengthening at the crack tip due to dissolved hydrogen with the concommittant decrease in plastic accommodation and blunting and leading to a decrease in K_{Ic}. In this model hydrogen impedes dislocation motion and increases the flow stress. It differs from other solution strengthening solutes only in its high mobility which enables it to move to the crack tip during crack propagation. In direct contrast to this point of view Beachem (146) has suggested that stress induced hydrogen segregation at the crack tip aids the plastic deformation processes (solution softening) which lead to failure. He views the fracture as an essentially plastic process which is aided by hydrogen. The various modes of "plastic failure", intergranular, quasicleavage or microvoid coalescence are considered to be manifestations of the differing microstructures. A detailed mechanism for the relation between the hydrogen enhanced local plasticity and the fracture process was not proposed and has not been forthcoming.

Lynch (150) has discussed a fracture mechanism for liquid metal embrittlement, stress corrosion and corrosion fatigue of aluminum alloys which is based on environmentally enhanced crack tip plasticity. While he has not specifically applied this mechanism to hydrogen embrittlement, it is very closely related to the suggestion put forth by Beachem (146). Lynch suggests that surface adsorption can lead to a decrease in the stress to generate dislocations at the crack tip and therefore to intense localized slip at the tip rather than to the more generalized slip field observed in the absence of the environment. He proposes that the crack advance is by a slip process similar to that proposed by Neumann (151) for fatigue crack propagation. In a fatigue test this slip mechanism has been observed to lead to propagation of sharp cracks along crystallographic planes even in the absence of any environmental effects (151, 152). In a tension test however, the mechanism necessarily leads to crack blunting. Furthermore, fracture on a {100}, as observed for Al alloys, requires slip on the intersecting {111} slip planes in precise amounts which depend on the orientation of the stress axis relative to the {100} fracture plane and the {111} slip planes. It is difficult to see how this slip ratio is maintained to produce {100} fracture over a wide range of stress orientations.

In applying a concept such as proposed by Beachem (146) and expanded upon by Lynch (150), a critical question is how the adsorption of solutes such as hydrogen reduces the stress to generate dislocations at the surface or alternatively how the presence of solute hydrogen decreases the stress to propagate dislocations. In view of the conflicting experimental observations previously discussed, it is not obvious that either of these necessary postulates can be supported. It may be further noted that adsorption of species such as H_2O, O_2, etc. serves to stop crack propagation due to the presence of hydrogen and that all other solutes serve to increase the flow stress of alloys. Further development of these concepts require that the effect of hydrogen on dislocation generation and motion be understood.

Gilman (153) has viewed the hydrogen embrittlement process as a competition between plastic slip and cleavage. In this view the occurrence of brittle fracture depends on the ratio of the cleavage plane energy and the shear plane energy and this ratio varies with the environment. Plastic failure occurs when the local stress at the crack tip is reduced by slip to a value below that required to satisfy the Griffith criterion and therefore inhibition of slip at the crack tip will lead to cleavage fracture. Gilman proposed that this inhibition will result from the formation of a surface hydride. Since slip will disrupt the postulated surface compound bonds (increasing the shear plane energy, i.e. increasing the stress for slip) and hydrogen adsorption is also postulated to decrease the cleavage plane energy, the formation of these surface hydrides shifts the failure behavior from ductile to cleavage. Gilman also argues that surface hydrides form even in those systems which do not form bulk hydrides. Evidence in support of this surface hydride mechanism is rather limited. Furthermore, the question of why other strongly bonded surface compounds such as oxides or nitrides do not lead to embrittlement has not been adequately addressed.

5.4 DECOHESION MECHANISMS

In contrast to the mechanisms described in Section 5.3 which describe hydrogen embrittlement as a plastic process, a class of mechanisms have been suggested which relate the failure to hydrogen effects on the bonding of atoms. These "decohesion" mechanisms were originally suggested by Troiano (154, 155) and have recently been expanded by Oriani and Josephic (115, 137, 140). They are closely related to the "hydride formation" mechanisms discussed in Section 5.5 and to the surface adsorption mechanisms discussed in Section 5.2. These similarities as well as a number of important differences will be discussed.

The basic postulates of the decohesion mechanism is that brittle fracture occurs when the local stress exceeds the atomic bond strength and that the presence of hydrogen as a solute decreases the atomic bond strength. In both the decohesion and the hydride mechanisms, the plastic deformation which precedes fracture and which occurs at the crack tip plays a role in the fracture process but does not lead to hydrogen embrittlement per se. The deformation can affect the K_I at the crack tip, may influence the rate of hydrogen transport to the crack (by disrupting the surface oxide, by dislocation dragging or hydrogen trapping) or may influence the fracture process in other ways. In this sense therefore, failure by decohesion is competitive with ductile rupture mechanisms. It is important to note that the decohesion process can occur in conjunction with general plasticity in the solid as well as with local deformation at the crack tip. This latter point has been emphasized by Thomson and Rice (156) who discuss the formation of an atomically sharp crack shielded by a plastic zone. Although the calculation is highly idealized and uses Hookean elastic elements to model the atomic interactions, they show that under the condition that the activation energy for spontaneous dislocation loop generation at the crack tip is greater than zero, the tip of the crack may remain atomically sharp despite the presence of a plastic zone around the crack.

The thermodynamic surface energy is related to the atomic potential energy, ϕ shown schematically in Fig. 9, whose depth is related to the surface energy/atom. The energy (defined as the "cohesive energy") required to reversibly break the atomic bonds across an atomic plane while maintaining all other atom spacings at their equilibrium values is the thermodynamic surface energy. Since the derivative of the lattice potential with respect to atomic separation is the external force, $F(x)$ required to affect this separation, the surface energy can be written

$$\gamma = (\tfrac{1}{2})n \int_{x_0}^{\infty} F(x)\, dx \qquad (6)$$

where n is the number of atomic bonds per unit area of the cleavage plane considered. Adsorption of hydrogen decreases this surface energy. The decohesion mechanism postulates that hydrogen produces a decrease in the maximum bonding force between atoms across an atomic plane as they are being reversibly separated (Fig. 9). Since the "cohesive stress", σ_c is given by

$$\sigma_c = n\, F_x^{max} = n\, \frac{d\phi}{dx}\Big|_{max} \qquad (7)$$

the basic assumption is that brittle fracture occurs a critical bond distance, r_c at which the local applied stress exceeds σ_c. The variation of σ_c and r_c with hydrogen concentration is not known but it is assumed that σ_c decreases as the local hydrogen concentration is increased.

