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MECHANISMS OF HYDROGEN RELATED FRACTURE OF METALS

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INTRODUCTION

The number of studies of hydrogen related fracture in recent years is quite impressive both in the variety of systems studied and in the amount of materials characterization which has been obtained ¹⁻³. Despite this effort there is still incomplete understanding of the mechanisms by which the hydrogen related failures occur and hence each material becomes a new and novel problem. The advantage of obtaining an adequate understanding of the failure mechanisms is that general rules of behavior can then guide the selection and application of new materials in aggressive environments.

In focussing on the understanding of the basic mechanisms of environmentally related fracture it is important to distinguish between those experiments and effects which are dependent on the kinetics of fracture and those which are mechanistically related. Kinetic studies can be applied to develop an understanding of the factors which determine the failure rates but should not be used to classify materials with respect to the mechanisms of failure. Thus materials which had been classified as insensitive to hydrogen effects, e.g. Al ⁴, stainless steels ^{5,6}, etc. have recently been shown to be highly susceptible to "hydrogen embrittlement" when exposed to a sufficiently high fugacity of hydrogen or tested at sufficiently low strain rates and the proper temperature range.

There has been no shortage of suggested mechanisms ^{1,2,7}; but few have stood the test of critical examination; particularly as new experimental and theoretical methods become available. At the present time several viable mechanisms remain, each of which can be supported by some experimental and theoretical evidence. The preponderance of evidence is that there are several hydrogen related failure mechanisms rather than a single dominant mechanism and that even within one material system several of these may be operative. In cases where this is true, the particular mechanism which leads to failure is controlled by kinetics. An example of this will be discussed subsequently. In the present paper three mechanisms will be discussed; embrittlement due to hydrogen related phase changes, hydrogen enhanced plasticity related fracture and the decohesion mechanisms.

HYDROGEN RELATED PHASE CHANGE MECHANISMS

A number of metallic systems have demonstrated hydrogen embrittlement due to stress induced formation of hydrides or other relatively brittle phases and the subsequent brittle fracture of these phases ⁸⁻¹³. Several types of phases may take part in this failure mechanism; e.g. hydrides, martensitic phases ¹⁴⁻¹⁷, etc. The basic requirements are that these phases be stabilized by the presence of hydrogen and the crack tip stress field ^{10,16,18} and that the phase which forms be brittle ^{19,20}. The

typical system which exhibits failure by this mechanism forms stable hydrides in the absence of stress and these hydrides, by virtue of their large $\Delta V_{\text{formation}}$, are thermodynamically more stable under the stress and hydride fugacity conditions at the crack tip¹⁸. In some cases hydrides can be shown to result from this stress stabilization even when they are not formed in the absence of the stress^{21,22}. Among systems which exhibit hydride embrittlement are the group Vb metals (Nb, V, and Ta)^{8-13,23-25}, Zr^{26,27}, Ti²⁸⁻³⁰ and alloys based on these metals.

There are also a number of alloys systems which form "pseudo-hydrides" under high fugacity conditions, such as cathodic charging. These "pseudo-hydrides" are in fact high concentration solid solutions formed in the presence of a miscibility gap^{31,32}. These systems often exhibit embrittlement in the presence of this high concentration solid solution (or by the stress induced formation of this high concentration solid solution) even though this phase is not a true hydride, i.e. it lacks the ordering of the hydrogen in the interstitial positions. Examples of these systems include Ni and its alloys³², Pd and its alloys³³, the Group Vb metals Nb, Ta and V at elevated temperatures³¹, and possibly stainless steels which form a "pseudo-hydride" phase at high hydrogen fugacity¹⁶.

Hydrogen embrittlement by stress induced formation of hydrides (or high concentration solid solutions) is observed under conditions where the hydrides can form at a rate sufficient to preclude other forms of failure. In these systems ductile rupture can occur if the strain rate is increased or if the temperature is decreased³⁴ since both cause ductile fracture prior to failure by hydride formation and cleavage. Similarly, if the temperature is increased the stability of the hydride may be sufficiently decreased so that it can no longer be stress induced and hence failure may again occur by ductile processes. The thermodynamics of these processes allow prediction of the conditions under which hydride related embrittlement can be observed¹⁸. Establishment of this failure mechanism requires direct evidence for the formation of a hydride at the crack tip of a propagating crack^{11,12,23,30}. In some cases, the stress induced hydrides remain at the fracture surface and can be detected^{12,35} while in others they disappear when the stress field of the crack tip is removed²³ and have to be observed while under stress.

