A NEW APPROACH TO DISCOVERING THE FUNDAMENTAL MECHANISMS OF HYDROGEN FAILURE

BY

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DISSEERTATION

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ABSTRACT

The recent interest in developing a hydrogen-based energy economy has put the need for hydrogen compatible materials to the fore-front. In particular, metals that are resistant to the effects of hydrogen embrittlement are needed. Despite the long history of study into the embrittlement of metals by hydrogen, there is little consensus as to the mechanism by which hydrogen degrades the mechanical response. Contributing to this situation is a lack of experimental data at the microstructural and atomistic scales. To begin to address this problem, this present work examines the microstructure immediately beneath fracture surfaces and relates it to the fracture surface in an effort to understand the microstructural deformation processes leading to failure. This was done through a variety of techniques, including scanning electron microscopy and atomic force microscopy studies of the fracture surface, and the adaptation of the lift-out technique on the focused ion beam microscope to extract thin foils from fracture surface features for examination in the transmission electron microscope.

A variety of structural materials under different loading conditions were studied to get a broad view of the underlying effects of hydrogen. The materials and loading conditions were chosen to represent materials of interest for a Hydrogen Economy and loading conditions likely to be encountered. Pipeline steels, considered for hydrogen transport, were loaded in compact tension configuration in high pressure hydrogen gas. Nickel, charged with a high concentration of hydrogen, was tested in uniaxial tension. Two stainless steel alloys, used in manifolds, fueling hoses, and valves, were fatigue loaded. To contrast the effect of hydrogen with that of liquid metals, which are considered by some to operate by similar mechanisms, a martensitic steel, candidate material for nuclear reactors, and a commercial purity iron were loaded in center crack in tension mode in contact with liquid metal. Each of these samples displayed fracture modes typical of hydrogen embrittlement.

The microstructures beneath these typical features are complex and showed striking commonalities between the different materials and loading conditions. The complexity and extent of the plasticity observed beneath “brittle” fracture features suggests that extensive plasticity occurs prior to cracking. The evidence suggests that hydrogen accelerates this plasticity. From this, it can be concluded that inferences about the underlying microstructure
based upon fracture surface morphologies tend to be erroneous, due to the overly simple models of deformation that are assumed to operate.

From these observations, a new mechanism for hydrogen embrittlement is proposed based upon previously published mechanisms. Hydrogen accelerates the plasticity, resulting in work-hardening of the material and redistribution of the solute hydrogen, leading to locally high concentrations. This leads to the weakening of local features by the combination of the strain and hydrogen concentration. The weakest microstructural features fail, and fracture follows the weakest path through the material.
In memory of

Gerald F. Martin

Engineer, Teacher, Grandfather
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CHAPTER 1
INTRODUCTION

The current state of the world favors the investigation of alternative energy systems to reduce dependence upon fossil fuels. There is a forecasted shortage in fossil fuel supplies, with conventional sources being replaced by heavy sources, such as tar sands, or remote sources, such as deep water sources which may also be limited in availability, or accessibility. Particularly in the United States, as domestic production of petroleum is slowly decreasing and consumption is rapidly increasing, Figure 1.1, there is a desire to move away from a dependence upon foreign “stable production” countries, such as the Middle East, with whom the political climate is less than favorable. Additionally, environmental concerns, such as climate change from carbon pollution, have pushed public opinion towards a more carbon neutral energy economy. While often a candidate for a large part of a carbon neutral energy economy, events such as the Fukushima disaster have led to an aversion to nuclear energy [1, 2], requiring an alternative source for the power that would have been produced by nuclear means, Figure 1.2. These factors are all responsible for the push for the development of alternative renewable energy systems of which the “Hydrogen Economy” will likely be a component.

The main thesis of the Hydrogen Economy is the use of hydrogen as a means of energy storage.

Figure 1.1. United States petroleum trends. Note that in the past couple of decades consumption has increased while production has decreased. [3]

Figure 1.2. Actual Japan energy sources in 2007 compared to proposed energy sources for 2030, prior to the March 11, 2011 [22]. After the Fukushima disaster, nuclear reactors have been shut down, and new reactor construction placed on hold. Another energy source must replace the shortfall due to the removal of nuclear sources.
Electrical energy captured from solar, wind or even fossil fuel burning is transformed into hydrogen fuel which can be more easily stored and transported to where it is needed [1]. In the case of solar and wind power, it is particularly important to store excess energy produced during peak production times for use during high demand/low production periods, such as at night or during periods of low wind speed.

A large focus of the Hydrogen Economy is the replacement of internal combustion engines with hydrogen-powered fuel cells, though the use of fuel cells as a means of power production for domestic and industrial uses is also included. Transportation has become a focus area because, as a sector, it is one of the largest consumers of fossil fuels, Figure 1.3, and one of the largest producers of pollutants, Figure 1.4 [3, 4].

As the other energy use sectors are powered by multiple energy streams, it is feasible to slowly introduce different energy sources while phasing out fossil fuel based sources. By contrast, the transportation sector is almost solely based upon a single energy stream: petroleum. Therefore, though hybrid technologies (current and future) will help as stop-gaps, the conversion to fuel cell powered vehicles requires building a complete infrastructure: from production facilities and the distribution system for the hydrogen fuel, to the vehicles themselves, both the engine and the fuel storage system. In order for this new system to become acceptable, the vehicles must perform similarly to current vehicles, and the cost of the vehicle and the fuel must be competitive. This becomes difficult if the cost of building the infrastructure for delivery is added to the cost of

Figure 1.3. Historical trends of energy consumption in the United States divided by sector [4]. Transportation is one of the largest consumers and the sector with the steadiest and most rapid growth.

Figure 1.4. Historical trends of CO₂ emission in the United States divided by sector [4]. In the past decade, transportation has surpassed the industrial sector to be the largest producer of CO₂ emissions.
the fuel or the vehicles. Several different delivery systems are under consideration to mitigate this problem.

In terms of hydrogen distribution, the most feasible system would be remote hydrogen production sites, from which hydrogen is distributed to end-user stations. There are several obstacles in terms of the distribution system. Creation of a new distribution system designed for hydrogen, while feasible, may not be practical in many regions as the design, production and installation of the miles of pipeline required, as well as that of the related infrastructure, would be expensive. As there are no internationally consistent codes for hydrogen pipelines, it may cause difficulties when connecting different networks. An alternative is to use the existing natural gas pipeline distribution system that delivers natural gas nationwide in the United States. Pipeline have been used worldwide to transport hydrogen for over 70 years, and there is around 3200 km of hydrogen pipelines currently in use [5]. However, these systems were built specifically for hydrogen transportation and are operated below 20 MPa [6], while the new system would need to operate at twice that pressure (or more). With the variability of material quality in the construction of the natural gas pipeline system, especially in and around older cities, often unknown, the challenge is to ascertain the susceptibility of conventional pipeline steels to hydrogen embrittlement under the intended use conditions and, if possible, to devise strategies to ameliorate the situation [7].

Hydrogen embrittlement is the degradation of the mechanical properties of a metal when exposed to hydrogen. It will usually result in the premature catastrophic failure of the material at very low stress intensities. In some cases, this can occur at stresses below the measured yield stress, making fracture completely unanticipated [8]. Approximately 25% of all equipment failures in the petrochemical industry can be attributed to hydrogen, resulting in an estimated loss of tens of millions of dollars each year [9]. The phenomenon of hydrogen embrittlement has been recognized since 1875 [10], and has been extensively studied [11, 12]. While a consensus on the fundamental mechanism of hydrogen embrittlement has not been reached in the scientific community [11, 13], the wealth of data on the effect of hydrogen on mechanical properties of different metals and their alloys made the selection of appropriate materials possible when hydrogen embrittlement was a concern. From this data set, a large effort has been put into the development of standards for hydrogen use of structural materials [5, 6].
However, with the implementation of a hydrogen economy, many structural components will be exposed to higher pressures than have been studied traditionally. Currently, Japan is building a system where the vehicle fuel tank is filled at 35 MPa, with a goal to increase this pressure to 70 MPa [14]. The goal with increasing the pressure is to increase the traveling range of the vehicles between refueling. However, concern has arisen that a different regime of hydrogen embrittlement may be active at these pressures, leading to a further deterioration of mechanical properties. This concern has been precipitated by the failure of a hydrogen bus fueling hose at EXPO 2005 in Nagoya, Japan. The hose, made of type 316L austenitic stainless steel, underwent fatigue with each fueling cycle when 35 MPa pressure hydrogen gas was pumped into a bus’s storage tank over an 8 minute fueling time. This alloy was chosen in part for its resistance to hydrogen embrittlement, as stainless steels are commonly used in hydrogen-rich environments in industry [15]. The hose cracked after 280 fueling cycles, and the fracture surface showed clear striations: strong support for hydrogen-accelerated fatigue being the cause of failure [16, 17]. It is thought that both the low frequency of the loading cycle and the high pressure hydrogen have led to conditions that are not well understood.

These have led to the concern that a better fundamental understanding of hydrogen embrittlement is needed. A microstructurally based model can provide a prediction of behavior under different conditions, and allow the development of new alloys without exhaustive testing of every possible candidate.
2.1 Effect of Hydrogen on Mechanical Properties

Hydrogen embrittlement is the reduction of the strength, ductility or fracture toughness of a metal due to the presence of hydrogen [18]. The hydrogen alone does not alter the microstructure of the metal [19], and therefore the reduction in mechanical properties is often recoverable with the removal of the hydrogen. As most metals, with the notable exception of gold and copper, experience hydrogen embrittlement, it is the primary effect of hydrogen which is of concern while developing the Hydrogen Economy.

There is sometimes a distinction made between external hydrogen embrittlement (EHE) and internal hydrogen embrittlement (IHE) based upon the source of hydrogen. In both cases, it is accepted that the fundamental interactions between metal and hydrogen are the same [20-22]. In general, the operating conditions of components of the Hydrogen Economy lead to external hydrogen embrittlement. However, mechanical testing in a hydrogen environment is challenging, so it is common for mechanical testing to be done in ambient environment on samples pre-charged with hydrogen [20]. It is important to consider the effect of the method of

![Crack growth rate in HY-100 low alloy steel as a function of hydrogen pressure.](image-url)

**Figure 2.1.** Fatigue growth rate in HY-100 low alloy steel as a function of hydrogen pressure [20].
charging. Electrochemical charging tends to be more aggressive than gaseous charging and may introduce near-surface damage, such as blistering, high dislocation density or hydride phases, into the sample prior to loading. In these cases, it is important to note that crack initiation may have already taken place, and crack propagation paths will be influenced by these existing cracks [23]. However, further mechanical behavior and cracking is due to the effect of the solute hydrogen [24]. The detrimental effect of electrochemical charging can be mitigated by controlling the charging current.

Increasing external hydrogen gas pressure leads to an increase in the severity of hydrogen embrittlement [20]. The dependence on pressure is usually strongest at lower pressures and becomes less sensitive with increasing pressure. In many materials, it has been found that there is a threshold pressure above which the mechanical properties are invariant [20], at least within the pressure range tested. However, in some cases, it has been found that there is a third regime at high pressures in which the mechanical properties are again strongly dependent upon hydrogen pressure [20], Figure 2.1. Concerns exist that the high pressures desired for the hydrogen economy may fall in this third regime, and that recent failures, such as the failure of a hydrogen filling station hose [16, 17], are due to this increasingly aggressive effect of hydrogen.

In addition to the pressure of hydrogen gas, the purity of the gas will affect the mechanical performance. The presence of certain gases, such as O₂, CO, or SO₂, can inhibit the entry of hydrogen into a material. As a result, these inhibitors can reduce the severity of hydrogen embrittlement, Figure 2.2. In contrast, the addition of H₂S will increase the severity of hydrogen embrittlement [25, 26], by increasing the influx of hydrogen.

![Crack growth resistance curves for a low alloy structural steel tested in various concentrations of oxygen](image-url) Figure 2.2. Crack growth resistance curves for a low alloy structural steel tested in various concentrations of oxygen [20]. With increasing O₂ content, the behavior approaches that of an inert environment.
Water vapor in the hydrogen gas has been shown to inhibit or to enhance the effect of hydrogen depending upon the conditions. Traces of inert gases such as nitrogen, argon, or helium generally do not alter the effects of hydrogen [20]. The varying effects of these gases are due to their adsorption on the metal surface, and the subsequent effects on the adsorption of hydrogen, which is discussed later.

Hydrogen embrittlement occurs within a specific temperature range that is dependent upon the metal [11], Figure 2.3. In ferritic steels, hydrogen embrittlement is most severe in the temperature range of 200-300 K, while above 423 K, the phenomenon generally does not occur. For austenitic stainless steels, the temperature range of most severe hydrogen embrittlement is typically slightly narrower: 200-250K [20]. Hence, austenitic stainless steels show greater resistance to hydrogen embrittlement at room temperature than ferritic steels. The range of temperatures can vary in extent between different metal classes; for instance, nickel alloys are typically susceptible to hydrogen embrittlement over the temperature range 170-600K, while titanium alloys are only susceptible in the range of 273-366K. However, both are most susceptible near room temperature, a trend that plagues most structural materials [20, 27, 28].

The effect of hydrogen is also dependent upon the dynamic loading rate [11, 29, 30], Figure 2.3. Lower loading or displacement rates lead to more severe hydrogen embrittlement, though for some materials, hydrogen may have the greatest effect at intermediate loading rates. The effect of strain rate saturates for most materials below $10^{-3}$ to $10^{5}$ s$^{-1}$ [29]. Hydrogen-assisted crack growth is governed by two parameters: the mechanical driving force, and the environmental degradation of fracture resistance. At high rates of loading, the effect of hydrogen may be overwhelmed by the effect of the mechanical driving force [20, 27]. This result leads to the
hypothesis that Fickian diffusion is not the rate-limiting process. As the material specific diffusivities vary by up to 8 orders of magnitude, if Fickian diffusion governed transport, the range of limiting strain rates should reflect this range [29], whereas most materials show similar strain rate dependence to HE. At low displacement rates, the mechanical driving force may not be sufficient to propagate the crack, even in view of the environmental degradation.

While HE gets its name from the premature and brittle appearing fracture, there is still often a certain amount of deformation related with the fracture. There are certain trends in the deformation which are common regardless of the loading conditions. A localization of the deformation has been observed in the presence of hydrogen, particularly when a stress concentrator, such as a notch or a crack, is present. Additionally, the slip is localized onto a limited number of slip planes leading to macroscopically planar slip [15, 31-35]. This has been concluded based upon slip traces on or near the fracture surface. However, as this phenomenology can be explained by several different possible effects of hydrogen, and as surface traces are not always considered to be an accurate measure of the deformation underneath, there is still debate as to the effect of hydrogen on the plastic deformation. As will be shown in the next section, hydrogen can produce contradictory trends in mechanical properties meaning that their use for predicting microstructural mechanisms may be limited.

2.1.1 Tensile Tests

Tensile tests are one of the simplest tests to determine mechanical properties. While the results of tensile tests are not useful for lifetime prediction models, they provide information on macroscopic quantities, such as strength and ductility, from which insight into general trends due to hydrogen can be drawn, and allow ranking by resistance to HE [15, 20]. Figure 2.4 shows these trends for a C-0.5Mo steel [19].
The most prominent trend is the strong decrease in sample elongation and reduction of area with increasing hydrogen content [19, 22, 36-40], Figure 2.4. Reduction of area is often the most affected property, and is generally used to quantify degree of hydrogen embrittlement [29]. As an example of the extremes, commercially pure nickel shows a reduction of area of 74-86% in air, but with a high concentration of hydrogen (~1000-3000 appm) shows a reduction of area of 6-29% [36].

The ultimate tensile strength is generally stable with hydrogen content [22], Figure 2.4. However, the ultimate tensile strength of notched specimens was seen to follow the same trends as reduction of area with hydrogen [22, 29, 39]. Notches provide a stress concentration, leading to higher local hydrogen concentration and a stronger hydrogen effect [22]. High hydrogen content has been associated with an increase in tensile strength in austenitic steels [41].
The trend in yielding behavior is less evident. In many stress-strain measurements, there has been an observed increase in the yield stress and the measured flow stress when hydrogen is present [15, 22, 33, 41-43]. This has led to the assessment that hydrogen generally leads to hardening of the material. Some studies have seen no effect on the yield stress [22, 38, 40, 44, 45], Figure 2.4, though there may be differences in the flow stress with and without hydrogen. Other studies have shown that softening occurs, with a reduction in the yield stress, the flow stress or both [21, 22, 46, 47]. Studies of stress relaxation have shown an increase in the rate of relaxation when hydrogen is present, which has also been interpreted as a softening occurring in the presence of hydrogen [48]. Similarly to the extent of hydrogen embrittlement, strong strain rate dependence has been observed for yielding behaviors [15, 47].

The influence on the yielding behavior due to hydrogen also depends upon temperature [28, 46, 47, 49]. In high purity iron, softening was observed in the presence of hydrogen at temperatures from 200 to 300 K. Below 190 K and above 300 K, hardening was observed. Within the transition range, serrated flow was observed [50]. Serrated yielding, an example in nickel [44] is shown in Figure 2.5, has also been observed in nickel within a specific temperature range [37, 38, 44, 45]. The range of serrated flow depends upon the temperature, strain rate and hydrogen concentration [45, 51]. This yielding behavior is classified as being due to the Portevin-LeChatelier effect: dynamic strain aging due to dislocations being intermittently pinned by solute hydrogen forming atmospheres around the dislocations and breaking away from the atmospheres. The Portevin-LeChatelier effect combined with hydrogen-influenced dislocation motion, whether due to effects on the elastic fields [52] or the Peierls barriers [47] of the dislocations, has been proposed explain the

Figure 2.5. Comparison of stress-strain curves with and without hydrogen for nickel at various temperatures [44]. Hydrogen generally causes a reduction in the strain to failure. Note that the two curves in the middle show serrated yielding due to hydrogen. Serrated yielding is limited to a specific temperature range which encompasses those two test conditions, but not the higher or lower temperatures of the outer tests.
range of yielding behaviors. The effect of hydrogen on dislocation behavior will be discussed later.

Another explanation for some of the different observations in yielding behavior is the effect of localization due to hydrogen [34]. In tensile tests, there is an assumption of uniform deformation along the gage length. If hydrogen causes local yielding (softening) due to locally high concentrations, the effective gage length is decreased, leading to an observed macroscopic hardening. In cases where the softening effect is greater than the effect of shear localization, then macroscopic softening will be observed [34]. In summary, in a particular range of temperatures and strain rates, hydrogen is proposed to enhance dislocation motion, allowing motion at lower applied stresses, but the macroscopic observed behavior may not reflect this microscopic behavior.