The main argument adduced to support this assumption is the decrease of γ with H adsorption on a clean surface. Since γ is related to the integral of the bonding force $F(x)$ (Eqn. 6), a decrease in γ does not necessarily require a decrease in F_x^{max} (and hence a decrease in σ_c) since the shape and scale of ϕ is also expected to depend on the hydrogen concentration. The assumption of a decrease in σ_c associated with a decrease of γ is however a reasonable one on the basis of the functions used to model ϕ in a number of solids.

The condition $\sigma > \sigma_c$ is necessary and sufficient for cleavage. If σ_c is reduced sufficiently by the presence of hydrogen in solid solution ductile behavior will be terminated by brittle fracture. The primary difficulty in developing this theory lies in relating σ_c to the local hydrogen concentration. Presently accessible physical parameters, such as γ, measure the depth of the potential well or relate to the shape of the potential well at the equilibrium lattice spacing (elastic constants, atomic force constants, etc.). The theory required to relate γ or these other small strain parameters to σ_c requires a knowledge of ϕ which is not yet available for metals.

It is nonetheless informative to examine the dependence of these parameters on the H concentration. If a model lattice potential of the form:

$$\phi = -\frac{A}{x} + Be^{-x/\rho} \tag{8}$$

is considered (A measures the strength of the attractive interactions between the ion core and the electrons, due to exchange interactions and other electron energy terms while B describes the repulsion of the closed ionic shells of radius ρ) we can write:

$$\gamma \alpha \, \phi_{x_0} = A\left[\frac{\rho}{x_0} - 1\right]$$

$$C_{ij} \alpha \left.\frac{\partial^2 \phi}{\partial x^2}\right|_{x_0} = \frac{A}{x_0^2}\left[\frac{1}{\rho} - \frac{2}{x_0}\right] \tag{9}$$

$$\sigma_c \alpha \left.\frac{\partial \phi}{\partial x}\right|_{max} = \frac{A}{x_c^2}\left[1 - \frac{2\rho}{x_c}\right]$$

where x_0 is the lattice spacing. Since x_0 depends only weakly on the hydrogen concentration, a decrease of γ with C_{11} implies a decrease of A and therefore C_{ij} and σ_c would also be expected to decrease. Although the real situation is significantly more complicated than implied by this model potential it does suggest possible trends.

One of the experimental complications is that those metals to which the decohesion theory of hydrogen embrittlement has been applied (such as ferrous alloys) have extremely low hydrogen solid solubilities. Measurements of parameters such as C_{ij} and phonon frequencies have generally been made on other systems such as the Group Vb metals and there is no assurance that conclusions based on these measurements can be extended to ferrous alloys. The effect of hydrogen on the elastic constants of a number of systems is shown in Table III (157, 158). For Nb and V alloys, the measurements extend to about 2.5 and 4 at.% H respectively and for Ta the measurements extend to about 20 at %; all of which are within the range of solid solubility. In contrast to these, a single measurement of the shear modulus of Fe-H alloys (made with a torsion pendulum) has been carried out at a concentration of about 170 at ppm in a highly supersaturated alloy (159). As seen in Table III, C_{44} and B are increased and C′ and G are decreased by hydrogen. The increase of C_{44} and B with hydrogen are particularly significant since the third order elastic constants of the b.c.c. metals (150) lead one to expect a decrease of C_{ij} due to the lattice expansion associated with H in solution. The large decrease of G noted for iron may be a significant indication of a decrease in lattice potential curvature which is expected to accompany a decrease in σ_c. In view of the experimental difficulties under which these measurements were obtained additional confirmation of this effect is needed. The elastic constant results therefore do not generally support a decrease in the curvature of the lattice potential at the equilibirum lattice spacing (Eqn. 9) and therefore do not provide substantive support for the decohesion theory.
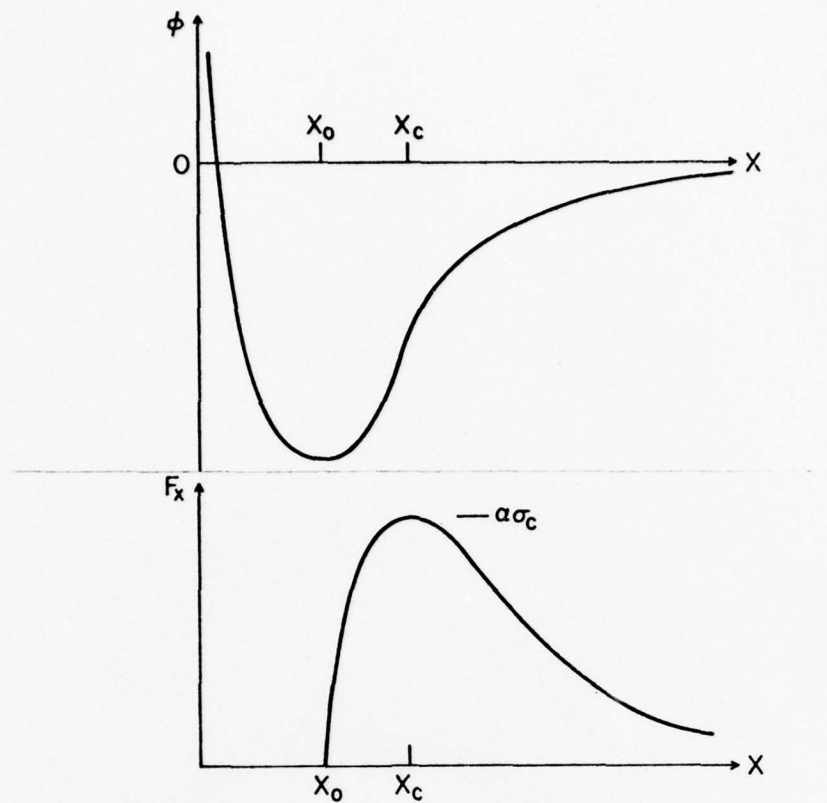
Fig. 9 Lattice potential curve (schematic) and the variation of the force required for separation of the atomic planes with the interplanar spacing.
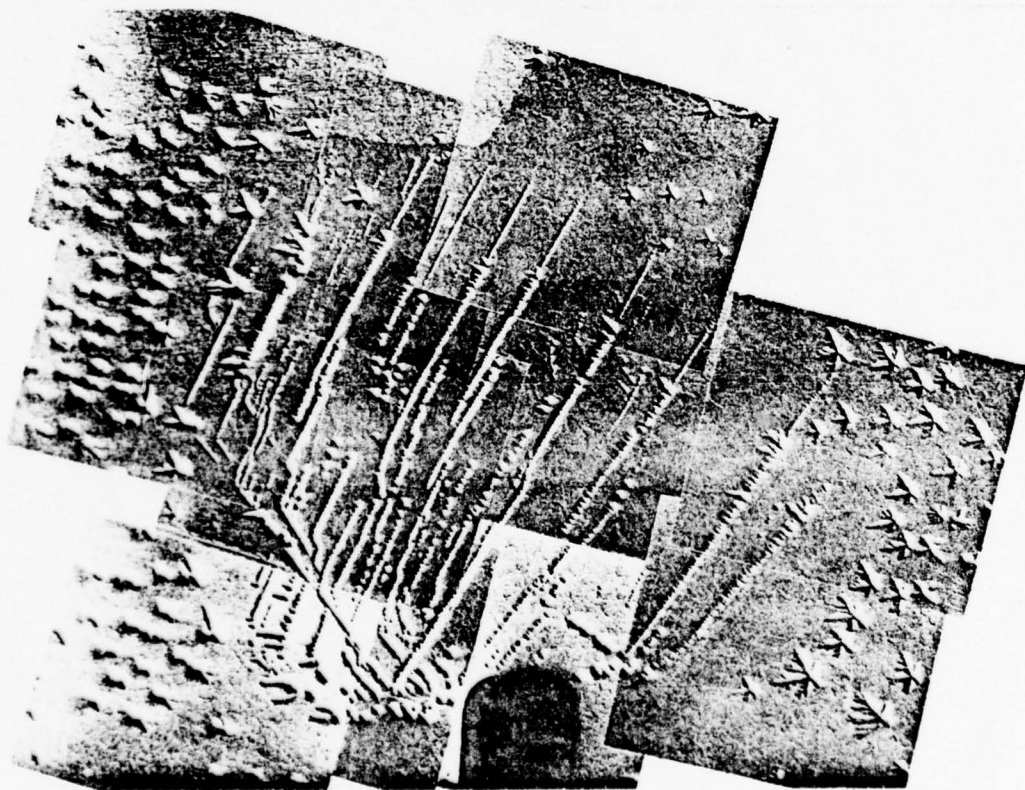