Another condition for hydride embrittlement is that the hydride be a brittle phase which undergoes "cleavage" fracture. In general this is not a restrictive condition as most of the hydrides exhibit very limited ductility due to restricted dislocation mobility resulting from the disordering of the hydrogen by dislocation motion^{19,20}.

The embrittlement mechanism may be qualitatively described as follows. Under the applied stress the chemical potential of the solute hydrogen and the hydride is reduced at tensile stress concentrations; such as crack tips. Diffusion of hydrogen to these elastic singularities and precipitation of hydrides at the crack tips then occurs. The phase change is accompanied by a decrease in the critical stress intensity for crack propagation as the hydrides are generally brittle phases. The crack may propagate into the hydride the formation of which is accompanied by a high

compressive local stress field due to the very large $\Delta V_{\text{formation}}$. This compressive stress field can give rise to "phase transformation toughening" ³⁰. However, the greatly decreased K_{Ic} allows rapid crack propagation when the applied stress is only moderately increased and the crack propagates by cleavage until the hydride-solid solution boundary is reached. At this point the crack enters a ductile phase having a high K_{Ic} and the crack stops until more hydride is formed. The process repeats itself resulting in discontinuous crack growth through the stress induced hydride phase and with hydride formation along the flanks of the cracks.

The stress induced hydride formation and cleavage mechanism can account for all of the observed characteristic of hydrogen embrittlement in those system where it is observed.

a. Hydride embrittlement occurs only over a limited temperature range with ductile behavior being observed at higher and lower temperatures ⁹⁻¹¹. The solvus temperature of the hydride forming systems depends on the local stress at the crack tip and the local hydrogen concentration ¹⁸. Therefore above a critical temperature the stress induced increase in solvus is not sufficient to cause hydride formation before ductile failure intervenes. At the lower temperatures previously precipitated hydrides crack under the applied stress. However the hydrogen diffusivity and the rate of hydride formation is too low to allow re-precipitation of the hydrides and ductile fracture intervenes.

b. The extent of hydrogen embrittlement is decreased as the strain rate is increased ³⁴. Ductile fracture and stress induced hydride formation and cleavage are competitive failure mechanisms. As the strain rate is increased, less time is available for the diffusion controlled hydride formation at the crack tip and ductile fracture intervenes. The temperature range over which hydrogen embrittlement is observed is increasingly restricted and the strain to failure increases as the strain rate decreases. A clear demonstration that the extent of hydride fracture is dependent on diffusivity controlled hydride growth rate was provided by studies which employed deuterium at low temperatures ³⁴. The deuterium diffusivity at low temperatures is very much lower than that of hydrogen (the diffusion is highly non-classical ³⁶) and the metal - deuterium alloy behavior is correspondingly much more ductile during fracture.

c. Pre-existing hydride precipitates do not necessarily cause severe embrittlement. In some systems, such as the Zr based alloys ³⁷, the presence of massive hydrides does not necessarily cause hydrogen embrittlement. While these pre-existing hydrides often crack under external stresses, the fracture proceeds between the hydrides in a ductile manner. The loss of ductility is then similar to that caused by other brittle phases. The solid solution in equilibrium with the pre-existing hydrides is inherently ductile and fails in a ductile manner unless new hydrides grow at the tips of the cracks which are formed by fracture of the hydrides. It is this stress stabilized hydride which is responsible for the propagation of brittle cracks. A continued fracture by the hydride mechanism may not occur for several reasons. The hydrogen diffusivity may be too low to allow significant hydride growth prior to ductile failure. Alternatively, the temperature may be too high

relative to the solvus of the solid solution to allow stress stabilized hydride at the crack tip.

d. Hydrides are not always observed at the fracture surfaces. Brittle fracture by a crack propagating through the hydride phase ^{11,12,30} will occur on the habit plane and/or the cleavage plane of the hydride. The presence of hydride at the sides of the cracks requires that the hydride be stable after removal of the crack tip stress field. In some cases e.g. Nb ^{11,12} and Ti ³⁰ this is possible because of the large thermal hysteresis between precipitation and reversion while in others e.g. V ²³ reversion occurs behind the crack. In the case of Zr alloys, reversion of precipitated hydrides occurs in front of the crack to supply hydrogen to the crack tip ³⁸ and therefore similar reversion of the stress induced hydride behind the crack may occur.