The contradictory nature of the yielding observations has also been attributed to surface damage during hydrogen charging [53]. The observed effect was found to strongly depend upon the charging conditions, with hardening often being attributed to more aggressive charging conditions. When these conditions were avoided by careful charging conditions, the temperature dependence of hardening and softening discussed above was observed [53, 54].

It is interesting to note that the effect of hydrogen on yielding is not always correlated to the amount of embrittlement observed [47]. Kimura and Kimura [47] observed embrittlement (loss of ductility and brittle fracture features) of high purity single crystal iron under conditions of softening and of hardening. Also, while the range of serrated yielding is often associated with embrittlement, similar levels of embrittlement were observed from different loading conditions, one of which had serrated yielding and the other did not [55].

2.1.2 Fracture Toughness
Hydrogen causes a drastic reduction of the fracture toughness of most structural metals [19, 21, 22, 56, 57]. The values of fracture toughness, both linear elastic (K) and elastic-plastic (J), generally follow the same trends with respect to temperature and hydrogen pressure as tensile test reduction in area measurements; typically showing a decrease in fracture toughness with
increasing hydrogen pressure [22, 29, 56]. As with tensile properties, the rate of loading is important, with fast testing methods, such as Charpy impact tests showing less of an effect than $J$ integral tests [57]. While fracture toughness tends to decrease with decreasing temperature, the fracture toughness ($J_Q$) in hydrogen of some materials stays constant with temperature, suggesting that the relative effect of hydrogen decreases with decreasing temperature [57].

Crack growth behavior tends to degrade in the presence of hydrogen. The threshold stress intensity factor for cracking was also found to decrease with increasing hydrogen pressure for most structural metals [22, 58, 59]. The extent of the effect appears to depend upon the strength of the material: materials with higher yield stresses were more drastically affected. Additionally, crack growth rates were significantly faster in hydrogen than in air [22, 59]. The degree depends upon the temperature, with the maximum depending upon the material but often occurring slightly above room temperature, with the effect dropping off at high temperature and tailing off at low temperatures [60]. The effect of hydrogen can be strongly dependent upon the microstructure, with different heat treatments causing different behaviors [60].

### 2.1.3 Fatigue

The application of cyclic loading often leads to accelerated failure, and the addition of hydrogen can exacerbate the effect. The presence of gaseous hydrogen in most structural metals can accelerate fatigue crack growth by as much as a factor of 10 or more [20, 22, 61-64]. The crack growth rates increase quickly with hydrogen pressure at low pressures, then reaches a plateau, such that change in hydrogen pressure does not cause an appreciable increase in crack growth rate [22]. However, recent studies have shown that a pressure dependence reoccurs at very high pressures, leading to a further acceleration of crack growth rates [20], Figure 2.1.

The acceleration of fatigue due to hydrogen causes the effect of fatigue at lower stresses than normally applicable, reducing the fatigue threshold ($\Delta K_0$) [20]. This phenomenon has been attributed to the dry hydrogen atmosphere precluding the development of oxide deposits at the crack tip which affect crack closure [65]. However, there is still generally a stress limit below which hydrogen enhanced fatigue is not an issue. In the case of vehicles and other applications
where weight is an important factor, hydrogen effects cannot be moderated by practices such as thickening tank walls to reduce stress [29].

Decreasing load frequency will cause an increase in crack propagation rates [20, 22]. Real-life applications often have low frequencies. For example, a hydrogen gas fueling hose would undergo one loading cycle for every vehicle fueling, which would be approximately 10 minutes. However, there is a limiting frequency below which crack growth rate is invariant [20]. At these low frequencies, there is sufficient time for H to diffuse to the crack tip and affect deformation processes.

2.1.4 Fracture Modes

Hydrogen can cause the transition from ductile transgranular failure (microvoid coalescence) to transgranular brittle failure to brittle intergranular failure; an example of this ductile to brittle fracture mode transition in nickel [38] is shown in Figure 2.6. In some materials, all of these fracture modes can occur, with the modes observed depending upon the temperature, strain rate and hydrogen content [27], with more brittle features (transgranular and then intergranular) tending to occur with increasing hydrogen content [33, 66, 67].

The addition of small amounts of hydrogen frequently does not change the fracture mode, especially in ductile materials where microvoid coalescence is expected. However, hydrogen has
been observed to cause a decrease in the microvoid size [39, 68-71]. In particular, the creation of very shallow microvoids is expected as hydrogen often causes a flattening of the voids during their growth [13, 62, 72]. Studies have shown that hydrogen accelerates the nucleation of voids, allowing nucleation at lower stresses than in the absence of hydrogen [73].

Intergranular failure is a common feature in HE, particularly at high hydrogen concentrations. The degree of polycrystalline failure can be controlled by the amount of hydrogen [67], as there is a critical amount of hydrogen needed at the boundaries to cause intergranular failure, though the amount is dependent on material factors. The addition of impurities at the grain boundary typically exacerbate this problem, and the combination of hydrogen and impurities is often more detrimental than either alone [74-77]. However, hydrogen alone can be sufficient to cause intergranular failure [36, 67, 77-79].

Other transgranular failures, such as facetted surface morphologies due to slip band parting, cleavage, or martensite lath failure [60], are also reported as being due to the presence of hydrogen [69, 80, 81]. The term “quasi-cleavage” is often used to label any brittle-looking transgranular failure, particularly associated with hydrogen embrittlement. Quasi-cleavage is a term that has been struggled with for a long time with definitions such as “a fracture mode resembling cleavage … but differing … in that the fracture facets are not known to be parallel to cleavage planes” [82] or “a fracture mode that combines the characteristics of cleavage fracture and dimple fracture” [83].

The trademark of fatigue is the existence of striations on the fracture surface. The area fraction of striations for a variety of materials in the presence of hydrogen is often observed to be decreased relative to in air [61, 62, 84-86]. Additionally, in cases where striations are distinguishable, the measured ratio of height to spacing was reduced resulting in wider and flatter striations [61, 84, 86].

2.2 Hydrogen Behavior in Metals

To understand hydrogen embrittlement, we need to understand the behavior of hydrogen in a metal. From the source of the hydrogen, how it interacts with the surface of the material and
how it is introduced into the material, how it diffuses, where it is likely to accumulate and the characteristics of these sites, and what the effect of the accumulated hydrogen will be on the elastic properties, the electronic structure, and, as a result, the effect on the mechanical properties.

### 2.2.1 Hydrogen Adsorption

Hydrogen is usually present as a diatomic gas molecule, H\(_2\), which is generally too large to enter metal crystal lattices. On metal surfaces, hydrogen molecules adsorb and then dissociate into hydrogen atoms, which can then enter the crystal lattice. High index planes, such as (211), (311) or (332), are preferred adsorption sites over low index planes such (100), (110), and (111) [87]. In most metals, there is an activation energy for the dissociative chemisorption of hydrogen; palladium, an exception, is considered to be a non-activated dissociative adsorption system, though a small amount of energy is still needed [87]. The kinetics of adsorption can vary greatly depending upon the surface. Conditions such as high temperature and high pressures of hydrogen gas enhance the kinetics to promote faster equilibrium between the hydrogen content of the metal and the atmosphere [88].

Most metal oxides impede adsorption processes, forming a barrier to hydrogen penetration. The oxygen tends to occupy hydrogen adsorption sites [89]. Because of this, the native oxide layer on many important structural metals, such as steels, prevents the ingress of hydrogen from the gaseous state at room temperature, reducing the likelihood of hydrogen embrittlement. However, any fresh surfaces such as cracks or scratches, which can be formed by high strains, could provide a location of ingress until the oxide layer reforms [29]. At the tip of an advancing crack, slip produces clean surfaces for hydrogen entry [90], potentially supplying the crack tip region with hydrogen. As with oxygen, other impurities, such as sulfur or carbon, on the surface can preferentially occupy hydrogen adsorption sites and block dissociation sites, leading to a reduction in the adsorption rate of hydrogen [87]. The most effective inhibitors are those which form an oxide, sulfide or carbide layer [89]. These surface impurities can come from gases dissociatively adsorbing on the surface, such as N\(_2\)O, CO, COS, SO\(_2\), CS\(_2\), H\(_2\)O [20, 89].
Hydrogen can also be electrochemically introduced. When cathodic protection is applied to structural materials in water, the current can produce atomic hydrogen which can potentially absorb into the material. However, in many aqueous environments, most of the atomic hydrogen recombines on the metal surface, forming hydrogen gas which bubbles off the surface. The presence of recombination poisons, notably H$_2$S, retards this process, leading to enhanced absorption of hydrogen into the metal [25, 26].

Both gaseous and aqueous sources are sources of external hydrogen. Hydrogen can also be introduced to the metal during the melt, creating internal hydrogen. The liquid metal can often accommodate more hydrogen than the solid. Upon cooling, the hydrogen becomes trapped in the metal as internal hydrogen, often for the lifetime of the metal part. Hydrogen can also be introduced by similar means during welding processes [91, 92].

On the surface, the hydrogen atoms typically rest on 3-fold or 4-fold symmetry sites [93], and form bonds with the underlying metal atoms. The formation of the metal-hydrogen bond upon adsorption is associated with a release of energy leading to a substantial local perturbation of the electronic structure of the metal surface [94]. This energy release often results in displacement or even rearrangement of the surface atoms, depending upon the cohesive energy of the material [94]. Higher cohesive energy materials show little rearrangement, but often the displacement of surface atoms is sufficient to alter surface relaxation, returning it to a more bulk-like configuration [87]. Lower cohesive energy materials can show extensive restructured surface phases, some of which can aid hydrogen uptake. Depending upon the material and conditions, significant subsurface populations of hydrogen have been detected [94].

### 2.2.2 Hydrogen Diffusion

Once adsorbed to surface sites, the hydrogen atoms can penetrate into the material. Within the bulk of the metal, hydrogen atoms are small enough to occupy interstitial sites instead of substitutional sites. In body-centered cubic metals, the tetrahedral sites are preferred, as they are twice the size of octahedral sites.
Due to its small size, hydrogen atoms can rapidly diffuse through the metal lattice. Compared to heavy interstitials, such as oxygen and nitrogen, the rate of hydrogen diffusion through a metal is 15 to 20 orders of magnitude higher at room temperature [95]. The behavior of hydrogen is modeled according to Fick’s laws:

\[ J = -D \frac{dc}{dx} \]  

(2.1)

\[ \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D \frac{\partial c}{\partial x} \right] \]  

(2.2)

where \( J \) is the flux, \( D \) is the diffusivity, and \( c \) is the concentration. The diffusivity, along with permeability and solubility, is a material property. The diffusivity describes how quickly hydrogen will move through the material. As an example of the differences between materials, the diffusivity in body-centered cubic ferrite (\( \alpha\)-Fe) is approximately one order of magnitude higher than in face-centered cubic austenite (\( \gamma\)-Fe); thus hydrogen is expected to move significantly more quickly through ferrite than austenite. This change can be seen in the change in diffusivity in unstable austenitic stainless steels with strain. As more austenite converts to \( \alpha'\)-martensite and produces more fast diffusion paths, accelerated diffusion is observed [96, 97].

The solubility \( (K) \) describes the amount of hydrogen that a material can contain for a given external hydrogen pressure \( (P) \):

\[ K = \frac{C_1}{\sqrt{P}} \]  

(2.3)

where \( C_1 \) is the concentration of hydrogen in the material. In order to take into account higher temperatures or stronger charging conditions, it is more appropriate to use the hydrogen fugacity \( (f) \) in place of the pressure [98]. The difference in the solubilities between different materials or phases can lead to local variations in distribution. For example, a high concentration of deuterium was observed in vanadium layers of Fe/V multilayers through atom probe tomographic analysis [99]. As vanadium has a high solubility, this is expected. Figure 2.7 shows the concentration, which is directly related to the solubility, of hydrogen in iron as a function of temperature [19]. While the solubility generally increases with temperature, there is
a noticeable jump between the values of the solubility of each phase, with the largest solubility being for the liquid phase, which would account for how a large amount of hydrogen could be introduced to the melt [19].

The diffusivity and the solubility are related by the permeability (Φ) of the material:

\[ \Phi = DK. \]  \hspace{1cm} (2.4)

Permeability is often used to describe the flux of hydrogen through a slab of material with a given thickness for a given hydrogen pressure. Some studies have tried to relate permeability with susceptibility to hydrogen damage [100, 101]. While these studies were successful in comparing similar alloys under different thermomechanical treatments, these trends are not always consistent [26] due to complications from microstructure which are described next.

Classical diffusion theory states that the diffusivity should follow an Arrhenius relationship with temperature [102]:

\[ D = D_0 \exp \left( -\frac{H_D}{RT} \right) \]  \hspace{1cm} (2.5)
where $D_0$ is the diffusion coefficient, $H_D$ is the enthalpy of diffusion, $R$ is the universal gas constant, and $T$ is the temperature. Likewise, permeability and solubility are expected to follow an Arrhenius relationship. For the diffusivity, this relationship has been observed at higher temperatures, but for several materials, most notably iron, this relationship appears to break down at lower temperatures. A wide range (several orders of magnitude) of diffusivities has been measured at room temperature for iron [95], Figure 2.8. However, this range only extends downwards from the Arrhenius trend observed at higher temperatures, suggesting that something is impeding the motion of hydrogen. This scatter has been attributed to the trapping of hydrogen at microstructural defects, though some argue that surface effects are a determining factor [95]. These microstructural defects include voids, impurity atoms, dislocations, precipitates and secondary phases and their interfaces, and grain boundaries [102, 103], Figure 2.9. High-purity annealed samples of iron, which would be expected to have the lowest number of trap sites, tend to have the highest diffusivities of the lower temperatures samples, fitting along the same Arrhenius relationship as the higher temperature data.

![Figure 2.8. Diffusion coefficient of α-iron as a function of temperature. The plotted line follows the Arrhenius relationship fitted at high temperature. (a-e are datasets reported in [95])](image)

![Figure 2.9. Schematic showing locations of hydrogen residency [103]: a) interstitial site, b) surface sites, c) sub-surface sites, d) grain boundary sites, e) dislocation core sites, and f) vacancy.](image)

Different microstructural features have different trapping characteristics, and thus, have differing impacts on the motion of hydrogen through the material. Pressouyre [104] first divided the traps into three different categories based on how the traps affect the
lattice energy: attractive, physical, and mixed. Attractive traps can be due to a stress field, electrical field, temperature gradient, or chemical potential gradient such that hydrogen atoms experience a local attractive force. Physical traps are more localized modifications to the crystal lattice such that hydrogen atoms are more energetically favored to remain after falling randomly into the trap. Examples include voids, high angle grain boundaries, and incoherent interfaces. Traps in a real lattice are likely to encompass both of these properties, especially as many physical defects in a lattice also have a corresponding stress field, but if one property doesn’t clearly dominate, the trap can be classified as having mixed character. An example of a mixed character trap would be an edge dislocation where the stress field is an attractive trap, and the core, due to lattice distortions, is a physical trap [104]. Traps can also be described by their trapping energy, which relates to the probability of hydrogen atoms escaping from the trap. For a given temperature, traps can be classified as reversible or irreversible. Irreversible traps remove hydrogen atoms from the diffusing population. Reversible traps retard the diffusion of hydrogen, but do not affect the effective concentration. Reversible traps may also exchange hydrogen with other traps. A common example would be dislocations exchanging hydrogen atoms with other defects, such as interstitials or carbides that it encounters [105].

The effect of trapping can be significant. For example, trapping in steel due to the addition of 1 wt% carbon can result in a two order of magnitude lower diffusivity due to reversible traps retarding motion, and at least an order of magnitude higher solubility due to the additional storage capacity of the traps [93]. Various studies have suggested that the diffusive and weakly trapped hydrogen have the greatest effect on mechanical properties and that irreversible traps remove hydrogen from the system, improving the resistance to hydrogen [30, 93]. However, modeling of the effect of different traps suggests that while the presence of traps modifies the rate of hydrogen supply, it is generally insufficient to mitigate embrittlement [106].

Identifying the type, the trapping energy and the number density of traps in materials is not trivial, and is needed to supply models with accurate parameters. Thermal desorption spectroscopy (TDS) and permeation studies are frequently used to determine trap density and energy [107-110]. With some sites, such as second phase precipitates, there is also concern about the actual trap location: whether it is within the second phase, at the interface and at which interface type, or in the strain field surrounding the precipitate. Techniques such as tritium
autoradiography, hydrogen microprint or secondary ion mass spectroscopy do not have sufficient spatial resolution to distinguish these possibilities. Techniques such as small-angle neutron scattering [111] and atom probe tomography [112] may be able to provide this information and are beginning to be applied to this field [93]. In the case of fine plate titanium carbides and vanadium carbides in steel, deuterium was observed along the flat faces, but not along the edges, of the carbides [112, 113]. Combined with the absence of deuterium around very small particles, this was interpreted as hydrogen not being trapped by strain fields around the particle, but trapped at the interface either at carbon vacancies on the surface or at the core of misfit dislocations along these large facets, with misfit dislocations proposed to be the most likely candidate. These results agree with previous TDS studies [108].

As mentioned previously, the diffusive and weakly trapped hydrogen appears to have the largest impact upon hydrogen embrittlement. Therefore, in attempting to understand hydrogen embrittlement, it is crucial to understand the location of the hydrogen, particularly as it relates to the crack tip. With hydrogen entering at the fresh surfaces created at crack tip, and being transported into the material by Fickian diffusion as well as by dislocations, the question is where does it go and how does it affect the crack tip progression. Hydrogen is attracted by high stress fields, and this will be highest ahead of the crack tip, and aided by the likely high number of trapping sites (dislocations) there [114, 115]. Multiple models of various complexities have been developed to describe the influence of trapping on diffusion [105, 116, 117]. Using these models for trapping, and accounting for the effect of stresses at a crack tip, hydrogen transport and distribution ahead of a crack tip can be modeled [114, 118, 119], Figure 2.10. In addition to knowing the location of the hydrogen, the effect of hydrogen on the metal at these locations needs to be understood.
2.2.3 Hydrogen-Metals Interactions

Hydrogen is assumed to reside at normal interstitial sites within the metal lattice where it produces a local stress field [120], due to its size compared to the site. In body-centered cubic metals, the preferred site at ambient temperatures tends to be the larger tetrahedral site, though octahedral sites are increasingly occupied at higher temperatures [121, 122]. The tetrahedral site is also the preferred site for hexagonal close-packed metals [122]. In face-centered cubic metals,
the octahedral site is preferred [121, 122], though tetrahedral sites will be occupied at higher concentrations [123]. A Snoek-like effect due to the interstitials has been observed in relaxation studies, where the solute hydrogen atoms shift position in response to an applied load. The result is described as Snoek-like, since it is likely that it is a reaction of either hydrogen-hydrogen pairs or hydrogen-metal complexes, as opposed to single atoms as expected in the usual Snoek effect [95, 124-126].