Fig. 10 Formation of hydrides along slip bands in a Nb -0.94 at%H specimen held at stress at 126K.

Table III. RELATIVE CHANGES OF THE ELASTIC CONSTANTS FOR 1at.% H FOR VARIOUS CRYSTALS

$\dfrac{\Delta C_{ij}}{C_{ij}}\left(\dfrac{10^{-3}}{1\,\text{at.\%H}}\right)$	$\dfrac{\Delta B}{B}$	$\dfrac{\Delta C_{44}}{C_{44}}$	$\dfrac{\Delta C'}{C'}$	$\dfrac{\Delta G}{G}$
System				
V-H	0.3	8.4	-18.3	
Nb-H	0.7	18.4	- 4.7	
Ta-H	0.55	1.4	- 1.2	
Fe-H				-80

Neutron scattering methods have been used to measure the phonon dispersion curves of a number of metal-H solid solution. In the Pd-H system the phonon frequencies are decreased by H in solid solution as expected from the lattice expansion (161). In the b.c.c. Group Vb metals however, hydrogen increases the phonon frequencies and therefore increases the atomic force constants (162, 163). Again there is no evidence for a decreased atomic bonding due to H in solution even for the very high hydrogen concentrations used for the neutron measurements.

Neither the elastic constants nor the atomic force constants are easily related to the cohesive stress σ_c, as previously discussed. Caglioti et al (164) have attempted to develop a theory of fracture based on the atomic force constants and have related the cohesive energy to the energy of the Brillouin zone boundary phonons. Application of their concepts to hydrogen embrittlement would require that the energy of the phonons at the Brillouin Zone boundaries be markedly reduced in the presence of solute hydrogen. The zone boundary phonons do not show any significant decrease in frequency except at H concentrations in excess of 45 at % in Nb-H alloys and even at concentrations as high as about 80 at % H the decrease is relatively minor (165).

In view of our inability to relate the elastic constants and the phonon dispersion curves to σ_c and of our inability to carry out these measurements on metals such as iron, the conclusions drawn must be rather tentative. The available evidence does not however suggest a marked decrease of atomic bonding due to hydrogen in solid solution. On the contrary, the measurements on the Group Vb metals are suggestive of an increased atomic bonding on alloying with hydrogen.

In addition to the uncertainty about the effects of hydrogen on atomic bonding in the ferrous systems, the concentration of hydrogen at the fracture tip is not well established. Embrittlement is observed at average concentrations of a few atomic ppm of H but as discussed by Oriani (137, 140), the actual concentration at the crack tip may greatly exceed this. The concentration in equilibrium with the crack tip stress field is given by Eqns. 3 (Section 3). The concentration enhancement, c/c_0 depends on factors such as plastic relaxation at the crack tip and can be related to the crack tip stress intensity. It can attain values of 10 to 100 at sufficiently high stress intensities and low temperatures. Since hydrogen embrittlement of steels takes place at average concentrations of a few parts per million, even at these enhancements the local concentrations are of the order of 100 at.ppm. In view of the rather modest effects of hydrogen on the crystal properties discussed above, it is difficult to see how this low concentration can affect the average lattice potential significantly. It must be realized however, that fracture does not reflect the average potential at the crack tip but rather the potential of the most highly stressed atomic bond and its immediate neighbors. In view of the lattice dilitation caused by a single hydrogen interstitial it is precisely at this point where hydrogen would have the lowest free energy. Hence, although the concentration enhancement due to the average local stress field at the crack tip may be insufficient to affect the average lattice potential significantly, the atomic bond which is most highly stressed can have a very high hydrogen concentration in its immediate vicinity and may be greatly affected by the presence of the hydrogen. It is thus misleading to consider average concen-

trations such as calculated with Eqn. 3. The effects of extremely high concentrations on individual atomic bond strengths are of prime importance even though the average local concentration is relatively low.