e. Hydrogen embrittlement of metal-hydrogen alloys is often seen at temperatures above the solvus temperatures. This observation is a natural consequence of the effects of stress on the solvus of the metal-hydrogen systems ¹⁸. The shift in the hydride solvus can be appreciable since the solvus temperatures published in the phase diagrams correspond to precipitation of hydrides which are constrained by the surrounding solid solutions ²². In some cases embrittlement results at high temperatures due to the stabilization of dihydrides ³⁹ by the applied stress.

In a qualitative sense all of the phenomena described above for hydride embrittlement can apply to the embrittlement caused by stress induced formation of other phases ⁴⁰. These may be oxides, nitrides etc. or may be phases stabilized by the enhanced hydrogen concentration at the stressed crack tips. In all cases the important factors are the same; a) the effects of stress on the stability of the precipitated phases (i.e.. the requirement that the precipitated phase have a significant and positive $\Delta V_{\text{formation}}$), b) the kinetics of phase transition, and c) the mechanical properties of the precipitated phases. One significant difference between hydride embrittlement and that due to the formation of other phases is that the diffusivity of hydrogen is much greater than that of other solutes at any particular temperature ³⁶.

One important case of hydrogen related second phase embrittlement of some importance is the embrittlement of stainless steels. This matter is still quite controversial and the mechanism(s) unproven. In a number of cases hydrogen embrittlement of metastable stainless steels (e.g. Type 304 and 316) have been associated with hydrogen enhanced transformation of the γ fcc phase to the α' bcc and ϵ hcp martensites ^{14-17,41-43}. In situ TEM studies ^{15,17} have shown that these martensitic phases are formed in front of the crack tip and along the crack sides. While the fracture surfaces of hydrogen embrittled stainless steels (which show a quasi-cleavage aspect) are clearly different than the microvoid coalescence fracture seen in the absence of hydrogen, the actual structure of the surface is a controversial matter. There are several difficulties in making a definitive association of hydrogen embrittlement with the formation of these martensitic phases.

a. The very presence of these phases along the hydrogen embrittled fracture surfaces has been disputed ^{44,45}. In part this may result from the fact that the martensitic phases occur only very close to the fracture surfaces (within 1 micrometer) and hence require detection techniques sensitive to surface phases.

b. The martensitic phases are present near the fracture surfaces even in the absence of hydrogen due to deformation induced martensites. The major difference is that the amount of transformation and the stress at which the transformation occurs is much less in the presence of hydrogen gas or hydrogen in solid solution ¹⁷.

c. While few studies have been carried out, it does appear that the M_s temperatures are not significantly affected by the presence of hydrogen in solid solution ⁴⁶ while the M_d temperature is markedly reduced by hydrogen ¹⁶.

d. While the presence of martensitic phases at the surface of hydrogen embrittled metastable stainless steels has been established, it has not been shown whether these phases are a necessary condition for fracture or whether they are consequence of the enhanced deformation caused by hydrogen ¹⁷.

In addition to the hydrogen enhanced martensitic phases the metastable and stable stainless steels both exhibit formation of a "pseudo-hydride" phase ^{16,47} at high hydrogen concentrations. This γ' phase has an expanded fcc structure and has been suggested to result from a miscibility gap in the Fe-Cr-Ni system ¹⁶. The role of this γ' phase in the fracture of the alloys is not known. While stable stainless steels generally do not exhibit hydrogen embrittlement, except possibly in very high hydrogen fugacities, (embrittlement has been observed in Type 310 stainless steel ⁴⁸) these stable steels do form the γ' phase during hydrogen charging and it is possible that this high hydrogen concentration phase may be associated with the fracture.