In general, there is an expansion of the crystal lattice due to the presence of interstitials [127], and this expansion is similar in most metals, ~3 Å [122]. This expansion is expected to affect the elastic properties of the metals [128]. A decrease of the elastic moduli due to hydrogen was observed in several materials by different techniques [32, 129, 130].

The presence of hydrogen in the metal lattice causes a change in the electronic structure [123]. This reorganization of the bonding states can form bonds between the metal and hydrogen atoms. Two simple opposing models for the hydrogen are suggested: anionic: the hydrogen pulls part of the conduction electron density from the metal atoms, becoming negatively charged, and protonic: the hydrogen loses its electron to the metal conduction band leaving a proton [131]. Experimental evidence exists both for and against these two simple models, suggesting a more complicated reality due to the delocalized character of electrons in a metal. However, evidence does support charge transfer between the metal atoms and the solute hydrogen, and that these interactions are highly localized.

The combination of the alteration of the electronic structure of the host metal and the elastic strain due to the presence of interstitial hydrogen will affect the properties of the different microstructural features in the metal.

The presence of hydrogen leads to an increased density of electron states at the Fermi level in the host metal, which results in a reduction in the strength of the metal-metal bonds [123]. The degree of bond weakening will increase with increasing hydrogen concentration, though the relationship, whether linear or non-linear, is still not fully understood [11]. While some propose that this weakening of the lattice bonding should lead to enhanced microcracking and failure [18, 132-134], electronic structure calculations and measurements show an increase in the metallic character of the interatomic bonds [135]: the number of free electrons in the material becomes
higher due to hydrogen charging. This change in character is argued to not enhance brittleness, but increase plasticity [123].

Solute hydrogen concentration tends to increase in the vicinity of tensile stress concentrators. This can be seen to occur either because the enlarged interstitial sites are more attractive due to electron-density considerations, or because of the volume change associated with the stress and the hydrogen interstitial [131]. As such, any effects, such as on the bond strength or character, will be more pronounced in regions of higher stress.

Thermodynamic considerations show that hydrogen lowers the surface energy of metals [136]. This is due to a preference of hydrogen to the surface due to the openness of the lattice at the surface, and a reduction in the electron density at the surface [131]. This will occur at both the surface and at any internal surfaces such as voids. This could potentially provide a driving force for the production of new surfaces. This reduction in surface energy also means a reduction in the energy to form steps or ledges on the surface. As hydrogen lowers the ledge energy, the energy needed to create more surface area, dislocation formation at the surface can be facilitated [131]. This would be most relevant at crack tips where stress would be concentrated. As the surface nucleation of a dislocation requires the formation of a surface step and a dislocation core, redistribution of the surface atoms is required. Hydrogen affects surface bonding and relaxation, and weak perturbations due to weak bonding of the hydrogen at the surface at a crack tip could favor the emission of dislocations [137].

In some materials, such as Ti, Zr, and Vb group metals, the low solubility of hydrogen leads to the formation of a hydride phase [138-141]. These will preferentially form in regions of high hydrogen concentration and in regions of high stress. The stress can be accommodated by the volumetric expansion of the hydride phase compared to the matrix. Metastable hydrides can also be formed in other metal systems under aggressive charging conditions [11, 142].

As hydrogen affects the local electronic structure, so will its distribution depend upon the electronic structure of the surrounding metal [131]. Hydrogen is attracted to regions of reduced electron density, which can occur at microstructural traps. One such location is a vacancy in the metal lattice. Simultaneously, there is an elastic effect, whereby the hydrogen, which is creating expansion in the lattice, is attracted to the open volume and relaxation of a vacancy. Similarly,
hydrogen interactions with solutes is typically a combination of effects due to elastic distortion caused by the solute atoms and electronic differences in bonding between the solute and host metal atoms [131]. The optimum binding site for hydrogen within a vacancy is a position displaced from the vacancy center [131]. Hydrogen has been shown to stabilize the vacancies which can form during plastic deformation, and this may lead to a superabundance (20 at. %) of vacancies compared to equilibrium \((10^{-16} \text{ at. } \%)\) [40, 143, 144]. As vacancies are traps for hydrogen, and the presence of hydrogen stabilizes vacancies, there may be a tendency for the formation of vacancies clusters which would otherwise be uncommon [143].

Hydrogen is strongly bound to dislocation cores. This is theorized to be due to vacancy-like defects at the core [131, 145]. Additionally, hydrogen is attracted to the elastic field surrounding the dislocation. This trapped hydrogen at the dislocations can resemble Cottrell carbon atmospheres [45, 51] and can pin the dislocations leading to behaviors such as dynamic strain aging and serrated yielding [49, 71]. The pinning behavior is due to the strong trapping: energy is needed to separate the hydrogen (whether as an atmosphere or as solute atoms) from the dislocation core, increasing resistance to dislocation motion [131].

Concurrently, the presence of hydrogen alters both the local electronic structure and the elastic field of the dislocation. In the metal lattice, the change in the electronic structure and the strain due to the presence of hydrogen leads to an alteration in the elastic constants, with one effect being a reduction in the shear modulus with hydrogen [123]. This in itself leads to a reduction in the stress needed to move dislocations. At the dislocations, the electronic structure change leads to a local weakening of bonding resulting in a reduction in the Peierls barrier. In body-centered cubic metals, this reduction in the Peierls-Nabarro stress could facilitate dislocation motion by enhancing kink-pair nucleation [46, 146-151]. However, in face-centered cubic metals, where the Peierls stress is already considered small, 650 MPa in FCC aluminum [152] compared to 2.5 GPa in BCC molybdenum [153], a reduction should not have a significant effect on dislocation motion [49].

The effect of the hydrogen on the elastic field of dislocations is less material specific [50]. The hydrogen modifies the elastic field, enhancing the field in some directions and reducing it in others. In the directions in which there is a reduction in the elastic field, the interaction energy
between the dislocation-hydrogen complex and other elastic obstacles is reduced, leading to a shielding effect [35, 120]. This shielding can lead to an enhancement of dislocation motion [120, 128, 154], which manifests as an increase in velocity at constant stress, with a 10 fold increase observed in iron [13] and a 2 fold increase observed in α-titanium [155]. Another consequence is the reduction in the equilibrium separation distance between dislocations, resulting in closer packing of dislocations in pile-ups, and a reduction in stacking fault energy [50, 120], potentially resulting in reduced cross-slip. A reduction of 20% was measured in 310s stainless steel [31, 50] and a reduction of 40% was measured in 304 stainless steel [156]. There is debate as to the extent that this reduction will influence dislocation behavior [157], and what effects might be due to changes in the stress fields of the bounding partial dislocations. The presence of hydrogen in the stress field of edge dislocations will also stabilize the edge component. As there is no driving force to remove the hydrogen, allowing the dislocation to shift to a screw configuration, cross-slip will be inhibited [146]. The combination of the two effects will lead to increased slip planarity. The temperature and strain rate regime in which these effects will dominate over the pinning effects is the narrow window in which hydrogen diffusion is comparable to dislocation motion, allowing the hydrogen atmospheres to remain with the dislocations. This window corresponds to the regime of hydrogen embrittlement.

In addition to being traps sites, it has been suggested that dislocation structures in cold-rolled materials could create short-circuit diffusion paths through the material [158], as higher diffusivity has been measured along dislocations than through the bulk [159]. However, dislocations play a more important role in transporting hydrogen as they move due to an applied stress [46, 118]. This has been observed by increased desorption and absorption of hydrogen during plastic deformation [71, 160, 161]. This may also lead to an increased apparent diffusivity of hydrogen [161]. The ease with which this occurs depends on the strain rate. When the diffusion rates and dislocation motion are similar, the Cottrell atmospheres will be transported along with the dislocations, and, correspondingly, have an effect upon the mechanical properties and the distribution of hydrogen. The range in which dislocation transport occurs frequently corresponds to the regimes of embrittlement. An important possible effect is the redistribution of hydrogen compared to the expected Fickian diffusion distribution [118], leading to different areas of locally high hydrogen concentration. While some studies have
shown a negligible effect of deformation [96, 128] on the distribution, it may be more important locally, particularly in front of advancing crack tips, although it is insignificant on a bulk scale.

Density function theory calculations of hydrogen atoms in an iron low angle grain boundary show a redistribution of electrons due to the presence of hydrogen [162, 163]. Electrons are removed from iron atoms near the boundary and one study showed removal of electrons from hydrogen atoms in the boundary and excess electrons on iron atoms in the boundary [162], while another studied showed excess electrons at the hydrogen atoms [163]. The net effect in both cases is a reduction in the number of electrons involved in bonding across the boundary, leading to a reduction in the cohesive strength of the boundary. These results are presumed to be more general, applying to general grain boundaries and secondary phase boundaries [164, 165]. Precipitates are often the nucleation site of voids; the addition of hydrogen may mean that the voids are able to nucleate at lower stresses [114, 154], reducing the stress for ductile failure. As mentioned previously, these are locations with high trapping energy, making these irreversible traps at most operating temperatures. Depending upon the secondary phase, its density, and the degree of trapping, precipitates can act as hydrogen sinks which remove hydrogen from the system, and thereby reduce the susceptibility to embrittlement [111, 154]. Unfortunately, in cases of high hydrogen concentration or continuous supply, saturation of deep traps may limit their benefit [106].

Impurities are known to collect at grain boundaries; a notable example being sulfur in nickel [166]. Sufficient sulfur segregation has been shown to be sufficient to cause a transition from ductile transgranular failure to intergranular cracking. The combination of hydrogen with grain boundary impurities has been shown to be greater than either species individually [8, 74]. The effect of different segregants on the strength of a boundary is shown in Figure 2.11, and it can be seen in the columns on the right that the combination of hydrogen with other impurities has a greater effect on boundary strength than either element separately [76]. This has also been shown in some steels, where the different combinations of segregants show slightly different trends. In particular, the effect of hydrogen is more noticeable in combination with weak embrittlers than with strong embrittling impurities [8, 75], though it can be sufficient in itself to cause intergranular failure [80].
Grain boundaries can also act as fast diffusion pathways through the material. Rates from 4 times to 2 orders of magnitude higher have been measured [131, 167]. When comparing different boundaries in nickel, it was found that grain boundaries with less order have higher diffusivities than highly ordered boundaries [168, 169]. This may not have a large effect on the bulk diffusion, as Fickian diffusion in the bulk may overwrite the effect of grain boundaries given sufficient time. However, it will be important on small scales, particularly in non-equilibrium situations [170]. The combination of accelerated diffusion along the boundary and the hydrogen sink properties of the boundary can lead to locally high concentrations along the grain boundary.

The combination of the various effects of hydrogen on the microstructural features of the material will determine the total effect of hydrogen on the mechanical properties. The effects reported here are based upon a combination of experimental observations, theoretical calculations, and computer modeling combining the two. The exact effect of hydrogen on the electronic structure of defects is still not completely understood, though its effects are observed. Additionally, there is still a lack of knowledge over the exact location of hydrogen with respect

Figure 2.11. First-principles calculations of the effect of various impurity elements on the cohesive strength of a nickel Σ5 (001) twist grain boundary [76].
to these defects. Still, what is available represents a large body of knowledge collected over
decades. And from this understanding of the effects of hydrogen on the microstructural features,
various mechanisms have been proposed to explain the effect upon the mechanical properties in
the presence of hydrogen.

2.3 Mechanisms of Hydrogen Embrittlement

Since the discovery of the effect of hydrogen on the mechanical properties of metals, many
mechanisms have been proposed to attempt to explain this phenomenon. With new discoveries,
these mechanisms have been modified or discarded, while others have been introduced. While
no mechanism currently explains all of the features of hydrogen embrittlement in every situation,
many account for large amounts of the observed behavior, and some have limited predictive
capabilities.

2.3.1 Hydrogen Blistering
Blistering or cracking can be caused by the precipitation of gaseous $H_2$ [46, 69, 171-176]. As $H_2$
gas builds in pressure, whether in internal voids or interfaces or beneath film layers, the internal
stress due to this pressure increases until local failure occurs. The morphology of the damage
depends upon the location of this internal gas build-up. The linking of parallel cracks, step-wise
cracking, formed by this mechanism is particularly damaging in pipes, where these cracks can
quickly reduce the remaining pipe wall thickness leading to catastrophic failure [25, 175, 176].
This phenomenon is more common in corrosive conditions when hydrogen fugacity is high. It is
proposed that hydrogen embrittlement due to solute hydrogen may contribute to blister
nucleation, crack growth, and crack linking [177, 178].

2.3.2 High Temperature Hydrogen Attack
At high temperatures (350°C or higher for steels), high temperature hydrogen attack (HTHA) can
occur. Hydrogen which dissolves into the metal reacts to form another phase (frequently a gas)
which can form pressurized cavities [69, 172]. In the case of steels, this phenomenon is also called methane reaction, as the hydrogen reacts with carbon atoms in the steel matrix or in carbides, leading to a depletion of carbon. The accompanying reduction of strength due to the decarburization combined with the formation of methane bubbles, often at grain boundaries, leads to the development of macrocracks or fissures causing failure that is preceded by very little ductility [19]. The addition of stress under such conditions can lead to creep processes exacerbated by the HTHA [179].

2.3.3 Hydrogen-Induced Phase Transformations

Perhaps the most widely accepted mechanism for hydrogen embrittlement, hydride fracture typically applies only to materials in which hydrides are favorable to form. This predominantly occurs in Group Vb materials [180-182], such as vanadium, niobium, and their alloys, as well as titanium and zirconium [56, 64, 155, 183] and their alloys, though metastable hydrides could potentially form in other metal systems [13]. The low solubility of hydrogen in the lattice causes the precipitation of hydrides in regions of high hydrogen concentration and high stress [183]. The high stress, and the associated plasticity, at a crack tip generally stabilizes the hydride, which will form preferentially in these areas. The stress due to the volumetric expansion of the hydride compared to the matrix further stabilizes the hydride and often precipitates further hydrides [155]. In some systems with stable hydrides, an extensive volume that is completely transformed into hydride can form [64], while in others, fine hydrides form immediately ahead of the crack tip [155, 183]. Hydrides are generally brittle phases, and cleave on specific crystallographic directions [181], Figure 2.12. In some cases, after cleavage, with the stress relieved, the hydride will dissolve, the hydrogen

![Figure 2.12. Schematic of crack tip hydride formation and fracture [155].](image_url)  
(a) Hydrogen diffuses to the crack tip.  
(b) Hydrides form ahead of the crack tip and, due to expansion of the hydride phase, the crack tip is stable.  
(c) Upon increasing the stress, the hydrides crack along cleavage planes.
atoms diffuse back ahead of the crack tip, and the hydride will be reformed, and cleavage can occur again [183]. This behavior may account for some cases of observed hardening due to hydrogen [15]. At high enough crack velocities, hydride forming processes cannot keep up, and hydrogen-influenced plasticity processes dominate [155]. Song and Curtin [134] have suggested that nanohydrides can form ahead of the crack tip even in non-hydriding materials. However, if this were the case, we would expect crystallographic cleavage, which is not observed.

Hydrogen-induced phase transformations are also possible in stable and unstable austenitic stainless steels. Hydrogen can assist the formation of different martensitic phases [15, 184, 185]. However, it is unclear whether these transformations are a critical part of embrittlement, or are a consequence of the plasticity prior to failure.

2.3.4 Hydrogen Enhanced Decohesion (HEDE)

First proposed by Troiano in 1960 [186], the Decohesion model postulates that dissolved hydrogen lowers the cohesive strength of the lattice, which enables bonds along a crystallographic plane to rupture at lower applied stresses. Alternatively, it can be viewed that hydrogen lowers the surface energy of atomic planes encouraging a more cleavage-like failure [133], though this surface consideration is necessary but not sufficient for lowering the fracture stress [187]. The decrease in surface energy, or the increase in the decohesion, becomes greater with increasing hydrogen concentration [133]. This brittle fracture process would be similar to that suggested by the Griffith criterion for brittle fracture [134]. The weakening of the cohesive force between bonds would permit nucleation of microcracks within the plastic enclave ahead of the crack tip, where the highest hydrogen concentration is expected. The microcrack progresses backwards to the main crack, either through decohesion or by ductile tearing, which is usually assumed to be unaffected by hydrogen [187]. Then the hydrogen diffuses to the new stress maximum ahead of the crack tip weakening the bonds and nucleating a new microcrack. The hydrogen on the new surface of the microcrack would lower the surface free energy [18]. The weakening of the co-linear force between the atoms should be accompanied by weakening of the shear-resisting force. This will lead to localized slip [18].
Because of the simplicity of the model and the overall brittleness of failure, it has been claimed that only the Decohesion mechanism is able to predict hydrogen-assisted cracking thresholds and rates [188]. The two primary variables to account for are trap modified hydrogen diffusivity and alloy yield strength.

A high lattice concentration of hydrogen is required for decohesion, but the amount of hydrogen needed for embrittlement can be quite low. It is argued that hydrogen collects at regions of high stress, such as around precipitates and in front of crack tips, in which case the local hydrogen concentration is high, though global concentration is still low. One calculation by Oriani and Josephic produced a local concentration of $10^4$ times greater than that in the unstressed lattice [132]. However, another model showed that the concentration due to stress ahead of a crack tip exceeded the bulk by only $10^2$ times [13]. Whether this enhancement of local hydrogen is sufficient to significantly lower cohesion and lead to fracture is still a subject of debate. Ab initio calculations support hydrogen reducing the cohesive strength of the lattice, although there remains uncertainty as to the specific relationship, linear or nonlinear, between hydrogen concentration and the magnitude of the reduction in the cohesive strength [133, 162, 189].