An indication of the importance of solute segregation at the crack tip may be obtained by varying the fracture made. Since hydrogen occupies the octahedral or tetrahedral interstitial sites it should have a non-spherical strain tensor, ϵ_{ij}. Therefore non-zero interaction energies may be expected with shear as well as with dilational stress fields. The distortion field around hydrogen interstitials in niobium has been shown to have cubic symmetry (166, 167) despite the occupancy of the tetrahedral interstitial site which has tetragonal symmetry. If this result is also valid for hydrogen in steels, concentration enhancement at the crack tip would occur for Mode I stresses but not for Mode II or III. Embrittlement has not been observed for Mode III stress fields under conditions which cause embrittlement under Mode I stresses (168) which is consistent with a cubic distortion field around the hydrogen interstitials in iron. This result also points out the importance of concentration enhancement by the crack tip stress field.

In a homogeneous elastic solid the decohesion mechanism would result in continuous crack propagation by bond rupture at the tip of the crack. Sonic emissions accompany the advance of a crack in a hydrogen embrittled steel (140, 170) indicating that the crack advance is in fact discontinuous. In a real material this would be expected due to the structural inhomogeneities and the plasticity which accompanies fracture in a material such as steel. Hydrogen assisted bond rupture could be expected both at the crack tip and at points in advance of the crack front at which particularly high stresses existed because of the crack tip plastic deformation or at which second phase interfaces existed. These cracks would link up with the main crack, possibly with some degree of plastic tearing of ligaments, giving rise to discontinuous crack propagation and sonic emission. A discussion of the decohesion mechanism applied to bond rupture in front of the main crack front has been given by Gerberich (90).

The existence of an equilibrium relation between H pressure, p and the stress intensity, K_I required for crack propagation has been demonstrated for high strength steels (115). Under clean surface conditions crack propagation could be initiated either by increasing K_I or the gas pressure down to pressures of 7.5×10^{-4} Pa (0.1 torr). The equilibrium relations differed for H_2 and D_2 gas. A variety of rationalizations (137, 140, 169) of this relationship have been presented in support of the decohesion theory but all *assume* that σ_c is reduced by hydrogen. The models can account for the measurements (if the above assumption is accepted) with reasonable values of the model parameters. In particular Oriani and Josephic (140) have incorporated adsorption thermodynamics and linear fracture mechanics into the formalism to derive the relation

$$\ln \left[\frac{p}{(K_{Io} - K_I)^2} \right] = \alpha_1 \left(\frac{K_I}{\rho^{1/2}} \right) + \alpha_2 \left(\frac{K_I^2}{\rho} \right) + \alpha_3 \tag{10}$$

where K_I is the stress intensity at which the crack propagates, K_{Io} is the critical stress intensity at zero hydrogen pressure, ρ is the crack tip radius and α_1, α_2 and α_3 are constants which are known from the material parameters. In order to fit the experimental data the crack tip radius was taken to be linearly proportional to K_I leading to the relation:

$$\ln \left[\frac{\rho}{(K_{Io} \cdot K_I)^2} \right] = \alpha_1' K_I^{1/2} + \alpha_2' K_I + \alpha_3' \tag{11}$$

A good fit to the data was obtained for reasonable values of the constants using Eqn. 11. A similar relation was derived by Van Leeuwan (169).

The ability of a relation such as Eqn. 11 to describe the experimental data is consistent with but not direct evidence for the reduction of σ_c by hydrogen which is the basic *assumption* of these theories. What the experiments do support is the stress effect on hydrogen solubility, the effects of crack tip parameters on hydrogen solubility and the existence of a critical hydrogen concentration for fracture. The issue of how the fracture actually occurs, be it by a decrease in σ_c, by hydride formation or by some other mechanism, remains to be settled by more microscopic experiments.

5.5 HYDRIDE FORMATION MECHANISMS

Many metals which exhibit severe hydrogen embrittlement are also known to form hydrides. In some systems, such as Group Vb metals and Zr alloys, precipitated hydrides have been shown to nucleate cracks but the propagation mechanism and the embrittlement mechanism in the absence of precipitated hydrides is still a matter of discussion. In other systems such as nickel and aluminum alloys, hydrides are known to form but only at much higher hydrogen fugacity than is thought to occur during hydrogen embrittlement. In the following sections the role of precipitated hydrides and stress-induced hydrides on fracture will be considered.

The mobility of hydrogen is sufficiently high in systems of interest to allow hydride formation in the temperature range where embrittlement is observed (27). Most of the hydrides form by an ordering reaction of the hydrogen interstitial solutes on a subset of the metal lattice interstitial sites. The metal lattice undergoes an elastic distortion and therefore the kinetics of hydride formation are governed by the rapid hydrogen interstitial diffusion.

In a number of systems, such as Ti-H and Zr H, the structure of the hydride which precipitates at low temperatures (6, 7) (the δ hydride (fluorite structure) or the metastable γ hydride (f.c. tetragonal structure)) appears to require correlated shears of the metallic lattice as well as ordering of the hydrogen interstitials. In these cases, the rate of formation of the hydride may be limited by the inhomogeneous deformation of the lattice rather than by hydrogen diffusion and ordering.