HYDROGEN ENHANCED LOCAL PLASTICITY MECHANISM

In many cases the definition of hydrogen related fracture as a "brittle fracture" is based on loss of macroscopic ductility and/or relatively low resolution studies of the fracture surfaces. It was C. Beachem who first suggested ⁴⁹, on the basis of careful fractographic examination, that hydrogen embrittlement of steels was in fact associated with locally enhanced plasticity at the crack tip. This viewpoint received little attention for many years. In recent years it has become evident that hydrogen "embrittlement" by means of locally enhanced plasticity is a viable fracture mechanism; the term Hydrogen Enhanced Local Plasticity (HELP) will be used as a descriptive phrase. While the concept of enhanced plasticity appears to be at variance with embrittlement, there is no contradiction when it is recalled that the distribution of hydrogen can be highly non-uniform under an applied stress. Thus locally the flow stress can be reduced, resulting in localized deformation which leads to highly localized failure by ductile processes, while the total macroscopic deformation remains small. In fact we are familiar with shear localization in many systems ⁵⁰⁻⁵²; the HELP mechanism proposes shear localization due to hydrogen.

From a macroscopic vantage point this type of failure will appear "brittle". Strain to failure measurements made over a macroscopic gage length will be greatly reduced despite the high degree of local plasticity. Examination of the fracture surfaces at low resolution will induce a conclusion of a "brittle" fracture surface because of the highly localized nature of the ductile failure.

In recent years this point of view has been supported by the work of Lynch^{3,53} and Birnbaum et al^{30, 54-64} on a variety of systems. Using both fractographic evidence and in situ environmental cell TEM deformation and fracture studies, it has clearly been shown that the HELP mechanism is a viable failure mechanism for a large number of systems, both pure metals and alloys based on: Ni^{54, 55, 60}, Fe⁵⁷⁻⁵⁹, In⁷¹⁸^{61, 65}, type 304¹⁷, A533b⁶⁶ and 316¹⁷ stainless steels, Al⁶⁴, 7075 and 7050 Al age hardened alloys⁶³, and α' Ti alloys³⁰. The phenomena is quite general having been observed in pure metals, solid solution strengthened alloys, precipitation hardened alloys, and in bcc, hcp and fcc crystal structures. In addition to the direct studies of fracture cited above there is a growing body of results which support the microscopic observation that the addition of hydrogen to a system can decrease the flow stress of that system⁶⁷⁻⁷² and lead to strain localization^{4, 73}. All of these points will be discussed below.

While there is agreement between Lynch and Birnbaum et al on the basic thesis that the presence of hydrogen increases the plasticity at the crack tip and leads to fracture, there are significant differences in that Lynch views the phenomenon as a surface effect while Birnbaum et al consider the hydrogen effect to occur in the volume of the material as well as near the surface. Since the views of Lynch have recently been reviewed⁵³, the following will primarily discuss the mechanism proposed by Birnbaum et al, the HELP mechanism. The systems to which this mechanism appears to apply are principally those which do not form hydrides. The HELP mechanism is competitive with the stress induced hydride mechanism as shown by the studies of α' Ti³⁰ (and possibly the metastable stainless steels¹⁷) where both failure mechanisms have been shown to apply in different regimes of crack velocities.

The HELP mechanism is operative for hydrogen in solid solution and for gaseous hydrogen environments. In both cases the application of a stress results in a non-uniform distribution of hydrogen with a high concentration in front of an elastic singularity such as a crack or a precipitate. The high local stress field at the tip of a crack reduces the chemical potential of solute hydrogen⁷⁴ and as a result of diffusion the concentration is locally increased. The tip of the crack is also the most likely place for hydrogen entry from a gaseous atmosphere since it is the place where plastic deformation first occurs and hence any surface barriers to entry are minimized. As will be discussed shortly, the resistance to dislocation motion, and hence the flow stress is decreased by the presence of hydrogen. Thus, in the regions of high hydrogen concentration the flow stress is decreased and slip occurs at stresses well below those which are required for plastic deformation in other parts of the specimen; i.e., slip localization occurs in the vicinity of the crack tip. This has been clearly shown for high purity Al⁴ and Fe-N alloys⁷². In addition to the local

decrease in flow stress, hydrogen has been shown to result in serrated yielding (Portevin-LeChatalier effect) in the temperature range in which hydrogen embrittlement is severe ⁷⁵. The region of serrated yielding is one of negative strain rate dependence, $d\sigma/d\dot{\epsilon} < 0$, and shear localization is a consequence ⁷⁶.