Modeling of the crack tip has suggested that dislocations emitted from the crack tip do play a role in the Decohesion process and aid in creating a high concentration of hydrogen [115, 190]. Taking into account the effect of strain gradient plasticity, significantly higher stress are calculated to occur ahead of the crack tip than calculated by classical continuum mechanics theory [190]. Modeling shows that dislocation emission shields the crack tip, slightly reducing the local stress ahead of the crack tip and moving the maximum to approximately 20 nm ahead of the crack tip [115]. At this location, large triaxial stresses are proposed to cause a very high concentration of hydrogen (as high as 1 hydrogen atom per metal atom), even with low bulk concentrations. As the interstitial hydrogen affects the bonds of all nearest neighbors and as the stress is near the theoretical stress of the material, only a relatively small reduction in cohesion is needed for failure. The concentration amount calculated may be high, especially when taking trapping into account [115], however, large effects due to hydrogen at the crack tip may be possible. The combination of the high stress with trapping has been proposed to cause a significant hydrogen enrichment [60].
Atomistic modeling has been applied to understand the effect of various parameters on likely hydrogen embrittlement mechanisms. Simulations looking at the thermodynamics of decohesion suggest that above a certain chemical potential of hydrogen, a first-order phase transformation occurs, from what they describe as dilute cohesive-zone phase to the saturated cohesive zone phase. This transformation results in a change in properties, and in particular, a drastic reduction the maximum stress for decohesion [191]. One model [134] suggests that this transformation leads to the formation of a “nanohydride” phase at the crack tip where the stress field leads to very high local hydrogen concentration. This “nanohydride” inhibits ductile mechanisms, leaving only cleavage of the hydride as a fracture path. However, this model was for nickel, which does not show cleavage fracture in the presence of hydrogen.

It is difficult to directly measure the loss in the cohesive strength, as well as to determine the exact location of the hydrogen in order to support the high concentration needed. As such, the effects on the cohesive strength have been calculated from first-principle methods, which are lacking this information, leaving an amount of uncertainty in the results. In addition, most calculations for cohesion effects on crack propagation assume equilibrium conditions, which is usually not the case for crack propagation.

The term decohesion has also been applied more generally to the lowering of strength of various microstructural features in a metal including slip bands, grain boundaries, and particle or second phase boundaries. These are often areas of high strain within the lattice, as well as traps for hydrogen. Both of these factors allow for the accumulation of potentially high levels of hydrogen at these sites. The decohesion of particles at lower strengths, nucleating voids that can grow by microvoid coalescence, could account for the lower fracture toughness, yet still ductile fracture observed in many cases [73]. In one notable example, the accumulation of hydrogen along ordered fine precipitates caused cleavage appearing failure, as the failure followed the particle boundaries which were aligned along crystallographic planes [192].

Similarly, the decohesion of grain boundaries due to the presence of adsorbed solute hydrogen describes the process for intergranular failure. Intergranular failure is a classical fracture mode associated with hydrogen embrittlement, as well as temper and liquid metal embrittlement. It is a fracture mode commonly observed in high yield strength materials. In these higher strength
materials, it is presumed that the local cohesive stress necessary for grain boundary decohesion can be more easily reached prior to other failure modes in the presence of hydrogen [78]. Thermodynamic considerations assume little to no ductility affecting the decohesion process for intergranular failure [193]. That hydrogen lowers the cohesive energy is supported by observations that a critical concentration of hydrogen is required at the grain boundaries before intergranular fracture dominates over ductile failure [67]. There is some concern about how a sufficiently high concentration would be reached in steels, as the impurity concentration needed to cause embrittlement in steel with a yield strength of 10^3 MPa is 10^{-2}-10^{-1} atomic fraction, yet the maximum hydrogen concentration in the lattice ahead of a crack, based upon \( C_H = C_0 \exp(\sigma_H V_M/RT) \), where \( \sigma_H \sim 3\sigma_Y \), would only be of the order 10^{-6}-10^{-5} atomic fraction [8]. In the case of steels, it was thought that it is the combination of hydrogen with other grain boundary segregants which causes a sufficient reduction in grain boundary strength to cause intergranular failure [8], however, recent studies have found intergranular failure to occur even in the presumed absence of segregated impurities [79]. Evidence of plasticity, such as slip traces, have been recently interpreted as possibly contributing to intergranular failure [36], however the extent of plasticity and its importance is still unknown. As such, the issue of critical hydrogen concentration has still not been completely addressed.

2.3.5 Hydrogen Enhanced Localized Plasticity (HELP)

Hydrogen Enhanced Localized Plasticity (HELP) was first proposed as an idea by Beachem in 1972 [194]. Through high resolution fractography, he noticed evidence of plasticity on hydrogen-assisted fracture surfaces. He suggested that hydrogen assisted the deformation processes and localized them leading to locally ductile failure with a macroscopically brittle appearance.

The HELP model is based on the concept of the hydrogen-enhanced shielding mechanism, which was developed to explain the enhancement of dislocation velocity observed during in situ TEM straining experiments conducted in a gaseous hydrogen environment [154, 157, 195-197]. Central to the shielding model is the hypothesis that hydrogen, in addition to being located in the dislocation core, forms an atmosphere around a dislocation, similar to Cottrell atmospheres in
steels [198]; in particular, the hydrogen atoms are proposed to agglomerate in the tension field of edge dislocations due to the dilatational interaction energy [35]. The calculated distribution of hydrogen around an edge dislocation [52] is shown in Figure 2.13a, and the distribution around two closely spaced edge dislocations with identical Burgers vectors is shown in Figure 2.13b. This is a result of the superposition of the stress fields of the two dislocations. The situation becomes more complex as more elaborate arrangements of dislocations occur, but with the similar result of hydrogen concentration becoming higher in regions of positive stress enhancement [52]. Hydrogen also accumulates around screw dislocations, although this is a second order interaction due to the change in moduli by solute atoms as opposed to the first-order elastic interaction with edge dislocations [120].

The dislocation-hydrogen complex can be treated as a unit with a different stress field compared to that of a dislocation. The shear stress due to hydrogen is negative, reducing the net shear stress on a dislocation from other elastic sources [52, 199]. The magnitude of the hydrogen effect increases with increasing hydrogen concentration [52]. Shielding, associated with the volumetric strain due to hydrogen in the dilatation field and hydrogen-induced changes in the moduli, reduces the repulsive force between dislocations on the slip plane [35]. Additionally, this effectively reduces, in certain directions, the interaction energy between a dislocation and an obstacle [35, 52, 120, 128]. An example would be a reduction of the interaction energy between

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**Figure 2.13.** Contours of normalized hydrogen concentration ($c/c_0$) around a) a single edge dislocation and b) around two parallel edge dislocations of the equal Burgers vector (b) on the same slip system at a separation distance of 6b. Nominal hydrogen concentration of $c_0 = 0.1$ and temperature of 300 K. Adapted from [52].
dislocation-hydrogen complex and solute carbon atoms, reducing the effect of solute hardening. These effects are short range, becoming weaker with increasing separation of the dislocations or dislocation and obstacle [52].

Due to the HELP mechanism being an elastic effect, the consequences should be independent of crystal structure and purity, which matches experimental observations on dislocation behavior in the presence of hydrogen [35, 50, 197]. The regime where this mechanism will be active will correspond to the temperature and strain rate ranges where H atmospheres around the dislocations retain high enough mobility to move with the dislocations; this temperature range corresponds roughly to the accelerated fracture regime [13, 35]. The reduction in the interaction energy between dislocation-hydrogen complexes and obstacles manifests as enhanced dislocation mobility at a constant stress. The enhanced mobility is greatest in regions of high hydrogen concentration, which leads to localization of plasticity [35, 54]. The dislocation-dislocation interactions will also result in closer spacing between dislocations within a pile-up [197], as shown in Figure 2.14. As these atmosphere form in the tension stress fields of edge dislocations, which are non-existent in screw dislocations, edge dislocations are proposed to be stabilized by these atmospheres, which would account for the suppression of cross-slip observed under hydrogen [128].

An argument against the HELP mechanism is that calculations show a high concentration of hydrogen is needed to cause the shielding effect [35]. A concentration of 10 at% is needed,
which suggests it should only occur in hydride forming metals [200], and that at the low concentrations at which HE occurs, the effects calculated would be too small to be measured. Others suggest that while shielding can occur at lower concentrations, high concentrations (10^{-2}) are needed in order to significantly affect mechanical properties [201].

New atomistic simulations have suggested a means to achieve this high hydrogen concentration locally [200]: by adding hydrogen-hydrogen attractive interactions, which are predicted by DFT calculations, and were suggested earlier by thermodynamic considerations [202], a locally very high (up to 4 orders of magnitude higher than matrix) concentration of hydrogen occurs at the dislocation core even with low lattice concentrations. Without the attractive interactions, only a diffuse atmosphere would accumulate around the dislocations. And with this high local concentration of hydrogen, the shielding effect is observed within the simulation, implying that HELP could operate under a wider range of conditions than otherwise predicted.

There is a difficulty in associating enhanced dislocation velocity with enhanced brittle fracture. The acceleration of ductile failure can be explained by hydrogen accelerating the growth of voids [72]. An explanation proposed for brittle failure was that the localization of slip, by the local reduction in the flow stress due to hydrogen, leads to locally ductile fracture which macroscopically appears brittle [154]. Glide-plane decohesion has been suggested, where hydrogen is gathered by the cores of gliding dislocations leading to lower cohesion on the slip plane [78]. Several atomistic studies [145, 203] have shown strong trapping of hydrogen at the core of the dislocation on the slip plane, which lowers the energy barrier for dislocation motion. One study [145] showed that as hydrogen accumulates along this slip plane and as dislocation separation distance is decreased, the cohesive strength along this plane decreases until fracture occurs. A physical-based statistical micromechanical model of intergranular failure [204] suggested that the three likely steps to failure, 1) dislocation pile-up at a grain boundary carbide, 2) interfacial failure of the carbide and 3) decohesion along the grain boundary, can all be influenced by the presence of hydrogen, but that the critical event may be the dislocation pile-up. As the presence of hydrogen can increase the number of dislocation in the pile-up, the stress at the carbide may be intensified, promoting failure. This may suggest that the HELP mechanism is needed to create dislocation structures and high hydrogen concentrations in order for decohesion processes to occur, creating brittle appearing fracture.
2.3.6 Adsorption Induced Dislocation Emission (AIDE)

By examining fracture surfaces created under different embrittling conditions (hydrogen, liquid metal, stress corrosion), Lynch [70, 205-207] noticed a strong similarity in features, which he interpreted as evidence of similar processes. Using carbon replicas to examine fine fracture features, Lynch found that liquid metal and hydrogen embrittled fracture features in the same material (whether in aluminum alloys, nickel, steels or titanium alloys) were nearly identical, and frequently contained fine dimples only discernible in the replicas [70]. Since liquid metal embrittlement can only be a crack tip effect, as the liquid metal cannot diffuse into the bulk metal, he proposed that hydrogen also must only impact the crack tip in order to produce identical fracture surfaces [18, 70]. This similarity had been noted before [38, 208, 209] and similar mechanisms suggested, though Lynch advanced the theory further. It is adsorption at the crack tip which is responsible for facilitating crack growth, and the adsorbed species can only affect interatomic bonds at the crack tips. Likewise, he proposed that the rate of crack propagation through material during hydrogen embrittlement is too fast for hydrogen diffusion to keep up, or indeed any other process other than adsorption to occur, which also supports the idea that it is a surface effect [70, 206]. The existence of dimples suggests that a ductile process is critical to these failures, with crack growth occurring by dislocation activity on the atomic scale [206].

The AIDE mechanism proposes that hydrogen, unlike oxygen, nitrogen or sulfur, on the surface of the crack tips lowers the surface energy allowing easier emission of dislocations [13, 205, 209]. Linear elastic considerations support this possibility [128]. These dislocations would travel away from the crack tip. Weak chemisorption weakens the interatomic bonds without forming strong directional bonds with the substrate [70]. This localized plasticity at the crack tip allows the advancement of the crack, and would account for fine features of plasticity on the fracture surface. The weakening of bonds due to the embrittling species would potentially contribute to both dislocation emission and decohesion processes, hence brittle failures with fine ductile features [206]. This is the explanation for the commonality of herringbone patterns on “cleavage-like” fracture features due to environmental failure [207].

Oriani claims that hydrogen would not be expected to enhance the nucleation of dislocations at the surface of crack faces [18]. The reduction in surface energy is insufficient. Others concur
that while AIDE may be an effect of hydrogen, the dislocations emitted from the crack tip are not as crucial as those moving ahead of it.

2.3.7 Hydrogen-Enhanced Strain-Induced Vacancies (HESIV)

Nagumo et al. [40, 144, 210-212] have suggested that vacancies play a crucial role in hydrogen embrittlement. The presence of vacancies was demonstrated by positron annihilation and thermal desorption spectroscopy techniques, and is due primarily to the movement and interactions of dislocations. By straining and heating in various combinations, with and without hydrogen, Nagumo et al. determined that defects (hydrogen traps) were created during straining, and that their creation was significantly accelerated by the presence of hydrogen, and that these defects were quickly removed by annealing [210]. They interpreted these weak trap sites as vacancies created by dislocation interactions and stabilized by the presence of hydrogen. Other evidence for hydrogen stabilizing vacancies has been reported [143, 213]. It has been proposed that hydrogen accelerates the formation of these vacancies by lowering the formation energy and by accelerating dislocation processes [148]. Clustering of atomic vacancies is expected to act as a potential source of fracture initiation by agglomerating to form microvoids or by destabilizing the crack front area by amorphization [40, 212].

Concern has been raised over the impact of the vacancies [11], particularly as the observation of amorphization does not correspond to in situ TEM results, and the result itself is debatable. Other interpretations suggest that vacancies could facilitate dislocation climb and cross-slip otherwise inhibited by hydrogen. This could lead to a local reduction in strain hardening [214], and be an assisting component of plasticity-based mechanisms. The connection between vacancy and plasticity-based mechanisms has been proposed, as accelerated plasticity due to HELP would help form vacancies and assist in the growth of “nanovoids” which nucleate from these vacancies [215].
2.3.8 Defactant Model

Kirchheim and coworkers [216-218] have developed the “Defactant model” as a thermodynamic explanation of hydrogen embrittlement. Similar to surfactants, which lower the surface energy of liquids, defactants (defect acting agents) analogously reduce the formation energy of defects. The surfactant treatment is used to describe the reduction of grain boundary surface energy due to the segregation of solutes; the defactant model is an extension of this model by considering the Gibbs adsorption isotherm:

\[ d\gamma = -\Gamma_A d\mu_A \]  \hspace{1cm} (2.6)

where \( \gamma \) is the surface/line energy of the defect, \( \Gamma_A \) is the excess of the (solute) defactant at the defect, and \( \mu_A \) is the chemical potential of the defactant. The Defactant model is general for solute-defect interactions [216]. In the case of hydrogen embrittlement, hydrogen, as a solute atom, is proposed to act as a defactant, and the higher the chemical potential, the greater the effect. Hydrogen atoms reduce their energy by finding trapping (lower energy) sites; it can also be viewed that the trapping defect gains energy by the trapping of the hydrogen. Vacancies would be stabilized, accounting for higher concentrations, and the accumulation of vacancies to form voids would be favorable, as hydrogen would lower the surface energy of the voids. The nucleation of dislocations is easier in the presence of hydrogen. By lowering the line energy of dislocations, kink formation would be easier, leading to enhanced dislocation motion. Therefore, the various HE models described previously can be considered specific cases of the Defactant model, with the specific circumstances determining which is dominant. The model is still lacking kinetic considerations, which may account for the current inability to predict which observations will be dominant.

2.3.9 Summary

The myriad of proposed mechanisms, and the supporting data for each, could suggest several possibilities. One possibility is that the different mechanisms operate at different regimes for different materials, such that which mechanism operates and is observed depends upon the material and the conditions [13, 114]. Another possibility is that the actual mechanism is a
combination of several of the proposed mechanisms, with different aspects being more prominent under different conditions. An example of this would be the atomistic simulations of shear band decohesion discussed previously [145].

A better understanding of the microstructure associated with hydrogen-assisted failures is needed to clarify the mechanism of hydrogen embrittlement. Studying different failure modes typically associated with hydrogen can allow for the finding of any commonalities. Using new tools, the microstructure immediately beneath the fracture surface has been correlated with the fracture features for several different materials under different loading conditions. It will be shown that features on the fracture surfaces do not reveal the details needed for microstructural fracture process interpretation, and that with the available resolution, assumptions of the effects of hydrogen on the microstructure were necessary. These interpretations of the microstructural mechanisms will be shown to be too simple. Based upon these observations obtain from the new investigative tools, a new dislocation-mediated mechanism for hydrogen-assisted failure based upon previous mechanisms is proposed.
CHAPTER 3
EXPERIMENTAL PROCEDURES

3.1 Samples
To investigate the operating mechanisms of hydrogen embrittlement, several different materials were tested under different loading conditions. These materials were chosen for their possible usefulness in a hydrogen economy, and the loading conditions were chosen to reflect different aspects of possible operating conditions. After failure, the fracture mode was determined and, from representative fracture surface features, thin foils were extracted in order to examine the microstructure immediately beneath the fracture surface. These were compared with the original microstructure in order to determine the microstructural processes leading to failure in these samples and the effect of environment upon these processes.

3.1.1 Pipeline Steel Compact Tension Tests
As the existing natural gas pipelines are being considered for the mass distribution of hydrogen, their behavior under high pressure hydrogen is being investigated. Two examples of high strength low alloy (HSLA) steels were used for this study. The compositions of the steels, designated ‘B’ and ‘D’, are given in Table 3.1. The fracture toughness of these steels was measured under high pressure hydrogen gas at Sandia National Laboratories in Livermore, CA. The yield strength of steels B and D, as reported by the mill, are 565 MPa and 434 MPa, respectively.

<table>
<thead>
<tr>
<th>Classification</th>
<th>API Grade</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cu</th>
<th>Ni</th>
<th>V</th>
<th>Nb</th>
<th>Cr</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>X70/X80</td>
<td>0.05</td>
<td>1.52</td>
<td>0.12</td>
<td>0.23</td>
<td>0.14</td>
<td>0.001</td>
<td>0.092</td>
<td>0.25</td>
<td>0.012</td>
</tr>
<tr>
<td>D</td>
<td>X60 HIC</td>
<td>0.03</td>
<td>1.14</td>
<td>0.18</td>
<td>0.24</td>
<td>0.14</td>
<td>0.001</td>
<td>0.084</td>
<td>0.16</td>
<td>0.014</td>
</tr>
</tbody>
</table>
Compact tension samples were used for fracture toughness testing, Figure 3.1. The samples were machined from rolled plate to be 12.5 mm wide, 33 mm long and 31 mm tall. In order to properly understand the effect of hydrogen, elastic-plastic fracture mechanics were employed for fracture toughness determination based upon ASTM standard E1820-06. The average fracture toughness measured in steels B and D in 5.5 MPa gaseous hydrogen are 110 and 85 MPa m$^{1/2}$, respectively.