Relatively little is known of the properties of most hydrides. The atomic bonding is usually metallic in nature although ionic bonding (e.g., alkali metal hydrides) and covalent bonding (e.g., MgH_2, BeH_2 and possibly AlH_3) are known to occur. The volume changes on forming the hydrides from the metal are often quite appreciable ranging up to about 25% and being negative for the ionic hydrides and positive for the metallic hydrides. Few of the hydrides have been grown in massive form due to their extreme brittleness and their tendency to powder as a result of the volume change on formation. Recent single crystal studies (171) and T.E.M. observations (172) of NbH have shown that (a) dislocations have very low mobility in the hydride and (b) the surface energy (as measured by fracture mechanics methods) is not particularly low; being about 5000 ergs/cm^2 for the {110}. In addition, the elastic constants (173) and phonon dispersion curves (174) of the β NbH have been measured and these do not indicate any significant decrease of atomic bonding compared to pure Nb. Nonetheless, the extreme brittleness of the hydrides is well established; the β NbH phase can be readily cleaved along the {110} for example and there is little plastic deformation which accompanies the fracture (171). While it has been suggested that the reason for the hydride brittleness is a resistance to dislocation motion rather than a decrease in atomic bonding (171), this is not well established. The high lattice resistance to dislocation motion in the hydrides may stem from the disordering of the H interstitials which accompanies plastic flow.

In the Zr-H system precipitated hydrides have been shown to crack at low temperatures while the solid solution α retains its ductility (110, 111, 175, 176). The hydride acts as a barrier to slip and the stress concentration at the head of the slip bands causes cleavage. Since the solid solution is ductile, the crack is blunted at the hydride-α interface and at normal tensile strain rates at room temperature the alloys fail by ductile tearing between the cleaved hydrides. This inability of the cleavage crack, which forms in the hydride, to propagate as a cleavage crack into the α solid solution may be due to low hydrogen diffusion rates in the α phase or to low rates of correlated shears of the metal lattice; either one of which can control the rate of hydride formation. At sufficiently low strain rates, the cleavage cracks in the Zr-H alloys do propagate in a low ductility mode (85, 87) as will be further discussed shortly. Thus, we may conclude that while precipitated hydrides can nucleate cracks they do not necessarily lead to low ductility failure in the solid solution. In this sense, the precipitated hydrides act as do any other brittle precipitate. They decrease the strain to failure by reducing the effective cross-section of the specimen when they crack. Completely brittle fracture, as observed in many systems, requires a mechanism for propagation of the cracks into the solid solution.

In discussing the role of hydrides in embrittlement cognizance must be taken of the fact that the metal-hydrogen phase relationships are extremely sensitive to stress (41, 42, 177-179). In fact the published "equilibrium" phase diagrams are "metastable" phase diagrams at zero applied

stress. This distinction is significant due to (a) the large volume change on forming the hydride from the solid solution, (b) the low ΔH of formation of the hydrides and (c) the low temperatures at which hydride precipitation can occur. Since the hydrides are constrained by the surrounding solid solution, a consequence of (a) is that they are under a high stress (compressive for $\Delta V_{formation} > 0$) and require both elastic and plastic accommodation (172, 177, 178, 180). The free energy of accommodation, $\Delta G_{accom} = \Delta G_{elastic} + \Delta G_{plastic}$, as well as the interfacial energy, $\Delta G_{surface}$, must be included in the equilibrium between the solid solution, α, and hydride, β which is governed by the equation:

$$\Delta G_{\alpha-\beta} = \Delta G_{chem} + \Delta G_{elastic} + \Delta G_{plastic} + \Delta G_{surface} \tag{12}$$

As a consequence, the $\alpha-\beta$ solvus temperature which is observed for hydride constrained by the α phase is significantly reduced compared to the true equilibrium temperature defined as the equilibrium between unconstrained hydride and the solid solution.

In a specimen volume under stress, σ_{ij}, the change in the hydrogen chemical potential causes a change in the hydrogen concentration given by Eqns. 2 and 3. Equilibrium between the solid solution and the hydride is also markedly affected by stress due to the volume change on forming the hydride from the solid solution. The true equilibrium or unconstrained solvus under zero stress is defined as the equilibrium between a stress-free solid solution and a stress-free hydride, i.e., one which is not constrained by the solid solution. This solvus is defined by the equation

$$C_e^{o} = A \exp{-[\Delta \overline{H}_H{}^{\alpha}/RT_e^{o}]} \tag{13}$$

where $\Delta \overline{H}_H{}^{\alpha}$ is the relative partial molar enthalpy of solution of hydrogen in the α solid solution relative to the β hydride and A is a constant which depends on the entropy changes on solution of H in the α phase relative to the β hydride. If a stress is applied to the system this solvus is altered due to the molal volume change on forming the β hydride from the α phase, $\Delta V_{\alpha\beta}$. The solvus under stress is given by

$$C_e^{o} = C_e^{o} \exp{-[\sigma_s \Delta V_{\alpha\beta}/RT_e^{o}]} \tag{14}$$

These solvus temperatures do not correspond to those observed experimentally as the hydride is normally constrained by the solid solution and the $\Delta V_{\alpha\beta}$ is partially accommodated elastically and partially by prismatic loop punching. The magnitude of these accommodation enthalpy (free energy) terms has been estimated (178) to be given by:

$$\Delta H_{accom} \approx \frac{2\mu}{3\gamma} \frac{(\Delta V_{\alpha\beta}{}^2)}{\overline{V}} \tag{15}$$

where $\gamma = 1 + 4\mu/3B$, μ = shear modulus, B = bulk modulus, and $\overline{V}$ is the molar volume. Thus, the solvus at zero stress with the hydride constrained by the solid solution is given by

$$C_s^{o} = C_e^{o} \exp[\Delta H_{accom}/RT_s^{o}] \tag{16}$$

This is the solvus which would be observed on precipitation of the hydride from the solid solution on the first cooling cycle. In the presence of an external stress the free energies of the solid

solution and the hydride are altered as discussed above. In addition, however, the magnitude of ΔH_{accom} will be affected by the external stress as part of the accommodation results from plastic flow around the hydride. The magnitude of this change in ΔH_{accom} due to external stress has been discussed for Nb-H alloys (178). The constrained solvus temperature under an external stress, T_s^σ lies between the values of T_e^σ and T_s^0 obtained from Eqs. 14 and 16. It is this solvus, T_s^σ, which determines whether precipitation occurs under stress. At temperatures below T_e^σ the α phase is metastable and if the accommodation free energy were reduced (by external work for example) the β would form. These shifts in the equilibrium between the α and β phases under stress can amount to several hundred degrees. It should be noted that while these effects of stress on phase equilibria are quite general, they are particularly large for hydrides due to their low enthalpies of formation and large ΔV of formation.