Continued localization of shear is expected to lead to fracture by the various plastic failure processes although the exact mechanism by which shear localization causes fracture is not known ⁷³. In the in situ TEM experiments, void formation is observed along the intense slip bands ^{58-60,63,66} and shallow microvoids have been observed along the fracture surfaces of macroscopic hydrogen embrittled specimens ⁵³. The in situ TEM experiments show fracture occurs along slip planes in a sawtooth morphology and three dimensional analogs, pyramidal features bounded by {111} slip planes, are observed on macroscopic fracture surfaces ^{54,55}. One consequence of the HELP mechanism is that the fracture surface is predicted to be that along which the shear localization occurs. In general this is the slip plane, as has been observed ^{53,54} but in cases where cross slip is prevalent or where special constraints are imposed by the stressing mode ^{3,77,78}, the fracture plane may differ from the slip plane.

The behavior of many systems observed during in situ environmental cell TEM experiments is consistent with the above description of the HELP mechanism. Deformation of the specimens in vacuum resulted in failure by plastic deformation in front of the crack tip with the region of deformation extending in front of the crack and being relatively broad. In general, the deformation occurred in several positions in the specimen and often ductile failure occurred at several different points. Propagation of these ductile cracks generally was preceded by voids opening in front of the crack front as well as appreciable thinning of the material in front of the crack.

The effects of hydrogen on fracture on these TEM specimens was studied for static cracks under stress. On adding hydrogen gas to the environmental cell dislocation sources were observed to begin to operate and dislocations to increase their velocities. Removal of the hydrogen gas resulted in a cessation of the dislocation motion; this cycle could be repeated many times. The effect of the hydrogen was to reduce the stress for dislocation motion ⁵⁶⁻⁶⁶. Similar effects were seen for dislocations in parts of the specimen which were of uniform thickness and were far from the cracks, and which were in thick (several hundred nm thicknesses) and in thin parts of the specimen. Enhanced dislocation velocities due to hydrogen were observed for screw, edge, and mixed dislocations and for dislocations which were in tangles, in slip bands, and far from other dislocations. Similar behavior was observed for dislocations in fcc, bcc, and hcp crystal structures and in alloys as well as in pure metals. In the case of a number of metals the effects of hydrogen are enhanced by the addition of small amounts of solutes ^{57,58}. One of the remarkable features of this phenomenon is its generality which suggests that the mechanism is not specific to a particular type of material or dislocation type. The effects of hydrogen on fracture results from these effects on dislocation behavior. Fracture in hydrogen was similar to that in vacuum but with several very important differences. In the presence of hydrogen the plastic deformation processes and the

resulting fracture took place at greatly reduced stresses and the plastic zones were more limited in extent. Thus hydrogen caused enhanced plasticity and local plastic failure at lower applied stresses, i.e. "hydrogen embrittlement".

Decreases in the macroscopic flow stresses due to the addition of hydrogen into solid solution have been interpreted as due to enhanced dislocation motion. These effects have been observed for hydrogen introduced by cathodic charging of pure iron⁶⁷⁻⁶⁹, by plasma charging of iron⁷¹ and by gaseous charging of pure nickel⁷⁰. Very significant decreases in the flow stresses were observed, particularly after cathodic charging of high purity iron and while these can result from dislocations introduced by hydrogen charging, the experiments were carefully carried out to avoid surface damage. Flow stress decreases in iron were interpreted based on decreases in the energy to nucleate kinks on dislocations thus decreasing the Peierls-Nabarro lattice interactions⁶⁷⁻⁶⁹. However, observations of the phenomena in systems in which there are no strong dislocation-lattice interactions suggests that this explanation is not correct. The generality of the phenomena suggests that an explanation must be based on interactions common to many systems; such interactions are the elastic interactions between dislocations and hydrogen solutes.

The reasons for the enhanced dislocation motion due to hydrogen is not yet established. One mechanism which is being studied is based on "elastic shielding" of dislocations and other elastic singularities by hydrogen atmospheres⁷⁹. In this mechanism the mobility of hydrogen allows it to diffuse to positions of lowest free energy and form high concentration atmospheres around dislocations, solutes and precipitates. The binding enthalpies for the hydrogen are typically of the order of 10 to 50 kJ/mole⁸⁰ which allows the atmospheres to form and to move with the dislocations in the temperature ranges where embrittlement is observed. Thus, in contrast to other solute atmospheres, when the dislocations move, the hydrogen atmospheres can move with them. The significant interactions are therefore between dislocations and defects which include the respective atmospheres. Furthermore, since the hydrogen remains mobile during the interaction the concentrations and configurations of the atmospheres respond to the stress fields of all the elastic defects taking part in the interaction. Thus for example, as two dislocations approach each other their hydrogen atmospheres reconfigure themselves, and the hydrogen concentration at each point responds to the sum of the stress fields of both dislocations; a reconfiguration which reduces the energy of the entire system. Similarly, in calculating the force one dislocation exerts on a second the contributions to this force must be summed over both dislocations and the hydrogen atmospheres.