![Figure 3.1. Compact tension fracture toughness samples. a) Schematic showing compact tension geometry and fracture surface. b) Optical image of fracture specimen.](image)

With a typical machined notch size of 0.5 in (1.3 cm), a precrack of an additional 0.1 in (0.3 cm) is usually desired. A sharp precrack is achieved by fatiguing the sample at 1 Hz. The stress applied is determined by the compliance of the material, measured after loading the sample. For the HSLA steels, precracking normally takes approximately 4 hours.

The testing machine is contained in a high pressure chamber which can be filled with hydrogen or helium gas with testing pressures in the range of 5.5 MPa to 105 MPa (800 psi - 15 ksi). After loading the sample, the chamber is purged three times with helium, and then purged with hydrogen three times before pressurizing the chamber with the desired amount of hydrogen. The sample is then cyclically loaded three times in the elastic zone to determine the compliance before having a slightly compressive load applied in order to ensure the zero strain point is measured. The load test is then run at the desired strain rate (displacement rate was approximately 3mm/hr). During the test, the crack length is determined by measuring the drop in potential across the sample. When sufficient data has been collected to determine the fracture toughness (crack length of approximately 0.5 mm) the test is stopped, the chamber vented, back-
filled with helium, and the sample removed. The sample is heat tinted at 275°C for 20-30 minutes. The sample is then cooled with liquid nitrogen before overloading for brittle failure. Occasionally, overloading was applied without cooling, leading to ductile failure. After cracking open by overloading, the heat tinted crack length is measured optically for the fracture toughness calculations. Figure 3.1 shows both a schematic of the sample and an optical image showing the effect of the heat tint. Samples were then stored in desiccator before being sent to the University of Illinois for fractography and microstructural analysis. Four samples were received: one sample was of B steel tested in 21 MPa H₂; three samples of D steel, one tested in 21 MPa H₂, and two in 103 MPa H₂.

### 3.1.2 Nickel Intergranular Failure

Nickel alloys are known for intergranular failure in hydrogen, a phenomenon which plagues high strength steels. Nickel is often used as a model system, especially for studying nickel-based alloys which are common in areas such as nuclear applications [76]. Ni-201 alloy, a commercially pure nickel supplied by ThyssenKrupp VDM USA, Inc., was studied. The impurities are (in wt.%) 0.11 Mn, 0.08 Fe, 0.02 Si, 0.01 Cu, 0.01 C and 0.002 S. The initial average grain size was 30 μm. The yield strength of the nickel was 55 MPa.

Uniaxial tensile tests were conducted using tensile bars with 4 mm diameter and 25 mm gage length. The samples were precharged in high pressure (~140 MPa) hydrogen gas at 150°C until the hydrogen lattice concentration was approximately 2000 appm (120 hours). Tensile tests were conducted at room temperature following ASTM Standard E8 M-08 using a servo-hydraulic MTS 810 mechanical testing machine (MTS Corporation, Eden Prairie, MN). A displacement rate of 0.01 mm/s was used in order to minimize hydrogen loss from the sample during testing, which corresponds to a strain rate of 10⁻⁴ s⁻¹. With hydrogen, the reduction in area dropped from 74-86% in the uncharged samples to 6-29% [219]. The failure became fully intergranular. The sample received had a strain-to-failure of 13%, corresponding to a test time of around 325s. Hydrogen charging and mechanical testing were done at Sandia National Laboratories in Livermore, CA.
3.1.3 Fatigue of Stainless Steels

Stainless steels are an important structural material and, while too expensive for use in a continent-spanning pipeline system, are likely to be used in smaller components such as local pipe systems, manifolds, valves, gas pumps and hoses, and vehicle parts: parts which undergo significant fatigue loading. As stainless steels are usually austenitic (face-centered cubic), they are considered to be more resistant to the effects of hydrogen embrittlement. However, recent events such as the failure of a hydrogen refueling station hose show that these steels are still susceptible to hydrogen-enhanced fatigue failure. Two common stainless steels, 304 and 316, were chosen for study. The compositions are given in Table 3.2. The yield strengths are 309 MPa and 271 MPa for the 304 and 316 stainless steels, respectively. With one exception, samples were precharged, as austenite holds hydrogen for extended periods of time, before fatigue testing. Sample fabrication and fatigue testing of tensile specimens was done at Kyushu University. Samples were of a tensile bar design with a diameter of 7 mm and a gage length, which was polished to a mirror finish, of 30 mm, Figure 3.2. A hole with diameter of 100 μm and a depth of 100 μm was drilled in the middle of the gage length to act as a crack initiation site. This geometry was chosen to facilitate a study of small crack propagation [220].

![Figure 3.2. Schematic of tensile specimen used for fatigue testing [220].](image)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>H*</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>0.056</td>
<td>0.43</td>
<td>1.72</td>
<td>0.03</td>
<td>0.025</td>
<td>8.87</td>
<td>18.26</td>
<td>0.22</td>
<td>2.2</td>
</tr>
<tr>
<td>316</td>
<td>0.045</td>
<td>0.3</td>
<td>1.36</td>
<td>0.026</td>
<td>0.029</td>
<td>9.91</td>
<td>17</td>
<td>2.05</td>
<td>3.4</td>
</tr>
</tbody>
</table>

There is the option of hydrogen pre-charging the specimens or testing in hydrogen. Gaseous charging, done after polishing the gage length to mirror finish, takes place in a pressure vessel which is heated while exposing the test piece to high pressure of hydrogen. After hydrogen charging, the sample is stored in a refrigerator to prevent hydrogen egression. The diameter of
the piece is measured in order to determine the applied force. Using a 100 micron diameter drill bit with a point angle of 120°, a 100 micron hole is drilled.

Two different machines were used for the testing of the samples, and apart from one having hydrogen atmosphere capabilities, they are equivalent. Both are electric hydraulic servo fatigue testing machines fabricated in Japan. One machine is a Shimadzu Servi-pulser. The other is a Saginomiya, which is capable of testing in a hydrogen environment. In order to ensure that the axis of loading is parallel to the axis of the sample, careful alignment is done when loading the sample into the testing machine. Four strain gauges are attached to the wider portion of the sample gage at 90° intervals. The sample is then loaded into the testing machine. The strain on the gauges is measured, and the sample adjusted as necessary until the strain is evenly distributed.

The testing occurs in increments, with crack length being measured after each increment. To measure crack length, replicas are made by melting acetylcellulose with methyl acetate (CH₃COOCH₃) over the crack tip, allowing the film to dry, removing the dried film and attaching it to a glass slide. These films can then be observed by optical microscopy. The replica picks up features from the hole and the crack, and will also reveal surface features such as slip bands, Figure 3.3. The crack growth rate is determined between replicas, and subsequent

![Figure 3.3](image_url)  
Figure 3.3. Optical images of replicas taken from fatigue crack after a) 0 cycles, b) 500 cycles (note slip band formation), c) 7000 cycles, and d) 9900 cycles. Original crack diameter was 100 microns.
intervals are calculated such that data is even and comprehensive. The crack is grown in this manner until it is approximately 3 mm in length. The test is then allowed to run until final failure.

Both 304 and 316 steels were tested with and without hydrogen to compare the effect of hydrogen on the crack growth and developing microstructure. Table 3.3 shows the test conditions of the four fracture samples studied. In both cases with hydrogen, the hydrogen content of the samples is approximately 10 wt. ppm. Additionally, two tests with hydrogen, one with 304 and one with 316, were interrupted when the crack length reached ~1.5 mm in order to study the microstructure ahead of the crack. These tests were conducted with hydrogen conditions matching those listed in Table 3.3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Test conditions</th>
<th>Maximum stress</th>
<th>Frequency</th>
<th>R ratio</th>
<th>Hydrogen charging conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A88</td>
<td>atmosphere</td>
<td>280 MPa</td>
<td>1 Hz</td>
<td>-1</td>
<td>None</td>
</tr>
<tr>
<td>A87</td>
<td>10 MPa H₂</td>
<td>280 MPa</td>
<td>1 Hz</td>
<td>-1</td>
<td>None</td>
</tr>
<tr>
<td>316</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D55</td>
<td>atmosphere</td>
<td>280 MPa</td>
<td>1 Hz</td>
<td>-1</td>
<td>None</td>
</tr>
<tr>
<td>D63</td>
<td>atmosphere</td>
<td>280 MPa</td>
<td>1 Hz</td>
<td>-1</td>
<td>10 MPa H₂ at 270°C for 400 hrs</td>
</tr>
</tbody>
</table>

3.1.4 Liquid Metal Embrittlement of T91 Martensitic Steel and Pure Iron

The connection between hydrogen embrittlement and liquid metal embrittlement (LME) has often been posited. The correlation between the two is based upon the abundant similarities between the fracture surfaces due to these two phenomena. To determine the similarity of the two mechanisms at a microstructural level, several cases of liquid metal embrittlement were examined. T91 martensitic steel is being used and is considered for future use as a structural material for neutron sources. The T91 steel was procured from the Industeel Arcelor group. The composition is given in Table 3.4. For comparison, a commercially pure iron (Armco) was used to determine the fracture mode for a purely ferritic steel. Two liquid metals were chosen to study this phenomenon: lead-bismuth (Pb-55 at.% Bi) eutectic (LBE) (melting point of 125°C) which
is a candidate material for use as a nuclear coolant fluid and spallation neutron target [221-223], and indium (melting point of 160°C).

Table 3.4. T91 martensitic steel composition (Fe balance)

<table>
<thead>
<tr>
<th>Element</th>
<th>Cr</th>
<th>Mo</th>
<th>C</th>
<th>Nb</th>
<th>V</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>Al</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>8.87</td>
<td>0.87</td>
<td>0.097</td>
<td>0.077</td>
<td>0.195</td>
<td>0.38</td>
<td>0.218</td>
<td>0.11</td>
<td>0.01</td>
<td>0.02</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

The T91 steel was received as 15 mm-thick plate which had been hot rolled and normalized at 1050°C for 30 min, quenched to room temperature, and tempered at 770°C for 90 min followed by air cooling. The resulting microstructure is fully martensitic with a mean prior austenite grain size of 20 µm.

To study LME crack propagation, center crack in tension, CCT, specimens with thickness of 1.5 mm and a centered notch 25 mm in height and 10 mm in width, with a notch root radius of ≈0.3 mm, were machined from the plate by electroerosion. As spallation sources use thin sheets and thin tubes of structural materials, this geometry mimics the in-service plane-stress loading conditions [224]. Additionally, this geometry allows direct measurement of the crack growth rate and the notch serves as a reservoir for the liquid metal. As the volume of liquid metal is small (≈0.1 cm³), surface tension is sufficiently strong to prevent loss of liquid metal to gravity. Capillarity ensures liquid-metal supply to the crack tip as it opens, provided the native iron-chromium oxide is disrupted sufficiently. Previous studies have shown that direct contact is needed between the liquid metal and the steel [222]. This was achieved by applying a soldering flux at the specimen notch at 200°C and then bringing a small amount of liquid metal into contact with the notch. The sample is then cooled, and, after the liquid metal freezes at the notch, the overflow is removed mechanically.

The samples were tested in a MTS 20/MH tensile machine. No pre-cracking of the sample was done, to avoid re-oxidation of the notch root, which would prevent wetting of the crack tip. Cracks would initiate during loading at the notch roots. During testing, a load would be applied for 30-60 seconds at a constant cross-head displacement rate (equivalent to 10⁻⁴ s⁻¹ strain rate). The specimen would then be unloaded of 10% of the maximum load achieved during the loading
sequence. The crack length was measured optically using a CCD camera to record the image. The liquid metal appears bright and mirror-like compared to the matte steel surface, giving a relatively low uncertainty to the length measurements. This sequence was repeated until one of the two cracks propagating from the center notch reached the edge of the sample, approximately 2 cm on each side [224].

The T91 steel specimens were tested at 160°C with LBE and at 200°C with indium, while the Armco iron was tested with indium at 200°C. The samples were heated by an internal heating (Joule effect) method [224], using a high intensity, low voltage current. The temperature was measured by infrared pyrometer focused ahead of the crack tip. The temperature field was homogenous along the sample width; a temperature gradient occurred at the ends (top and bottom) of the samples where the grips acted as heat sinks. To prevent oxidation of the liquid metal and dewetting due to oxide formation, testing was performed in a reducing atmosphere of Ar-5%H₂.

For fractographic examination, the liquid metal was removed via chemical dissolution in order to preserve the fracture surface. The LBE was removed by a solution of equal parts acetic acid, hydrogen peroxide and ethanol [221]; this solution does not affect the fracture surface. The indium liquid metal was removed by exposing the sample to mercury at room temperature for 5 minutes, and then using ultrasonic cleaning to remove the mercury-indium amalgam. As iron has a very low solubility in mercury, the fracture surface was unaltered.

### 3.2 Microstructural Analysis

Optical, scanning electron (SEM) and transmission electron microscopy (TEM) were used to identify, at different length scales, microstructural features of the pipeline steels that may act as hydrogen trap sites. This approach is necessary to ensure identification of the maximum number of microstructural features, and obtain a measure of the density. Optical analysis allows determination of grain size and percentage of pearlite grains compared to ferrite grains. It can also be used to confirm the presence and determine the density of large particles such as sulfides. SEM allows resolution of the cementite plates in the pearlite and determination of the density.
and compositional analysis of large (~1 μm) particles. TEM allows the dislocation density to be determined, as well as the density and chemical composition of small (~100 nm) particles.

Optical microscopy and scanning electron microscopy were done on bulk samples of the pipeline steels that were polished and etched with a 2% nitric acid in methanol solution. A JEOL 6060LV General Purpose SEM with an Oxford Instruments ISIS EDS System was used for imaging and for chemical analysis of larger inclusions.

For TEM analysis, the steels were sliced and thinned to 100-150 microns and 3 mm-diameter discs were punched from the thinned foil. These discs were thinned to electron transparency using electrochemical jet polishing. A solution of 10% perchloric acid in methanol at -40°C was used with an applied potential of 20 V. These samples were examined in either a JEOL 2010 LaB$_6$ transmission electron microscope operating at 200 kV or a Philips CM12 TEM operating at 120 kV. Energy Dispersive Spectroscopy with an EDAX Dx4 30mm ATW detector on the CM12 was used for chemical analysis. This system has a systematic error of a large copper signal due to the sample holder. This was confirmed by inserting a pure gold sample which still showed a strong copper Kα and Kβ signal, Figure 3.4. As the steels do not contain copper, this signal does not affect the analysis.

Grain size of the stainless steels was determined by electron backscattered diffraction (EBSD) in a JEOL 7000F analytical SEM with an HKL Technology EBSD detector. The tensile specimen was sectioned away from the fracture zone (~ 5 cm) and polished to a mirror finish prior to insertion into the SEM.

![Figure 3.4. EDS spectrum of gold sample showing strong copper signal due to TEM sample holder.](image)
3.3 Fractography

Characterization of the fracture samples was performed using scanning electron microscopy. While the pipeline fracture samples were able to fit into the microscopes as-received, the tensile bars (nickel and stainless steel fatigue samples) were cut using a diamond saw. Samples were attached to SEM mounts using superglue, with carbon tape used for conductivity. This allowed the samples to be loaded into various microscopes and be examined at various magnifications, rotations and tilts without significant drift. Fractography of samples was done in a JEOL 6060LV General Purpose SEM, a JEOL 7000F Analytical SEM, and in a FEI Dual Beam 235 FIB (focused ion beam) operated in electron mode. EBSD analysis to determine fracture planes was done in the JEOL 7000F using an HKL Technologies EBSD detector and software.

In order to fully understand the fracture surface, help is needed to visualize it and transform two-dimensional flattened images into three-dimensional reconstructions of topography that can be manipulated. Stereographic reconstructions of the fracture surfaces were created by taking three images of the features of interest, at 0°, -5° and +10° sample tilt. These images were aligned and reconstructed using the program MeX by Alicona. The program measures the change in position of features compared to the tilt of the sample and calculates a height based upon this change. The program produces a properly aligned stereo-pair, and a three-dimensional reconstruction of the fracture surface. The reconstruction can be rotated in three-dimensions. Several forms of analysis are available, such as line scans from which height differences and angles between planes can be measured.

To examine the finer features of the fracture surface, atomic force microscopy (AFM) was employed. An Asylum Research MFP-3D AFM was used to examine the nickel fracture surfaces, while a Digital Instruments Dimension 3100 AFM was employed for the pipeline steel fractures in order to accommodate the larger sample sizes. Both were operated in tapping mode using BS-Tap300AL tapping tips. As sample positioning on both of these microscopes is done with low magnification optical imaging, sampling of the fracture surface was random. Due to the overall flatness of the pipeline steel failures, measurements were possible of several areas of interest. The roughness of the nickel intergranular failure resulted in difficulties such as taller areas preventing the tip from making contact with the surface and the tip being unable to track the surface due to the steepness of the features.
3.4 FIB Lift-out Technique for TEM

In order to correlate the fracture surface features with microstructural processes, transmission electron microscopy samples were extracted from the fracture surface using a focused-ion beam (FIB) microscope. The samples are thin foils lift-out approximately perpendicular to the fracture surface. Thinned to electron transparency, they allow examination of the microstructure immediately beneath the fracture surface. While this process had been developed for use on flat, preferably polished, surfaces [225-227], for this work, it has been adapted for use on rough fracture surfaces.

The FIB microscopes used were dual beam microscopes from FEI: an FEI 235 FIB at the University of Illinois, an FEI Nanolab 600 Quanta at Brigham Young University, Provo, UT, and an FEI Helios Nanolab 600i at Colorado School of Mines, Golden, CO. Dual beam FIB machines consist of an electron gun situated perpendicular to the sample plane (usual SEM configuration), and a Ga source ion beam gun aligned at an angle of 52° from the electron gun. The accelerating voltage of the Ga ion gun is 30kV. A gas-phase Pt source allows beam activated chemical vapor deposition patterning in both electron and ion mode. For the lift-out process, a micromanipulator (Omniprobe) made of tungsten-plated nickel is used.

Many samples were able to be accommodated within the FIB microscopes without alteration, such as the pipeline steel compact tension specimens, and the Armco iron CCT specimens after the indium was removed to expose the fracture surface. However, some of the fracture samples required preparation prior to FIB sample extraction. The nickel and stainless steel tensile bars were too tall to fit in the microscope, so the fracture surfaces were removed from the rest of the tensile bar by diamond saw cutting approximately 1 cm below the fracture surface. In all of these cases, the FIB samples were extracted directly from the fracture surface features.