Experimental verification of these effects has been obtained in a number of systems. Hydride precipitation has been induced by the application of stress at temperatures above the T_s^0 in the Nb-H system (42). In addition, the application of stress has been shown to cause reorientation of hydrides in several systems due to resolution of hydride plates which are in an unfavorable orientation relative to the applied stress and precipitation of favorably oriented hydrides (181, 182). Preferential precipitation of hydrides has been observed along slip bands in a number of systems presumably caused by a decrease in ΔG_{accom} (42). An example is shown in Figure 10.

A qualitative mechanism for the stress-induced hydride embrittlement was proposed by Westlake (183) and extended by a number of other authors. The mechanism is shown schematically in Figure 11. Application of a tensile stress decreases the hydrogen solute chemical potential at stress concentrators (which may be notches or dislocation pile-ups) and results in a flux of hydrogen to the region. The hydrogen concentration increases until it attains a value given by Eqn. 3 at which time the stress-induced chemical potential gradient is removed. However, the stress also decreases the free energy of the hydride and when $\Delta G_{\alpha-\beta} = 0$ hydride precipitation occurs. The kinetics of this process are controlled by the flux of hydrogen to the stress concentration. As discussed above, the stress-induced precipitation can occur above the stress-free solvus, T_s^0. Once the brittle hydride forms, it cleaves (Figure 12), the crack runs to the β-α interface at which point it is blunted by deformation in the ductile α matrix. The process described above repeats and the brittle fracture propagates by repeated stress-induced hydride formation and cleavage.

Direct confirmation of this mechanism has been obtained in a number of hydride forming systems. In the Nb-H system formation of hydrides under stress at stress concentrations and at slip bands has been directly observed using SEM both above and below T_s^0 (41, 42). Crack propagation through the stress-induced hydride and continuous formation of the hydride at the crack tip has been observed. The hydride was identified morphologically, and with electron diffraction and with S.I.M.S. At temperatures below 300K the stress-induced hydride was shown to be NbH while at elevated temperatures the embrittlement was shown to be consistent with NbH_2 formation (124). The hydride was present on both sides of the crack surface and the crack plane was the {110} consistent with that obtained from hydrogen cleavage. Hydride formation at crack tips has also been observed in the V-H (184) and the Ti-H (108) systems using T.E.M. methods. Less direct but nonetheless convincing demonstrations of stress-induced hydride formation associated with crack propagation during hydrogen embrittlement of Ti alloys have been reported (185).

Crack propagation kinetics in Zr-H alloys have been shown (186, 187) to be quantitatively consistent with a model based on stress induced flux of hydrogen to the crack tip and stress induced hydride formation. This theory accounts for the common observation of a cleavage to ductile fracture transition as the strain rate is increased or the temperature decreased on the basis that the crack propagation is controlled by hydrogen flux to the crack tip. At high strain rates, ductile fracture behavior is obtained because insufficient time elapses before ductile fracture to allow hydride formation. The same phenomena, i.e., the return of ductility and ductile fracture, occur on decreasing the hydrogen diffusivity by lowering the test temperature or by using deuterium alloys. Recent crack propagation studies in Nb-H (D) alloys have been in general agreement with the theory developed for Zr-H alloys (120). While the kinetic studies are consistent with the stress induced hydride mechanism they do not provide direct support. However, in combination with the direct hydride observations the total support is very strong.
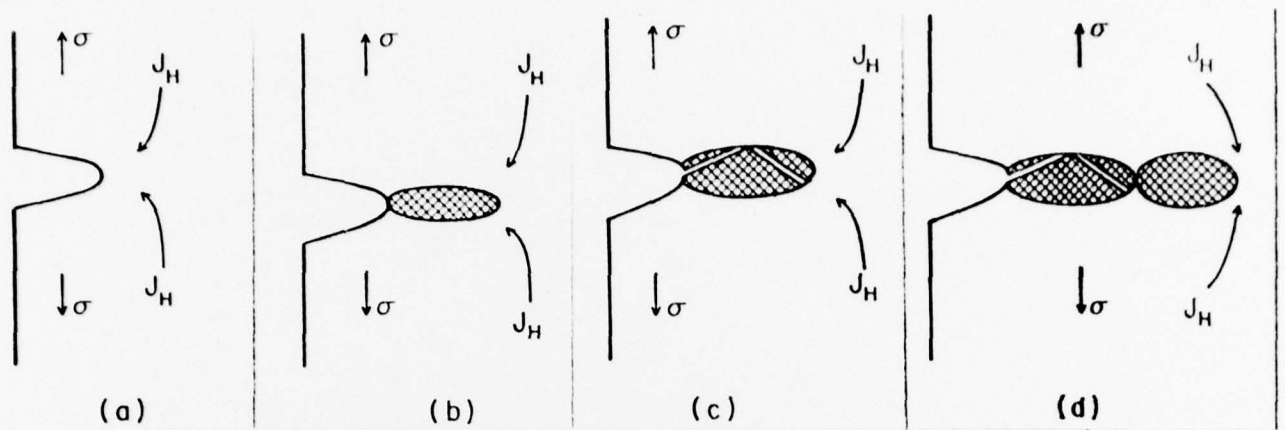
Fig. 11 Schematic showing the mechanism of hydride embrittlement by stress induced hydride formation. (a) flux of hydrogen to the crack tip due to the reduction of the hydrogen chemical potential in the tensile stress field (b) formation of the hydride due to the reduction of the hydride chemical potential by the applied stress (c) cleavage of the hydride along its cleavage plane resulting in crack advance.
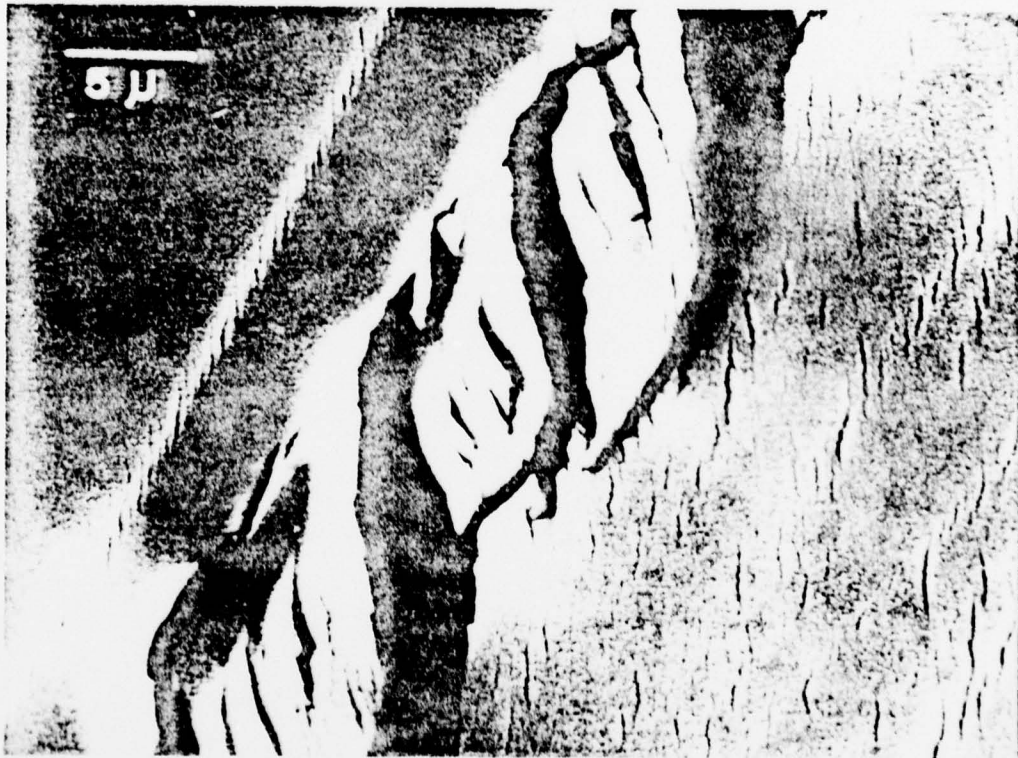