Self consistent elasticity calculations using finite element methods were carried out to study the hydrogen atmosphere configurations, the interaction energies, and the forces between elastic singularities⁷⁹. In general, the effects of hydrogen atmospheres at dislocations is to decrease the interactions of elastic defects at short range and to have no effect at large distances. This spatial dependence is a consequence of the result that the hydrogen atmosphere interactions vary as $1/r^2$ while the dislocation stress fields vary as $1/r$. The magnitude of this decrease of the

interaction stress can be of the order of the dislocation stresses at distances of about 10 Burgers vectors for reasonable hydrogen concentrations.

The magnitude of the hydrogen effect increases as the concentration of hydrogen in the atmosphere increases, i.e. as the lattice hydrogen concentration increases and as the temperature decreases. As a consequence, the "elastic shielding" effects are small at high temperatures where the concentration of hydrogen in the atmospheres is small and are small at low temperatures where the atmospheres are not mobile. In the intermediate temperature range and at low dislocation velocities the effects are largest as the atmosphere rearrangements can occur in phase with the dislocation motion.

These shielding effects correspond well to the macroscopic softening which has been observed, e.g. the softening is greatest at temperatures around 200 K in Fe⁶⁷⁻⁶⁹, is largest at low strain rates, and increases as the number of short range obstacles such as solutes are increased^{58,59}. In nickel and Ni-C alloys the temperature range of hydrogen enhanced dislocation motion is also that in which serrated yielding is seen; indicating that hydrogen atmospheres can move along with the dislocations. Direct elastic shielding effects have been observed using the N anelastic relaxation in iron⁸¹.

The general dependence of hydrogen embrittlement on temperature and strain rates is similar to that observed for hydrogen softening of the resistance for dislocation motion. The *in situ* TEM studies directly show that the hydrogen enhanced dislocation motion leads directly to fracture by slip localization, opening up of voids and thinning of the material along slip bands. This slip localization also leads to fracture in macroscopic specimens although the detailed mechanism is not established. A detailed connection between the hydrogen effects on dislocation behavior, slip localization and hydrogen "embrittlement" is not well established and remains a major issue.

No distinction was made between transgranular and intergranular fracture in the above discussion. Many of the non-hydride forming systems exhibit primarily "intergranular" fracture as observed by relatively low magnification optical and SEM fractography. On observation with higher resolution instruments, in many cases these "intergranular" fractures exhibit features which suggest that the fracture paths are not confined to the grain boundaries. One of the important issues is whether the intergranular and transgranular fractures are in fact caused by different mechanisms or whether they are variants of the same fracture mechanism. This cannot be answered with great certainty as in many systems the intergranular fracture in hydrogen environments is intimately related to the segregation of other solute species to grain boundaries and interfaces. The synergistic effects of solute segregation complicate an already difficult situation. In the case of Ni and Fe the interaction of H with segregants such as S and P have been studied⁸²⁻⁸⁴ and it has been shown that segregation of species such as S at the grain boundaries reduces the fugacity and amount of H required for intergranular fracture.

In Ni the causes of intergranular fracture due to hydrogen have been extensively studied⁸⁵⁻⁸⁸. Transgranular fracture by the HELP mechanism is observed on slow rate straining in a hydrogen atmosphere at temperatures in the vicinity of room temperature while the same testing conditions lead to "intergranular" fracture when hydrogen is present as a solute⁵⁵. The basis for this difference in behavior can be seen in experiments which have used Secondary Ion Mass Spectroscopy (SIMS) to determine the distribution of hydrogen in Ni⁸⁹ and in Nb-V alloys⁹⁰. Very large segregation of solute H (D) was observed at external surfaces and at some grain boundaries. Furthermore, studies of "intergranular" fracture using in situ TEM straining techniques have shown that in the presence of hydrogen the "intergranular" fracture was in fact fracture by the HELP mechanism which occurred in the vicinity of the grain boundaries and occasionally along the grain boundaries⁹¹. Furthermore, this hydrogen segregation occurred over appreciable regions (about 100 nm thick) adjacent to the surfaces and grain boundaries. Sulfur segregation at external surfaces had the effect of increasing the amount of hydrogen segregation in the vicinity of these surfaces.