A diamond saw was also used to cut the unfractured fatigue tensile bars approximately 2 cm on either side of the crack. This ~4 cm long

Figure 3.5 SEM micrograph of fatigue crack in 316 stainless steel. Trenches remaining from lift-out process show where samples were extracted along the crack flank and immediately ahead of the crack tip.
bar was attached horizontally to an SEM stub with the crack initiation site pointing upwards. Samples were extracted from the polished surface of the bar at various points along the crack, immediately (< 1 μm) ahead of crack, and approximately 5 μm ahead of crack tip, Figure 3.5.

The T91 steel samples, left with their frozen liquid–metal layers covering the fracture surface, were cut at 45° to the fracture surface to expose an area with a high likelihood of containing a fine crack filled with frozen liquid metal [228], Figure 3.6a. Samples were extracted ahead of visible cracks filled with the embrittling metal at a position corresponding approximately to a crack tip, Figure 3.6b. The polished surface shows evidence of mechanical damage from the polishing, however, TEM examination concentrated on an area 5 μm below this surface where the liquid metal was present, Figure 3.6c.

![Diagram showing sample preparation](image)

**Figure 3.6.** a) Schematic showing location of FIB extracted volume. b) FIB micrograph with approximate location of Pt strip marked. c) FIB micrograph showing thinned membrane prior to lift-out. Sample edges marked by dotted line. [228]

After identifying the location of interest, the sample is tilted to 52° to align it with the ion gun. To protect the fracture surface from irradiation damage during machining, a strip of platinum is
deposited by ion beam with dimensions of approximately 30 x 4 x 1.5 μm, Figure 3.7a. The length of the strip can be varied from 25-40 μm to accommodate the fracture feature of interest. The thickness of the strip helps ensure that the layer still remains after the process is complete, preserving the contour of the fracture surface. The first 0.5 μm of the Pt strip is deposited at low ion current density (50 pA) to reduce the dose of the irradiation damage to the fracture surface and to ensure slow deposition with good coverage of the fracture features. For expediency, once the surface is sufficiently covered (~0.2-0.5 μm thick), the deposition rate is increased (current density of 100-300 pA). Using the ion beam, trenches of approximately 10 μm in depth are milled on either side of the Pt strip until the width of the remaining membrane is approximately 1.5 μm, Figure 3.7b. The sample is returned to 0° tilt. A u-shaped cut is made in the membrane to define the dimensions of the sample, Figure 3.7c. The Omniprobe micromanipulator is attached to the membrane with platinum, and the sample is cut free, Figure 3.7d. The sample is transferred to a copper grid and attached by platinum and cut free from the micromanipulator, Figure 3.7e. The sample is then thinned to electron transparency (~100-200 nm), and the surface

Figure 3.7. SEM micrographs showing FIB lift-out process. a) Deposition of Pt layer to protect surface. Pt strip highlighted in red. b) Milling of trenches on either side of Pt layer. c) Milling of u-cut to define sample dimensions. d) Lifting-out of sample on micromanipulator. e) Attachment of sample to 3mm copper grid. f) Thinning of sample to electron transparency.
carefully polished as smoothly as possible, Figure 3.7f. Care is taken to thin the entire depth of the sample.

Because of the roughness of the fracture surface, consideration is needed when choosing sample locations. Unlike on polished surfaces, the topology of rough fracture surfaces can complicate or prevent the extraction process. If the sample location is surrounded by tall features, it may be impossible for the micromanipulator needle to reach the sample, or may block viewing of the sample area when tilted. Local topology is also crucial. Small tilts, undulations and protrusions may be indistinguishable in plan-view, but may block viewing of the sample, preventing the milling of the u-cut, Figure 3.8a. This problem can often be solved by milling longer trenches to remove the higher areas. Additionally, if one trench is deeper than the other and the u-cut is being milled from the deeper side, the u-cut may be positioned such that it is digging into the thick portion of the sample instead of through the membrane. Local tilts in the other direction can also cause problems, Figure 3.8b. If the trenches are not deep enough, it is difficult to form the u-cut and have a sample with enough depth from the fracture surface. Because the sample cannot be too thin before lift-out, it is difficult to deepen the trench at this juncture. Evidently, while sample roughness can be overcome, the lift-out process is easiest if the average plane of the fracture feature is perpendicular to the electron beam (0° tilt), which is a factor to consider when selecting regions for sample extraction.

Figure 3.8. SEM micrographs showing sample geometry issues which may occur. a) Local rise in surface topology obscures side view of sample making milling of a u-cut impossible from this direction. b) Sample extracted from slanted surface (~20°). If trenches are not milled deeper, finished sample may have too small of sampling depth.
Specific locations of interest were chosen to examine based upon fractographic examination, Figure 3.9. In most cases, multiple samples were lift-out from equivalent locations (based on SEM observation), often with different orientation; for example, parallel and perpendicular to fatigue striations, Figure 3.10.

There is some concern over the amount of irradiation damage that can be introduced to the lift-out samples [229]. The typical penetration depth of Ga ions into most structural metals (steel, Ni) is approximately 34 nm for a current of 1000 pA, for irradiation normal to the sample [230], and this damage typically forms small loops. Using low currents helps limit the dose, and the platinum layer protects the material below during operations with higher doses. The fact that fine features from the fracture surface are preserved and can be observed in the TEM gives confidence that the fracture surface is relatively undamaged. Additionally, during thinning/polishing, layers containing large amounts of damage are removed, and, as the final stages are done at lower current densities, successively lower doses of gallium ions are introduced while removing layers which received higher doses. Surface roughness can occur, and cause confusion in the interpretation of the microstructure, but is also reduced by using slower milling rates. The samples themselves show significantly different microstructures depending upon the material and loading conditions. This gives confidence to the interpretations discussed later.
These samples were examined in a JEOL 2010 LaB₆ TEM operated at 200kV in diffraction mode, or using a Hitachi H9000 TEM operated at 300 kV in diffraction mode at Argonne National Laboratory.

Figure 3.10. FIB fractographs showing orientations of platinum strip determining lift-out sample locations a) perpendicular and b) parallel to fatigue striations.
4.1 Pipeline Steel Failure

4.1.1 Microstructural Analysis

The B steel is an API X70/X80 pipeline steel. It is mostly polygonal ferrite with approximately 10% acicular ferrite, Figure 4.1. The average grain size is 3 μm. The steel contains several large (1-5 μm) particles comprised of either MnS or Al₂O₃, both with amounts of calcium, as identified by EDS, Figure 4.2. These particles have a low distribution density. Smaller particles (100 nm) were observed in the TEM, and have a higher distribution density. Several of the particles were identified by their diffraction patterns to be cementite, Figure 4.3. Chemical analysis of these particles revealed only iron. Other small particles were found to contain Ti, Nb, or a mixture of both. These particles are likely carbides or carbonitrides, though their small size makes confirmation by diffraction difficult. They come in a variety of morphologies, Figure 4.4. These carbides are typically intragranular, with a population of approximately 1 per grain. The ferrite grains have a uniformly low dislocation density, Figure 4.5.

Figure 4.1. SEM micrograph showing grain size and shape in B steel. a) wide view. b) higher magnification micrograph showing acicular nature of grain shape.

1 Some of the data presented in this chapter has been published previously. Pipeline steel results were published in Martin, Fenske, Liu, Sofronis and Robertson, Acta Materialia 59 (2011) 1601-1606 and Martin, Robertson and Sofronis, Acta Materialia 59 (2011) 3680-3687. Nickel results were published in a paper in Martin, Somerday, Ritchie, Sofronis and Robertson, Acta Materialia 60 (2012), 2739-2756. Liquid metal results were published in Martin, Auger, Johnson and Robertson, Journal of Nuclear Materials 426 (2012), 71-77. Reprinted with permission of the publisher.
Figure 4.2. SEM micrographs and EDS spectra of inclusions in B steel. a) Manganese sulfide particle. b) Aluminum oxide particle.

Figure 4.3. TEM micrograph showing cementite particle. a) Bright field image of particle. b) Diffraction pattern showing cementite [010] zone axis (marked by box). Larger spots correspond to ferrite background.
Figure 4.4. TEM micrographs and EDS spectra of carbides in B steel. a) Square precipitate containing titanium and niobium. EDS of the matrix shown for comparison. b) Two round carbides and the accompanying EDS spectrum for each. Note: in each spectrum, copper signal is due to background signal from the sample holder.

Figure 4.5. TEM micrograph showing microstructure in B steel. Two precipitates are noticeable in the center of the frame. A low dislocation density is observed in the surrounding grains.
The D steel is an API X60 HIC pipeline steel. It is predominately polygonal ferrite, Figure 4.6. The average grain size is 5 μm. Similar inclusions to those in the B steel also exist in the D steel. The ferrite grains exhibited limited evidence for dislocation activity, Figure 4.7a. Small carbides are common, either cementite or (Ti,Nb) carbides, Figure 4.7b. These carbides typically reside within the grain, with a population of approximately 1-3 per grain.

![Figure 4.6. Grain size analysis of D steel. a) Optical micrograph showing grain structure. b) SEM micrograph showing morphology of grains.](image)

![Figure 4.7. TEM micrographs showing initial microstructure of D steel. a) Low dislocation density observed. b) Typical carbide observed in D steel.](image)
4.1.2 Fracture Overview

Compact tension specimens of the pipeline steels were received from Sandia National Labs in Livermore, CA. These samples were pre-cracked in air, tested in gaseous H$_2$, heat tinted, and then overloaded to fracture in LN$_2$, or in some cases, overloaded in air at room temperature. One sample was of B steel tested in 21 MPa H$_2$. Three D samples were tested, one in 21 MPa H$_2$, and two in 103 MPa H$_2$, one of which was also overloaded in air. There did not appear to be a significant difference in fracture toughness behavior between the tests at different pressures of hydrogen gas, Figure 4.8. The average fracture toughness measured in steels B and D in gaseous hydrogen are 110 and 85 MPa m$^{1/2}$, respectively [231].

The three areas of the fracture surface are distinct in both optical and SEM observation. In optical, the smooth fatigue pre-crack is easily distinguished from the roughness of any further fracture. The heat tint of the hydrogen cracked region makes it easily distinguishable from the fast fracture region following it, Figure 4.9. The interface between the hydrogen fracture and overload regions is slightly curved, showing the thumbnail shape of the hydrogen fracture crack. The fast fracture region is typically faceted in appearance, and there is little evidence of global plasticity. In the case of overload at room temperature, the ductile fast fracture region appears much rougher, and evidence of ductile tearing is evident at the back end of the sample.
In SEM observation, the differences in the areas of the fracture surface are distinct, Figure 4.10, with a noticeable change in the texture and type of features observed. The hydrogen fracture is often delineated from the fatigue pre-crack by a secondary crack running into the surface, though this feature is not always there, Figure 4.10b. In the case of ductile rupture, the interface to the ductile rupture is clearly marked by a tall (~100 μm) shear lip leading to the ductile rupture, Figure 4.10c and Figure 4.11. Upon closer inspection, the shear lip appears to be composed of stretched voids, Figure 4.11b. The overload regions are of interest because they demonstrate features typical of failure, both brittle and ductile, when environment, other than temperature, is not a contributing factor.

Figure 4.10. Low magnification SEM fractographs showing the different areas of failure: fatigue pre-crack on the right, hydrogen fracture crack in the middle, and final fast fracture on the left.  a) SEM fractograph showing curvature of thumbnail-shaped crack.  b) SEM fractograph showing secondary crack delineating part of boundary between fatigue pre-crack and hydrogen crack.  c) SEM fractograph of sample that was fast fractured in air producing ductile failure, sample tilt is 52°. Note that large secondary crack in image is within the hydrogen failed region, not at fatigue boundary.
4.1.3 Ductile Overload

High strength low alloys steels would be expected to fail by ductile processes at room temperature in the absence of hydrogen. This is observed in the fast fracture region of a D steel sample, where microvoid coalescence appears to be the primary fracture mode, Figure 4.12. The dimples appear uniform in size, at approximately 20 μm in diameter, and circular in shape. Closer inspection shows a second set of dimples around the edges of the large dimples with diameters of approximately 1 μm, Figure 4.12b,c. The insides of the dimples are rough, with occasional shear lips suggestive of where several smaller voids combined to form a larger one. Upon tilting, the voids only flatten slightly, suggesting they are marginally deeper than they are wide, Figure 4.12c. This is supported by the 3-D reconstruction showing a typical dimple to be approximately 30 μm in depth, Figure 4.13.
To examine the microstructure underneath, a FIB sample was extracted from the basin of a dimple. Beneath the rough surface, a complex cell structure exists consisting of bands separated by dislocation walls, Figure 4.14. The bands vary in contrast along their lengths; sub-walls are not evident in most microbands. The bands primarily run nearly parallel to the local fracture surface, though this varies, particularly with distance from the fracture surface, Figure 4.14a. There is a variation in band thickness with larger bands approximately 500 nm in thickness and finer bands less than 100 nm in thickness, Figure 4.14b. The bands immediately beneath the surface have a tendency to be thinner than those further from the fracture surface, Figure 4.14c, though there does not appear to be a direct correlation between band width and distance from the fracture surface. The microstructure extends for more than 10 μm (limit of FIB sample) with
local variations in shear band orientation and thickness, Figure 4.14d, though the microstructure becomes difficult to resolve past 10 μm in depth due to sample thickness.

Figure 4.13. 3-D reconstruction from SEM stereo pair of ductile fracture feature.

Figure 4.14. TEM micrographs from FIB sample extracted from void basin. a) Area immediately beneath fracture surface. b) Area immediately beneath different region of fracture surface. c) Closer view of microstructure immediately beneath fracture surface. d) Microstructure approximately 2 μm from fracture surface.
4.1.4 Brittle Overload

The low temperature overload region is easily defined by the large facet features, Figure 4.10a,b. At higher magnification, the interface between the two areas is not smooth, but there is a clear difference between the features in the hydrogen-assisted failure and the liquid nitrogen induced cleavage features, Figure 4.15.

Figure 4.15. SEM micrograph showing transition region between hydrogen-assisted crack (right) and the cold fast fracture surface (left). The cleavage features are significantly larger than most features observed in the hydrogen-assisted crack region.

At liquid nitrogen temperature, iron has undergone a brittle-to-ductile transition, and the primary fracture mode is by cleavage. This is evident in the fractographs shown in Figure 4.16, where cleavage features are evident with various orientations relative to the sample normal. The fracture plane was determined by EBSD spot analysis. The zone axis was identified for several features which were nearly perpendicular to the detector. The fracture planes were within 10° of {001} which is the expected body-centered cubic cleavage plane; the deviation is due to tilt of the fracture plane relative to the detector.
The features in D steel are typically on the order of 10 μm, Figure 4.16b, with a similar size observed in the B steel. As these features are larger than the grain size of either steel, they are likely due to the coplanar failure of several adjacent favorably aligned grains, Figure 4.16c. While some areas in planar view appear to consist of features that are all within a few degrees of perpendicular to the view direction, others clearly show faceting in various directions, Figure 4.16b. The large variation in facet orientation is more evident after tilting. The cleavage fractures are typically fairly smooth in texture, with very little contrast, Figure 4.16c. However, certain features display a rough texture suggesting parallel plane failures connected by steps, Figure 4.16d. Inclusions do not appear to have had a large impact on the fracture path or mechanism, Figure 4.17.
Samples were extracted from cleavage facets in both the B and D steel. In both cases, a low dislocation density was found beneath the fracture surface, Figure 4.18. This density does not appear to vary greatly with distance from the fracture surface. Individual dislocations are imaged, and are in random orientations, not organized slip systems. Irradiation damage can be seen as the speckled contrast particularly evident in Figure 4.18a, however, it is distinct from the dislocation contrast. In the sample from steel D, grain boundaries were observed, Figure 4.18b, confirming the hypothesis that these large facets are due to nearly coplanar failure across several adjacent grains.

In the sample from the B steel, twins were observed, Figure 4.19. It is difficult to determine whether twinning significantly impacted fracture. The fracture surface does change direction to follow a larger twin, Figure 4.19b, but the fracture surface does not follow the entire length of the twin, suggesting a local effect due to the presence of the twin rather than cracking along the twin boundary. The arrangement of the twins suggests that they were formed ahead of the crack tip and are incidental to fracture [232]. Though twins were not observed in the D steel, this may...
simply be an issue of the limited sampling by the FIB-TEM technique. Given the similarity in microstructures and chemistry, it seems unlikely that the steels would deform in a significantly different manner.

![TEM micrographs showing twins beneath cleavage fracture in 'B' steel.](image)

**Figure 4.19.** TEM micrographs showing twins beneath cleavage fracture in 'B' steel. a) Twin intersecting fracture surface (bottom left). Diffraction pattern of [011] zone axis with twin spots shown in inset. b) Two parallel twins of different thicknesses near the fracture surface (upper right). Note how the fracture surface changes direction upon encountering the larger twin.

### 4.1.5 Hydrogen Fracture

The region of hydrogen fracture is macroscopically flat, but textured. Different regions show

![SEM fractographs of secondary cracks.](image)

**Figure 4.20.** SEM fractographs of secondary cracks. The primary crack propagation direction is to the left. a) Large secondary crack (lamination) running into the fracture plane and extending parallel to the main crack direction. b) Small secondary crack running into the fracture plane and extending perpendicular to the main crack direction.
height differences of tens of microns between them. These are often separated by rough regions, likely due to the joining of parallel cracks through rapid failure processes such as tearing. Within the hydrogen fracture region, several different distinct features are evident.

Secondary cracks are present throughout the hydrogen fracture region, Figure 4.20. Some cracks might be more accurately labeled as laminations. Laminations are proposed to open up in order to relieve stress in the sample over a large scale. They run into the fracture plane, and their propagation direction is parallel to that of the main crack, Figure 4.20a. These cracks tend to be large, often more than 500 μm in length, and show significant crack opening. Ductile fracture modes are sometimes observed to have occurred within these cracks. Other smaller secondary cracks are present, often showing branching from the main crack away from the main fracture plane, Figure 4.20b. These cracks tend to show limited crack opening, and appear to fail due to similar processes as the main crack.

Figure 4.21. SEM fractographs showing failure features due to inclusions. a) Inclusion sitting in void. b) Void failure that occurred around an inclusion with the inclusion missing. The inclusion is likely either on the other side of the fracture, or fell out during testing.