Fig. 12 Appearance of region in front of the main crack tip in a Nb -0.15 at.%H specimen tested at 150 K. The cracks are along {110}planes of the stress induced NbH. (Ref. 42)

The observation of embrittlement in hydride-forming systems above the stress-free solvus has led to suggestions that embrittlement may occur with hydrogen in solid solution or as a result of pre-precipitation clustering (38, 39). The existence of two ductility minima in Nb-H alloys (38, 41) was accounted for in this manner (38). In view of the demonstrated shifts in the solvus temperature by external stress, it does not appear appropriate to invoke a different solid solution mechanism for fracture above T_s^0. The stress shifts in the solvus T_s^0 were shown to be adequate to account for embrittlement above T_s^0 and the double minima in the strain to failure was shown to be consistent with the changes in hydride ordering in the β NbH hydride (41, 42, 124). Stress induced hydride cracking was also shown to be the crack propagation mechanism above T_s^0 (41, 42).

The occurrence of large amounts of plasticity prior to cleavage fracture (Figs. 2 and 8) has been suggested to be a reflection of the shifts of the solvus temperature during work hardening (41, 42). In this view plastic deformation and hydride precipitation and cleavage are competing processes. The solid solution is ductile and would fail in a ductile manner unless the stress during deformation shifts T_s^0 sufficiently to allow stress-induced hydride to form. Occurrence of the hydride forms and therefore the strain to failure depends on the thermodynamics of the hydride in the deforming specimen as well as the kinetics of H transport. A convincing demonstration of this is provided by the work of Sasaki and Amano (188) who showed that solute trapping which stabilizes the solid solution relative to the hydride decreases the hydrogen embrittlement.

While the stress-induced hydride cracking mechanism is strongly supported by the behavior of a number of metal-hydrogen systems, its range of applicability is not yet established. In Ti alloys, for example, the complexity of the microstructure has confounded attempts to obtain direct confirmation of stress effects on the hydrogen solvus or of the mechanisms of embrittlement. In $\alpha + \beta$ alloys containing H, the fracture appears to occur along the α-β interfaces and it has been proposed that this results from the formation of hydride (185). The H solubility and diffusivity is much greater in the β phase than the α and the β may act as a high diffusion conduit to bring hydrogen to the crack tip at which point it precipitates as a hydride in the α phase and cracks. A layer of titanium hydride has been observed along the fracture surface for titanium alloys having a Widmanstatten structure which were fractured in dry hydrogen gas (185).

In other alloy systems where hydride formation is possible, the evidence in support of any embrittlement mechanism is rather conflicting. Bursle and Pugh (3) reviewed the evidence for Mg alloys and for Al alloys which were fractured in hydrogen gas and in stress corrosion environments. While there is increasingly strong evidence that hydrogen enters into the stress corrosion fracture of these alloy systems, and while there is some evidence for possible hydride formation during the fracture, the situation remains rather inconclusive. In these alloys there is no direct evidence for stress-induced hydride formation.

In nickel-base alloys, hydride (NiH) can form by cathodic charging or at high H_2 pressures ($\sim 10,000$ atm) (189, 190). The hydrogen fugacity under the conditions of external H_2 gas pressure or internal charging which lead to embrittlement is generally considered to be too low to form the hydride. However, it should be pointed out that the formation of NiH hydride at high pressures overestimates the required fugacity. The stress free energy terms, $p\Delta V_{formation}$ (where $\Delta V_{formation}/V_0 \cong 0.16$) inhibit the hydride formation, whereas in the tensile field of a crack this term would assist the hydride formation. Direct observations of the phenomena at the crack tip are not yet available. In nickel alloys, embrittlement by solute hydrogen and by simultaneous cathodic charging during deformation leads to intergranular fracture. Transgranular embrittlement has been reported in sharply notched single crystals (191). Latinison and Opperhauser (130) have suggested that the failure at grain boundaries under conditions of simultaneous cathodic charging may be associated with the presence of hydrogen recombination poisons, such as sulfur, which aid hydrogen entry, thereby increasing the local fugacity. Alternatively, for both internal hydrogen and cathodic charging conditions, the hydrogen fugacity at the boundaries may be increased by dislocation transport processes. In either case, the effect of stress on stabilizing the hydride and its possible role in fracture remains to be determined.