These results are consistent with the view that in Ni, and perhaps in other systems, hydrogen enhanced "intergranular" fracture is in fact transgranular fracture by the HELP mechanism which occurs in the vicinity of the grain boundaries. Localization of the enhanced dislocation mobility to regions near the grain boundaries and therefore localization of the fracture which results from this enhanced dislocation mobility is a consequence of the hydrogen segregation in the vicinity of the boundaries. Fracture occurs near the grain boundaries because that is where the greatest extent of hydrogen softening occurs. Under relatively low magnification these appear as intergranular fracture but with higher resolution examination features on the fracture surfaces which are consistent with plastic failure adjacent to the grain boundaries are observed.

The importance of H segregation to grain boundaries was clearly shown in a study of the fracture of Ni - H alloys at 77 K⁸⁵⁻⁸⁸. Ni - H alloys in which segregation of the H to grain boundaries did not occur were completely ductile. As the extent of segregation increased the amount of intergranular fracture increased until the specimens exhibited completely intergranular fracture at a critical grain boundary hydrogen concentration. It was the achievement of this critical concentration which controlled the fracture at the grain boundaries rather than to overall concentration in the lattice. Achievement of this critical grain boundary concentration was controlled by diffusion of H to the grain boundaries either before or during the tensile tests (if they were carried out at temperatures at which H could diffuse.) At any segregation temperature the lattice H concentration determined whether this critical grain boundary hydrogen concentration could be achieved by segregation. Synergistic effects of S and H segregation were observed similar to those observed by cathodic charging^{82,83}. In the presence of S segregation, the amount of solute hydrogen required to achieve the critical grain boundary concentration for fracture was greatly decreased⁸⁷.

HYDROGEN EFFECTS ON THE COHESIVE ENERGY

One of the oldest and most commonly referred to mechanism of hydrogen embrittlement is the "Decohesion" mechanism⁹²⁻⁹⁴. In general outline, decohesion associates hydrogen embrittlement with a decrease in the atomic bond strength due to the local concentration of hydrogen. Thus the fracture is cleavage which occurs when the applied stress exceeds the "cohesive stress"; a material parameter which is assumed to be decreased by the presence of hydrogen in solid solution. This cleavage fracture is generally accompanied by plastic deformation⁹⁵ which greatly increases the total energy of fracture and hence the macroscopic K_{Ic} . In the systems where fracture occurs intergranularly, failure is expected to be along the cleavage planes and to exhibit the fractography of cleavage while intergranular fracture should occur directly along the grain boundary surfaces. In intergranular fracture the relevant parameters are the cohesive energy and cohesive force of the grain boundary which are also postulated to be decreased by the presence of hydrogen as well as the segregation of many other solutes.

There are a number of "open issues" relating to the observational base on which the decohesion mechanism is founded. Intergranular fracture by decohesion due to hydrogen implies that the fractography should reveal the morphology of the grain interfaces whereas most high resolution fractography shows a great deal more structure on the hydrogen embrittled intergranular fracture surfaces than is expected from brittle fracture along the grain boundaries. In situ TEM observations of the hydrogen related intergranular fracture of a number of systems⁹¹ shows that the fracture occurs mostly along slip planes in the vicinity of the grain boundaries often crossing the grain boundary to follow slip planes in the adjacent grains. In contrast to this behavior associated with hydrogen assisted fracture, hydrogen assisted failure in the Ni-S system with S segregated at the grain boundary does occur by crack propagation along the grain boundary albeit accompanied by significant plasticity on both sides of the boundary^{87,96}.