Another set of large fracture features on the surface is due to the presence of inclusions, Figure 4.21. Inclusions are found along the fracture surface sitting in pits or voids larger than the diameter of the inclusion, Figure 4.21a. In some cases, the void is present although the inclusion is missing, Figure 4.21b. These cases may occur due to the inclusion being left on the opposing fracture surface, or the inclusion may have fallen out during failure. Chemical analysis shows
that the inclusions are typically composed of aluminum oxide, Figure 4.22, though sometimes including elements such as magnesium or calcium. Failure likely occurred by decohesion of the inclusion interface, possibly helped by hydrogen, followed by limited void growth. These features typically do not impact the fracture features surrounding them, generally appearing as isolated features that have incidentally intersected the fracture plane. In a very few cases, secondary cracks were seen extending from the failed inclusions, Figure 4.23. These cracks did not extend very far (< 50 μm) from the crack origin at the inclusion. If this is a typical mechanism of secondary crack initiation, it was not evident, though initiation of other larger secondary cracks may have occurred at inclusions not on the main crack plane and therefore are not visible to plan-view fractographic techniques.

Figure 4.22. EDS spectrum of oxide inclusion containing aluminum and magnesium.

Figure 4.23. Secondary cracking extending from an inclusion (a) and from an inclusion pit (b).
There are two features of interest on the fracture surface, one which has river patterns, and one which does not, Figure 4.24. The feature with the river pattern is labeled as “quasi-cleavage” and the other is labeled as “flat” in order to distinguish them. Both of these features appear to be approximately equal to the grain size of the samples, and thus are different for each steel type due to the different grain sizes. In the B steel samples, which have a smaller grain size than the D steel, feature sizes were smaller. In the B steel, the “quasi-cleavage” features appeared to be rarer than in the D steel, those this perception may be based upon the features being very small and difficult to distinguish. Occasionally in both samples, unusually large features (~20 μm) were observed. These are quite likely cases where adjacent grains are separated by low angle boundaries, allowing nearly continuous fracture to occur. This is supported by features where the ridges of a quasi-cleavage feature continue across a short step likely indicating the presence of a low angle grain boundary, Figure 4.25. In the case of different mode features, they are often separated by a shear lip. However, in some cases there is a nearly perfect continuous plane transition from one feature to the next, Figure 4.26. What allows the continuous fracture across these two features, but with a change in fracture mode is not evident from the fractography. In the following, each of the two feature types is investigated in depth.
4.1.5.1  "Quasi-cleavage"

"Quasi-cleavage" features have several different morphologies, Figure 4.27. In the majority of cases, the river pattern markings appear to be parallel to the crack propagation direction, with a few exceptions, Figure 4.27a; variations are probably due to local deviations in the crack path due to local stress state and grain orientation. The river markings can be nearly evenly spaced and parallel, Figure 4.27b. In several of the features, branching of the markings can be seen, which then become nearly parallel with similar spacings between them, Figure 4.27c. The average separation between ridges is around 1 μm. The markings can be continuous along the length of the feature, or discontinuous, Figure 4.27d. In some cases, the markings seem to radiate outwards from the base of the feature, in some cases resembling fan spines and in others more closely resembling a herringbone pattern, Figure 4.27e. While sometimes transitioning smoothly from one feature to another, there are sometime shear lips or rough steps separating adjacent features, Figure 4.27f.
Figure 4.27. SEM fractographs of morphologies of "quasi-cleavage" features. a) Two neighboring features with different river pattern directions. Main crack propagates right-to-left. b) Feature with straight parallel continuous river markings. c) Feature with highly branched continuous river markings. d) Feature with straight parallel discontinuous river markings. e) Feature with radiating pattern. f) Several adjoining quasi-cleavage features separated by rough boundaries.
Figure 4.28. a) SEM image showing the quasi-cleavage fracture surface at 0 tilt; b) same feature at 55° tilt; c) Reconstructed model of a select area on the surface, showing the presence of the ridges, arrowed features, and the undulating nature of the area between the ridges; d) feature in c) rotated by 180°. Adapted from [233].
Closer examination of the white striations at various tilts reveals that they are ridges, usually 100-200 nm high, Figure 4.28 [233]. Stereographic reconstructions were conducted to confirm this topology, Figure 4.28c-d. These ridges typically exhibit a distinct v-shape. The areas between ridges show a certain amount of contrast, and lift-out samples suggest that they are not entirely flat. This topology was confirmed by AFM measurements, Figure 4.29. These ridges are topped by saw-teeth peaks thin enough to be electron transparent to a 12 keV electron beam, Figure 4.30. This suggests that the saw-teeth are less than 100 nm in thickness. These peaks are reminiscent of ligament failure seen at the final phases of failure during in situ straining experiments, when material that was initially opaque to the electron beam (400 nm) necks down to electron transparency by extensive plastic deformation, then finally fractures along slip bands, Figure 4.31.

![Figure 4.29](image1.png)

Figure 4.29. a) Depth map generated from AFM of “quasi-cleavage” fracture region. (b) Line scan taken perpendicular to ridges. Height difference measured between markers is 170 nm.

![Figure 4.30](image2.png)

Figure 4.30. SEM micrographs of electron transparent saw-teeth topping the ridges in a) D steel and in b) B steel.
Point scans using EBSD were done to attempt to identify the fracture plane. Shadowing from surrounding features was problematic. Though decent quality Kikuchi patterns were taken, they were unable to be identified. It is possible that the strain in these areas distorted the patterns too much for proper identification. Additionally, as these were spot patterns, it would be difficult to sample a sufficient number of points such that there would be confidence in the zone identification.

TEM analysis was conducted on samples extracted from the quasi-cleavage features. An important feature to notice is that the ridges are preserved by this process and that their dimensions and spacing match those acquired through the surface techniques, Figure 4.32. In samples taken perpendicular to the ridges, there is evidence of extensive deformation that extends for microns from the fracture surface; this distance is determined by the sample size and is not an indication that the microstructure ends at this depth. Immediately beneath the ridges on the fracture surface, densely packed slip bands were observed parallel to the ridge faces, Figure 4.33. The projected direction of these lines on the TEM foil surface is parallel to traces of the \(\{321\}\) family of slip planes in the body-centered cubic system. The roughness on the surface would be consistent with fracture along closely spaced slip systems. Other views show areas of high dislocation density, Figure 4.34. This difference may be due to a local difference in

Figure 4.31. a) TEM micrograph of an initially electron opaque region of an Al TEM foil strained to failure in situ in the microscope. b) SEM micrograph of fracture surface produced in an initially electron opaque region in a Cu-Co alloy deformed at room temperature in situ in the TEM. Images courtesy of G.S. Liu. Adapted from [233]
dislocation structures, or due to the angle allowing viewing of the dense dislocation density on the slip bands, such as those observed in Figure 4.33, as opposed to observing them edge-on.

In samples taken parallel to the ridges, slip bands were observed with a limited amount of dislocation activity observed between slip planes, Figure 4.35. In certain views, the slip bands appear to form cell boundaries, Figure 4.35a, however, in other cases, they appear as discrete parallel, or nearly parallel, slip bands, Figure 4.35b. The dislocation density appears to be lower in samples taken in this direction, suggesting that slip is limited to certain directions.
While fine carbides (Ti/Nb carbonitrides or cementite) were observed, Figure 4.36, they did not appear to impact fracture. Carbides within 100 nm of the fracture surface appear to have no influence on the local fracture surface morphology, Figure 4.36a. Some carbides were found on or very near to the fracture surface, Figure 4.36b. In most cases, the fracture surface was unaffected, even if the carbide was sitting on the surface, suggesting that the crack coincidentally intersected a carbide. In none of the cases observed were there any voids associated with carbides, suggesting that these fine carbides are not a significant nucleation site for local failure.

![Micrograph](image1)

**Figure 4.34.** TEM bright-field micrograph of microstructure beneath "quasi-cleavage" feature in B steel. Sample was taken perpendicular to ridges.

![Micrographs](image2)

**Figure 4.35.** TEM micrographs of samples taken parallel to "quasi-cleavage" ridges. a) Wide-view showing dislocation bands with minimal dislocation activity in between. b) Parallel dislocation bands with individual dislocations apparent in between.
4.1.5.2 **“Flat” Features**

Flat fracture features are large features, typically 5-20 microns in diameter, Figure 4.24 and Figure 4.37. They are often leaf shaped, with a thinner, sometimes obscure, beginning, and a wider, rounder and sharply defined end, often marked by a tear ridge, though these features can become more obscured leading to a more round or oval appearance. In other areas, and particularly in the B steel, these features are more elongated with shear lips on each edge of the features, Figure 4.38. The shape of these features may be due to the more acicular nature of the ferrite grains in the B steel. While macroscopically flat in appearance, particularly in plan-view, there is some contrast observed within the feature. Most flat features have a “flat” base running parallel to the net crack growth direction (along the center vein of leaf). From this base, the edges appear to slope gently upwards, Figure 4.37b, with tilting this slope can be seen to be significant. In some cases, branching of the deeper center vein is observed, Figure 4.37c, leading to multiple changes in the slope of the feature. Closer examination after tilting the sample reveals that certain features have a smooth rolling contour, Figure 4.39.
Figure 4.37. a) SEM micrograph of flat feature. b) SEM micrograph of feature in a) at 52° tilt. c) Large flat feature. d) Same feature as c) at 52° sample tilt. Note that while the feature in b) has a center vein with the feature tilted on either side of it, the feature in d) has several changes in plane direction.
Figure 4.38. a) Fractograph of hydrogen fracture surface in B steel with the flat features marked by arrows. Note the elongated shapes common to these features. b) Elongated flat features in D steel.

Figure 4.39. SEM fractograph of 'flat' feature with sample tilted at 70° showing the rolling nature of the feature.
High magnification fractography reveals further surface texture to the flat features, Figure 4.40. This texture is more evident when the surface is tilted relative to the incident beam. Fine dimple-like features approximately 100 nm wide cover the surface. While the contrast at higher magnification, Figure 4.40d, does suggest fine dimples with shear lip-like edges, the contrast and amount of detail still leave some ambiguity. The fineness of the scale makes accurate stereo reconstructions difficult. AFM measurements confirm the presence of these features, Figure 4.41, but were unable to remove the ambiguity of their shape (mounds vs dimples) due to the resolution of the AFM tip. The height of the features was measured to be on the order of 5nm.

Point scans using EBSD were attempted in order to identify the fracture plane. While shadowing from surrounding features proved problematic, several areas with clear lines of sight were found.
However, clear Kikuchi patterns could not be resolved on any of the features scanned. It is presumed that the strain in these areas is too great for resolvable Kikuchi patterns.

TEM examination of FIB lift-out samples from these features confirm that the fracture surface is not a flat plane, but curved, Figure 4.42a, preventing the assignment of a fracture plane. Additionally, it was confirmed that the edges of the fracture features generally correspond to grain boundaries. The microstructure was observed to consist of massive amounts of plasticity, Figure 4.42. Distinct dislocation tangles, along with loops, form a structure with a spacing of approximately 100 nm, Figure 4.42b. This length scale is similar to that of the fine surface features. This dislocation density continues unabated across grain boundaries, Figure 4.42a.
This high dislocation density continues undiminished for at least 10 microns from the fracture surface (the sample size), showing no sign of a gradient in density, and suggesting it continues even deeper into the sample. A collection of cementite particles was observed near to the fracture surface, however, the fracture surface appears unaffected by their presence, and no voids were observed around the particles, Figure 4.43.

Figure 4.42. TEM micrographs showing dislocation structure underneath 'flat' fracture features. a) The dense dislocation density is evident immediately beneath the fracture surface. At the right side of the lower grain, the contrast shows that a similar dislocation density is present at that depth as well. Note that the fracture surface is curved with two short waves visible in this view. B) Higher magnification micrograph immediately beneath a ‘flat’ fracture feature (left side) in a different grain from a). Note the presence of loops along with the tangled dislocations.

Figure 4.43. TEM micrograph showing cementite particles beneath the fracture surface. Note how the fracture surface does not appear to be affected by the presence of the particles, nor are there any voids visible along the boundaries of the particles. Also note that the change in direction of the fracture surface (left) can be associated with the grain boundary, suggesting a change in fracture direction in the differently oriented grain.
4.2 Nickel Intergranular Failure

The Ni-201 alloy chosen for this study has an original grain size of 30 μm, as measured by EBSD, Figure 4.44. In the EBSD image, boundaries are marked by type: black boundaries are random, red boundaries are Σ3 twin boundaries, and blue boundaries are Σ3” special boundaries. The special boundaries comprise approximately 1/3 of the boundaries measured. However, most of these consist of Σ3 twin boundaries within grains defined by random boundaries. The texture is approximately that of a random polycrystal [219]. As the material was received in the “soft annealed” condition, and the ESBD maps show little distortion due to strain [219], the initial microstructure is likely to be clean with a low dislocation density.

Samples charged with 2000 appm hydrogen failed with a mean reduction in area of ~13%. This is a significant decrease from the original range of values of 74-86% reduction in area for the unexposed samples [219]. The sample received had a strain to failure of 13%, by which point yielding had occurred. The failure did not occur at the midpoint, but at approximately ¾ of the gage length, Figure 4.45.
Failure is nearly completely intergranular, Figure 4.46. The grain size can be seen to correspond to the original grain size of 30 μm. While most facets are flat, or slightly concave, a few peaks show signs of significant deformation, Figure 4.47. Nearly all facets are covered with slip traces, but the area between the slip traces tends to be rather smooth and unmarked, Figure 4.48. In most cases, only one set of slip traces is visible, though different sets may be visible in different areas of a facet, Figure 4.49. However, in some cases, two or three sets can be seen intersecting. The density of the visible slip bands appears to vary from facet to facet. At some grain boundary intersections, slip traces can be seen to propagate from one grain to the next, though if multiple sets encounter a grain boundary, often only one is visibly transmitted, Figure 4.50. In the example [234] shown in Figure 4.50b, there are two parallel twin boundaries, evidenced by the peaks on the facet. A set of slip traces encounters the first boundary (B), and is transmitted, though deflected from direction 1 to 2. At the second twin boundary (A), the slip traces are again transmitted, and deflected back to their original direction (3). These results closely parallel those observed during in situ straining where dislocation slip systems passed through two parallel twin boundaries: a change in direction was observed after the first boundary, and the slip returned to the original propagation direction after passing through the second boundary [235].
Figure 4.46. SEM micrograph showing wide view of nickel intergranular failure due to hydrogen.

Figure 4.47. SEM micrographs showing different morphologies of the intergranular failure. a) Clean "brittle" appearing fracture. b) Heavily deformed facets.
Figure 4.48. SEM fractographs showing facet texture. a) Slip band texture on three different facets. b) High magnification image of left facet showing texture between slip bands.

Figure 4.49. SEM micrographs of intergranular facet in nickel due to hydrogen. a) Facet with at least three different sets of slip traces visible in different regions of the facet. b) Higher magnification of the facet showing the intersecting slip bands.
Atomic force microscopy measurements were taken of a peak, likely a twin boundary where slip bands are observed continuing on both sides of the peak, Figure 4.51. The steps average 150 nm in height, which corresponds with SEM measurements. With the lattice constant of nickel being 3.25 Å, and a Burgers vector of type $\frac{a}{2}(110)$, this would translate to ~600 dislocations having passed through the grain boundary to produce each step.

While the SEM and AFM results suggest that plasticity is significant for intergranular failure, they do not address the role of the plasticity. To determine the relationship of the slip traces and dislocation activity to the intergranular failure, FIB lift-out samples were taken from facets on the fracture surface for examination in the TEM.
TEM samples were extracted from an intergranular facet, perpendicular to the visible slip bands, Figure 4.52a. In the case of the region shown in the figure, classical interpretation would have concluded that only one slip system was active. The microstructure immediately beneath the fracture surface shows evidence to the contrary, Figure 4.52b. There is a high dislocation density which is organized into a well-developed cell structure that extends for several microns below the fracture surface. The average cell size is on the order of 200-400 nm. This cell size, and the
dislocation density, do not appear to change for several microns from the fracture surface, Figure 4.53. As there is no evident gradient in the dislocation density with depth over the 10-15 microns of the sample, and given that the grain size is on the order of 30 microns, it is strongly suggested that this high dislocation density is continuous through the entire grain.

![TEM micrograph showing the dislocation cell structure ~5 μm from the fracture surface.](image)

The steps on the fracture surface appear sharp and defined, and the step heights correspond to the AFM measurements. The form suggests that they are the result of periodic shearing of the grain boundary caused by significant slip across the grain boundary. It appears that the steps in the grain boundary coincide with cell walls. As would be expected with the 1 μm spacing of the steps, and the 200-400 nm diameter of the cells, steps do not coincide with every cell wall intersection with the fracture surface. This also supports the idea that the steps correspond with shearing of the grain boundary, and not by the emergence of dislocations associated with the crack advance. There is some evidence of the cells stretching towards the steps on the fracture surface, Figure 4.52b. This may be due to the shearing of the cell when the step was formed or due to relaxation after fracture occurred.

It is worth noting that there is no evidence of a grain boundary immediately beneath the fracture surface. Although samples were only taken from one side of the fracture, they were sampled from different grains. This supports the idea that the failure was true intergranular failure, not failure parallel and immediately adjacent to the grain boundary.
Slices were cut from the sample gage between 3 and 6 mm from the fracture surface to examine the microstructure of the bulk. These slices were ground, polished, and jet polished using a solution of 20% sulfuric acid in methanol to produce conventional 3 mm disk TEM samples. The resulting microstructure, Figure 4.54, consists of dislocation cells with average cell diameters of 400-800 nm. This size varied slightly with location, with the smallest cells observed having diameters on the order of 200 nm and the largest having diameters near a micron. As this cell size is slightly larger than that observed immediately beneath the fracture surface, it would suggest that the effective strain at the fracture surface was slightly higher than in the bulk. However, these results suggest that the plasticity is extensive throughout the gage length of the sample.

![Figure 4.54. TEM micrographs showing bulk microstructure (at different distances between 3-6 mm from intergranular fracture surface) consisting of dislocation cells.](image)

### 4.3 Fatigue of Stainless Steels

The 304 stainless steel microstructure is fully face-centered cubic austenitic with an average grain size of ~15 μm, Figure 4.55. The material has a number of annealing twins present. The 316 stainless steel microstructure is fully FCC austenitic with an average grain size of ~13 μm, Figure 4.56. The material also has a number of annealing twins which break up some of the large grains.
Figure 4.55. EBSD orientation map showing grain size and orientation of 304 stainless steel.