Embrittlement in ferrous alloys is even less likely to be associated with the formation of a hydride. FeH is a stable compound in the vapor phase but the solid hydride appears to have even less stability than NiH. Fujita (19) as suggested a model for transgranular fracture based on

segregated H interstitials which form an interstitial platelet. This is formally similar to a hydride but evidence in support of this concept is lacking.

In summary, the stress induced hydride mechanism seems well established for systems which form hydrides and appears to account for the behavior both above and below the solvus temperature. In systems which have metastable hydrides (NiH, AlH, etc.) this mechanism may be applicable when the effects of stress on the hydride stability are taken into account. In these systems, direct support for the mechanism is lacking. In systems such as FeH, where hydrides are not stable, the applicability of the mechanism is rather questionable.

6. SUMMARY

The diversity of behavior observed for hydrogen-metal systems is too great to allow a complete mechanistic understanding at this time. Several general conclusions can however be drawn as summarized below. In attempting to understand the failure mechanisms it is important to distinguish between kinetic effects and fracture mechanisms.

The occurrence of hydrogen embrittlement depends on the attainment of a critical hydrogen chemical potential at points of stress concentration. The factors which determine the hydrogen chemical potential are the fugacity of the hydrogen source, the thermodynamic properties of the metal-hydrogen system, the hydrogen transport processes and the nature of the stresses applied. Based on these factors it is possible to understand why embrittlement is often observed in high fugacity environments where hydrogen is present at the crack tip and not under conditions where the hydrogen fugacity is low or where its mobility is limited by low diffusivity.

Hydrogen has been shown to have an effect on the ductile fracture process of microvoid coalescence as well as on the occurrence of low ductility fracture processes such as cleavage or intergranular fracture. The fracture morphology is determined by a variety of factors such as the system considered, the hydrogen chemical potential, the metallurgical structure and the segregation of particular solutes to grain boundaries. In a number of systems it appears that the effect of the hydrogen is to modify fracture processes which occur in the absence of hydrogen rather than to introduce new processes. In other systems hydrogen changes the nature of the fracture process from a ductile to a brittle one.

After removing kinetic factors from consideration it appears possible to categorize the hydrogen related brittle fracture processes into groupings based on hydride forming systems, systems in which hydrides are not stable and systems in which normally unstable hydrides may be stabilized by the applied stress. In the hydride forming systems the fracture mechanism has been shown to be the stress induced hydride formation and cleavage. Direct observation of hydrides at crack tips as well as the thermodynamics of stressed solid solutions and hydrides support this mechanism. Kinetic models based on the stress induced flux of hydrogen to crack tips are consistent with the hydride fracture mechanism. One result of observations on these systems is that hydrogen solid solutions are ductile and the cleavage fracture mode occurs only when hydrides are formed.

The hydride stability relative to the solid solution is influenced by the applied stress as well as by the hydrogen chemical potential at the crack tip. If hydrides are stabilized by crack tip stresses, the stress induced hydride fracture mechanism may apply to systems such as Ni-H in which hydrides are not normally expected to be stable under the conditions of hydrogen embrittlement. The range of metal-hydrogen systems which have metastable hydrides to which the stress induced hydride mechanism applies has not been established. To do so requires kinetic studies to show agreement with the stress induced flux to crack tips, thermodynamic studies to examine the stress effects on hydride stability and microscopic studies to examine crack tip processes.

In non-hydride forming systems the fracture mechanism is less clearly established. Adsorption mechanisms based on reduction of the surface energy by adsorbed hydrogen cannot account for the experimental observations. The same conclusion can be drawn for mechanisms based on hydrogen effects on the plastic properties of the metals. In this case the effects are not as clearly established since contradictory evidence for the effect of hydrogen on deformation parameters has been obtained. These effects appear to be too small to account for the drastic changes in fracture modes observed and no adequate mechanism for the fracture processes based on plasticity effects has been proposed.

The decohesion mechanism is consistent with the observed kinetics of embrittlement and with the thermodynamic requirement of a critical hydrogen concentration for fracture. However, this mechanism postulates the decrease of the lattice cohesive stress and no evidence in support of this postulate is available. Measurements of hydrogen effects on small strain parameters such as the elastic constants and phonon frequencies indicate an increase in atomic force constants due to hydrogen in solution. Establishment of this mechanism requires an understanding of the effect of hydrogen on the lattice potential which is not yet available.

In establishing the validity of the decohesion mechanism, or any of the others, it is not sufficient to examine the kinetic aspects of the model. For example both the stress induced hydride mechanism and the decohesion mechanism have similar kinetics which are based on hydrogen flux to the crack tip. Both have similar thermodynamic requirements in that a critical hydrogen concentration is necessary at the crack tip. In the decohesion mechanism this critical concentration is required to reduce the cohesive stress to below the crack tip stress while in the stress induced hydride mechanism a hydrogen concentration sufficient to form the hydride in the crack tip stress field is required. The essential difference between the two mechanisms is the detailed process of bond rupture. It requires either microscopic observations or a knowledge of hydrogen effects on lattice potentials to establish this process. Even in this point the two mechanisms have a great deal of similarity. Thus although the presence of a hydride at the crack tip may be established, the basic question of why the hydride is brittle is identical to the basic question in the decohesion mechanism.

ACKNOWLEDGEMENTS

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13. ABSTRACT

The literature pertaining to hydrogen related failure of metals is reviewed. Emphasis is placed on those experiments which relate directly to the failure mechanisms. The possible failure mechanisms are discussed and evaluated.

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