The fractography of transgranular fracture due to decohesion should be cleavage fracture whereas most observations can be classified as "quasicleavage". This term, whose meaning is somewhat illusive, generally describes a fracture surface which shows evidence of significant local plasticity and fracture features which resemble those on cleavage fracture surfaces but which are considerably less crystallographic. The differences with true cleavage surfaces are often ascribed to plastic deformation; an explanation which is somewhat specious since plastic deformation is crystallographically conservative, at least on a local scale. Thus cleavage of a pre-deformed material should show similar crystallographic features to those seen in an undeformed specimen. This is not generally true of the fractures cited as evidence for the decohesion mechanism. The other observation cited as evidence for decohesion is that the fracture surface corresponds to what is believed to be the cleavage plane of the system rather than the slip plane. However, the actual macroscopic plane will reflect the nature of the macroscopic stress tensor and may reflect fracture on a combination of slip planes on a fine scale which sum to an overall fracture plane corresponding to the supposed cleavage plane. This can only be determined by careful high resolution fractography which generally has not been carried out.

The principal issue in determining whether the decohesion mechanism has any validity is whether hydrogen decreases the "cohesive energy" or the "cohesive stress". Evidence for a hydrogen related decrease in the "cohesive energy" may be sought in the elastic constants, atomic force constants derived from phonon dispersion curves, surface energy measurements, fracture surface energies and theory. Direct support for this postulated decrease does not exist except in the realm of theoretical calculations⁹⁷. The elastic constants of Group Vb metals with hydrogen have been extensively determined⁹⁸⁻¹⁰⁰; in the case of Nb up to compositions of the order of $H/Nb = 0.8$. The general result is that significant increases in C_{11} and the bulk modulus B and decreases in the shear modulus C' are observed. For the same metals the phonon frequencies and the corresponding atomic force constants are all increased by the addition of H to solid solution¹⁰¹. These increases in the elastic constants and phonon frequencies are all the more remarkable as they occur despite the very large volume increases which accompany H in solid solution; these volume increases normally cause decreases in the elastic and atomic force constants (as observed in the FCC metals). Both the elastic constants and the phonon frequencies correspond to "small strain" parameters and describe the effect of hydrogen on the part of the lattice potential curve close to the equilibrium positions. Despite this limitation, the dependencies of these parameters on H concentration in BCC metals are not consistent with hydrogen related decreases in the cohesive energy or the cohesive force. In fcc metals the situation is somewhat different in that hydrogen decreases the elastic parameters¹⁰¹; principally as a result of the volume increase on adding H to solid solution.

Since the elastic and atomic force constants pertain to the initial part of the atomic force - displacement curves, an increase in these parameters does not necessarily imply an increase in the cohesive force, i.e. the maximum of the force - displacement curve. A direct measurement of this parameter is not yet possible. The area under the atomic force displacement curve is $2\gamma_f$ where γ_f is the fracture surface energy. This parameter has been measured in the brittle β $NbH_{0.8}$ hydride phase¹⁹ and shown to be equal to the equilibrium surface energy of Nb. Thus even at $H/Nb = 0.8$ there was no significant decrease in the surface energy due to hydrogen. A similar conclusion was drawn from measurements of the equilibrium surface free energy of Ni + 300 appm H¹⁰².

Recent theoretical discussions of this problem have suggested that H causes a significant decrease in the bonding of atoms, i.e. a decohesion during stressing. While these calculations, based on a cluster variational method¹⁰³ and on the Embedded Atom Method⁹⁷, support the Decohesion mechanism, they remain the only support for it in the absence of direct experimental measurements. What is required is a sounder basis for this fracture mechanism before it is accepted as a viable embrittlement mechanism.

CONCLUSIONS

Several theories of hydrogen related fracture have been discussed in the context of critical experimental measurements. While the discussion of the

voluminous literature was limited to those experiments designed to challenge and test the theoretical concepts, the evidence presented clearly shows support for two mechanisms of "hydrogen embrittlement"; "Stress Induced Hydride Formation and Cleavage" and "Hydrogen Enhanced Localized Plasticity". A third mechanism, "Hydrogen Induced Decohesion", remains a possible failure mechanism as no definitive support be mustered nor can completely convincing counter evidence be adduced.

The existence of several "hydrogen embrittlement" mechanisms is clearly established. In a sense these are competitive with each other and with ductile (non-hydrogen related) fracture. Several mechanisms may even operate in a single system. The observed fracture mechanism is controlled by the thermodynamics and kinetics of the various fracture processes.

All of the observed environmental fracture characteristics can be accounted for on the basis of the above three fracture mechanisms.

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