Figure 4.56. EBSD orientation map of 316 stainless steel showing grain size and orientation.
The addition of hydrogen to the system leads to degradation of fatigue properties. A comparison of the crack length as a function of number of cycles for the 304 steel in air and in a hydrogen environment is shown in Figure 4.57. As can be seen, the crack grows significantly faster in a hydrogen environment than in air, and fails after a fewer number of cycles. In this case, the reduction of fatigue life is nearly 30%. Previous data [62] suggests that a similar relationship should hold for the 316 stainless steel, though the effect of hydrogen will be less.

![Figure 4.57. Crack growth as a function of cycles of 304 stainless steel both in air and in a gaseous hydrogen environment.](image)

### 4.3.1 Effect of Hydrogen on Fracture Surface

SEM examination showed that the fracture surface was comprised predominantly of striations. Fractographs, acquired approximately the same distance (~1 mm) from the crack origin, from the uncharged and hydrogen-charged steels are compared in Figure 4.58 for the 304 stainless steel tested in air and in gaseous hydrogen environment and in Figure 4.59 for the uncharged and hydrogen-charged 316 stainless steel. From a simple visual inspection, it is obvious that the test environment influences the striations in both steels, with the distance between striations as well as the striation height decreasing when hydrogen was present either in internal or external form. Quantitatively, the striation spacing decreased from 1 μm to 300 nm in 304 stainless steel and from 3 μm to 700 nm in 316 stainless steel due to the presence of hydrogen. The striation height
in 304 stainless steel could be up to 200 nm in uncharged material compared to ~50 nm in the presence of hydrogen. In 316 stainless steel, the striation height decreased from 175 nm to 80 nm due to solute hydrogen. Other differences attributable to the presence of hydrogen include the overall roughness of the fracture surface, Figure 4.60. In uncharged samples, the fracture surface was more uniformly flat with different areas of striations at approximately the same height, Figure 4.60a, whereas, in the presence of hydrogen, steps a micrometer or more in height separated different sets of striations, Figure 4.60b. Furthermore, flat features with barely perceptible striation bands, Figure 4.61, were observed in the presence of hydrogen but not without. This feature might suggest that rubbing during closure is greater in the presence of hydrogen and this, in turn, generates the flatter surface with less distinct features, or it might be indicative of failure along an interface such as a martensitic interface or a twin boundary [63, 236]. This latter possibility is suggested by the facet-like quality of the feature in Figure 4.61b. At higher resolution, it is seen that such surfaces are covered with fine striation markings; compare Figure 4.61d, which is the boxed area in Figure 4.61c at higher magnification, with Figure 4.59b. If these features were attributable to rubbing contact, the microstructure beneath the fracture surface would be different from under striations.

Figure 4.58. Striations on the fatigue surface in 304 stainless steel fatigued in a) air and in b) 10 MPa gaseous hydrogen.
Figure 4.59. Striations on fatigue surface in 316 stainless steel fatigued in air a) uncharged and b) charged with hydrogen.

Figure 4.60. a) Wide view fractograph showing smoothness of the 304 fracture surface in air. b) Fractograph showing roughness of fracture surface in presence of hydrogen. Crack propagation direction in both images is approximately up.
4.3.2 Microstructure beneath 304 Stainless Steel Striations

In the case of 304 stainless steel tested in a high-pressure gaseous hydrogen environment, the microstructure beneath the striations evolves with distance from the fracture surface. As shown in the bright-field micrographs presented in Figure 4.62, immediately beneath the striations, there exists a layer 0.5 - 1 μm thick of irregularly shaped sub-grains with dimensions between 50 - 200 nm, which is a significant reduction from the original grain size of 15 μm, Figure 4.62c. The diffraction pattern from this area, Figure 4.62c inset, shows splitting of the diffraction spots. This indicates the misorientation between adjacent sub-grains is a few degrees. Occasionally, as evident in Figure 4.62b, immediately below the fracture surface, shear bands are seen to extend.

Figure 4.61. a) Flat features on 304 fracture surface in hydrogen. b) Flat facet-like features in hydrogen-charged 316. c) Flat feature in hydrogen-charged 316. d) High magnification image of feature in c) showing striation-like markings.
directly from the fracture surface, through the layer of refined grains, to a depth of at least 15 μm; this depth is set by the size of the extracted sample and does not suggest that this microstructure terminates at this distance. Dislocations, but not other phases, exist within these bands.

Figure 4.62. TEM micrographs showing microstructure immediately beneath striations of 304 stainless steel fatigued in a 10 MPa gaseous hydrogen environment. a) Overview of microstructure showing fracture surface in upper right corner. b) Shear band extending from fracture surface. c) Fine grain structure immediately beneath fracture surface. Inset shows diffraction pattern (<111> zone axis) taken from area showing splitting of spots due to small rotations between grains. d) Martensite laths approximately 5 μm from fracture surface.

Beneath the layer of sub-grains, and extending through the depth of the FIB sample (10-15 μm in depth), is a microstructure consisting of planar features and dislocations, see Figure 4.62a and d. Analysis of selected area diffraction patterns revealed the presence of a BCC structure within a FCC matrix, which is consistent with the planar features being laths of strain-induced α’ martensite, Figure 4.63b. The laths are approximately 100 nm-wide with an inter-lath spacing on the order of 100 - 500 nm. As shown in the micrographs presented in Figure 4.63a-b, which was from a sample extracted perpendicular to the striations, several intersecting martensite lath variants coexist. At lath variant intersections, one variant is displaced suggesting that they
formed sequentially with the last formed cutting through and displacing the others. The martensite laths appear to line up with the surface striations, but the surface layer of refined grains interrupts the intersection and prevents a direct correlation. The microstructure of samples extracted parallel to striations, as shown in Figure 4.63c, was similar to that in samples extracted perpendicular to the striations, although more variants of martensite were apparent in the perpendicular slices.

In uncharged 304 stainless steel fatigued under ambient conditions, the microstructure is again refined but to a significantly lesser extent than when the tests are conducted in a high-pressure gaseous hydrogen environment. The resulting microstructure, as shown in the micrographs presented in Figure 4.64, consists of elongated grains with a diameter of ~500 nm and extends at
least 10 – 15 μm from the fracture surface; again, the depth is set by the size of the extracted sample, and should not be interpreted as indicating that the microstructure ends at this depth. A similar microstructure exists in samples extracted parallel to the striations. Analysis of selected area diffraction patterns confirms that these grains have a predominantly BCC structure with only a few exhibiting an FCC structure. This was confirmed by EBSD on the FIB sample. That is, much of the volume beneath the fracture surface and extending 10-15 μm from it has been transformed to martensite, which is in marked contrast to the evolved microstructure produced when tests were conducted in a gaseous hydrogen environment. As in the case of 304 stainless steel deformed in a gaseous hydrogen environment, there was no obvious correlation between the refined microstructure and the features on the fracture surface, as shown in Figure 4.64b.

4.3.3 Microstructure beneath 316 Stainless Steel Striations

The depth dependence of the evolved microstructures beneath the fracture surface of hydrogen-charged 316 stainless steel is presented in the electron micrographs of Figure 4.65. This microstructure consists of a refined sub-grain structure with grains 100 – 200 nm in diameter existing to a depth of 1 μm beneath the fracture surface, Figure 4.65a. Again, this is a significant decrease from the original grain size of 13 μm. It is also consistent with the effect of a gaseous hydrogen environment on the microstructure immediately beneath striations in 304 stainless steel; compare the micrographs presented in Figure 4.62 and Figure 4.65. With increasing distance from the fracture surface, the microstructure transitions from a refined sub-grain structure to one consisting of dislocations and planar features that lie perpendicular and parallel
to the fracture surface. An example of this microstructure is shown in the micrograph presented in Figure 4.65b; examples of the planar features are indicated by arrows. As can be seen from the micrograph, the planar features perpendicular to the fracture surface appear to be more closely spaced than those parallel to it. Diffraction pattern analysis revealed austenite and twinning in the FCC system, Figure 4.66. The lack of martensite in the hydrogen-charged 316 stainless steel is expected and is in marked contrast to the evolved microstructure in 304 stainless steel tested in a gaseous hydrogen environment. Similarly to the martensite laths in the 304 steel fatigued in hydrogen, the twins in the hydrogen-charged 316 steel show evidence of displacement relative to other sections of the twin, consistent with sequential formation of different sets of twins, Figure 4.67.

Figure 4.65. TEM micrographs showing microstructure beneath striations of 316 stainless steel precharged with hydrogen and fatigued in atmosphere. a) Fine grains immediately beneath fracture surface. b) Planar features extending approximately 5 μm beneath fracture surface, examples indicated by arrows.
The microstructure beneath fatigue striations in uncharged 316 stainless steel fatigued in air is different than that produced in the presence of hydrogen and, also, different than that produced in 304 stainless steel deformed in the presence and absence of hydrogen. Again, there is a refinement in the microstructure immediately beneath the fracture surface, Figure 4.68a, b and Figure 4.69a. However, immediately beneath and extending a distance of between 400 and 600 nm the refinement takes the form of a banded structure with the bands tending to lie parallel to

Figure 4.66. a) TEM micrograph showing fine grain immediately below fracture surface (marked by arrowheads) and twins below the layer of fine grains. b) Diffraction pattern showing twin spots (blue pattern) on a [011] zone axis (white pattern). c) Diffraction pattern shows splitting of spots in an [011] zone axis due to fine grains near fracture surface.

Figure 4.67. TEM micrograph of intersecting twins displacing each other in 316 stainless steel pre-charged with hydrogen. Notable examples of this displacement are circled.
the fracture surface, Figure 4.68b. The inter-band spacing is 50 - 100 nm and between the bands exist dislocations cells and dislocations. This microstructure is strikingly similar to that produced by compressive loading or rolling to high strains [237]. Further from the fracture surface, these bands exist but now lie inclined to the fracture surface, Figure 4.68b. Below this level, a mosaic pattern (2 μm in spacing) exists, composed primarily of deformation twins, Figure 4.68c and d. The angle between the sides of the mosaic pattern corresponds to the angle between {111}-type planes and diffraction analysis confirms the presence of twins. This configuration of twins is simpler in samples extracted parallel to the striations with one dominant set of twins, and evidence of the emergence of a second set of twins, Figure 4.69b. This structure extends for more than 7 μm from the surface (depth limit is due to sample size, and is not an indication that the evolved microstructure ends at this depth).

Figure 4.68. TEM micrographs showing microstructure underneath (taken perpendicular to) striations in uncharged 316 stainless steel. a) Region immediately beneath fracture surface showing refinement progressing into planar structures. b) Region immediately beneath the fracture surface showing banded structure parallel to fracture surface and beneath that a banded structure at an angle to the fracture surface before progressing to planar structures. c) Planar structures 2 μm from fracture surface with diffraction pattern (inset) of a [011] zone axis showing twin spots at appropriate spacings. d) Two different regions showing close-packed planar structures and region of widely spaced twins.
4.3.4 Flat Features

The flat features observed in both steels with hydrogen are covered with what resemble fine striation markings, Figure 4.61. However, the morphology of the feature suggests a different failure mechanism from the striations described above. To determine the underlying microstructure, samples were cut from the 316 surface perpendicular to the markings such that several would be evident in an electron micrograph. As shown in the bright-field images presented in Figure 4.70, the microstructure beneath the surface consists of a high density of dislocations interspersed with fine planar features that extend 2 μm from the surface. Electron diffraction analysis shows that these planar features are twins, Figure 4.70c. A second set of fine features exists between the twins extending from the fracture surface. These are nearly parallel to the fracture surface. The angle between the two sets of features matches that between different \{111\}-type planes (70.5°), suggesting that the features are both twins. Examination of the cross-section of the fracture surface, top of Figure 4.70a, shows that it is not flat but contains undulations that are approximately 50 nm in height and irregularly spaced. These correspond to the fine striation markings seen in the fractograph presented in Figure 4.61d. In comparison with the underlying microstructure, it is seen that the twins appear related to the undulations, although the correspondence is not one-to-one as more planar features than undulations exist, see Figure 4.69.

Figure 4.69. TEM micrographs showing microstructure beneath (taken parallel to) striations in uncharged 316 stainless steel. a) Refined and banded structure immediately beneath the surface with twins deeper into the sample. b) Twin structure approximately 3 μm from surface. Diffraction pattern of [011] zone axis showing twin spots inset. Note that twins were also visible in a second direction (marked with arrows).
4.70a. This microstructure, while also produced in hydrogen, is significantly different from the microstructure beneath the hydrogen-induced striations.

![Figure 4.70](image.png)

Figure 4.70. a) TEM micrograph showing microstructure immediately beneath flat fracture feature of 316 stainless steel precharged with hydrogen. b) TEM micrograph with a closer view showing fine features perpendicular to planar features seen in a). c) Higher magnification view of twins with diffraction pattern (inset) showing (\(\overline{1}1\)) twin spots (circled) on [011] zone axis.

4.3.5 Fatigue Crack Tip Microstructure

To understand the chronology of how the microstructure evolves in the hydrogen-charged material during the fatigue cycles, FIB samples were extracted from the polished surface 1 μm and ~5 μm ahead of arrested cracks from fatigue tests interrupted after 8000 cycles. An example
of the resulting microstructure in 304 stainless steel is shown in the micrographs presented in Figure 4.71. Figure 4.71a shows the relationship of the extracted sample (Pt strip) to the arrested crack and the resulting microstructure is shown in Figure 4.71b. Within ~1 μm of the crack, planar features (martensite plates) coexist with dislocations although there are regions in which only dislocations exist. The microstructure approximately 5 μm ahead of the crack tip consists of dislocations only. The microstructure ahead of an arrested crack in 316 stainless steel showed a similar dependence on distance from the crack, although the planar features were not martensite but twins.

**Figure 4.71.** a) FIB image showing location of Pt strip ahead of crack tip of 304 stainless steel tested in hydrogen; this indicates the location from which the sample was extracted. b) TEM micrograph showing microstructure immediately ahead of crack tip. Right region shows example of martensite laths, while left region shows area with just dislocation activity.
4.4 Liquid Metal Embrittlement of T91 Martensitic Steel and Armco Iron

4.4.1 T91 Steel in Contact with Lead-Bismuth Eutectic and Liquid Indium

The T91 steel is a fully martensitic steel with a mean prior austenite grain size of 20 μm, Figure 4.72 [228]. The dislocation density is low.

![TEM micrograph showing the initial microstructure of the T91 martensitic steel. The steel is martensitic with a low dislocation density. Image courtesy of T. Auger. [228]](image)

In the temperature range investigated (160-200°C between indium and lead-bismuth), T91 steel is fully ductile. However, in contact with either indium or lead-bismuth, the mechanical properties display liquid metal embrittlement. Lead-bismuth (LBE) causes a 30% (±10%) decrease in fracture toughness of the T91. Indium causes a 50% (±10%) decrease in the fracture toughness of this steel. The difference in susceptibility of this steel to the two liquid metals is shown in the J-R curves in Figure 4.73, where a reference case is shown for comparison. The stated error in the curves is due to uncertainty in the crack measurements, not the 40°C difference in temperature [228].
Figure 4.73. Crack growth (J-R) curves for T91 as a reference, T91 in contact with PbBi, and T91 in contact with In. Graph courtesy of T. Auger. [228]

Figure 4.74. SEM fractographs of T91 steel in contact with (a) and (c) indium and with (b) and (d) LBE. Image courtesy of T. Auger. [228]
As shown in Figure 4.74, the fracture surfaces of the two samples show strong similarities. Both display a river pattern typical of LME fracture, particularly in plane-stress loading condition [238]. That indium may be a stronger embrittling agent than lead-bismuth is also suggested by the presence of intergranular failure with respect to prior austenite grains after contact with indium but not with LBE, Figure 4.75. However, this failure mode represents only a small fraction of the total fracture path, and, correspondingly, should not have a strong effect on the reduction of fracture toughness [228].

FIB samples taken ahead of the crack tip reveals a complicated three-dimensional crack network. The liquid metal penetrates deep beneath the surface. As can be seen in Figure 4.76, liquid indium filled the cracks which recrystallized upon cooling, though FIB milling removed much of the filling of the large cracks. However, a coating of indium remains on the crack edges, which consists of fine to nano-sized crystals. The indium also delineates grain boundaries ahead of the crack, Figure 4.76. In general, the indium appears to penetrate several hundreds of nanometers ahead of the crack tip. The crack path closely follows martensite lath boundaries, Figure 4.77. Penetration of the indium occurs along the boundary, slightly past the crack tip that is evident due to opening in the bright field image, Figure 4.77d. Orientation mapping was used to confirm that these were martensite boundary relationships, Figure 4.78. The example in Figure 4.78 indicates a high misorientation (~45°). Other examples, not shown, had misorientations typical of martensite variants and were in the ranges of 10-50°.
Figure 4.76. Dark field TEM micrograph of indium-embrittled T91. Black arrows indicate the indium coating the crack. White arrows indicate indium penetration through the grain boundary. Arrowheads mark martensite lath boundaries.

b) Corresponding electron diffraction pattern for the indium. Image in (a) was taken using the $\{110\}$ ring of the tetragonal indium. Higher order rings are also visible suggesting a fine grained and textured structure. [228]
Figure 4.77. TEM micrographs of T91/In showing martensite boundary failure.  a) Dark field micrograph showing cracking occurred along martensite boundaries (arrowheads) connected by an intergranular crack between two randomly oriented grains (arrows). Inset shows corresponding diffraction pattern of indium; images were formed with [110] ring. b) Dark field micrograph of close-up of martensite boundary marked by right-most arrowhead. c) Dark field micrograph close-up of martensite boundary marked by left-most arrowhead. d) Bright-field micrograph corresponding to same area as c) showing the lath boundary. [228]
Examination of the microstructure surrounding the crack tip, Figure 4.79, reveals dislocation activity. The resulting dislocation density is several orders of magnitude higher than in the initial microstructure. This dislocation density does not appear to vary with distance from the crack tip, over the scale observed. Additionally, evidence of surface activated sources was not found, either around crack tips, or along crack flanks. It is important to note that cracks or voids do not appear to have opened up ahead of the crack tip.

Not every boundary showed evidence of extensive cracking. Cases of crack arrest were investigated more closely. In the example shown in Figure 4.80, chemical mapping reveals the presence of indium along crack flanks, but no indium along the grain boundary ahead of crack tip. At the crack tip, corresponding to a dark contrast feature, there is an area rich in chromium and carbon. This carbide is the likely reason for the crack being arrested. This particle is typical of T91 carbides [239].

Figure 4.78. a) Orientation map of indium-filled crack along martensite lath boundary. b) Image quality map. c) Misorientation across indium filled crack. Line scan position marked in a). Images courtesy of T. Auger. [228]

Figure 4.79. a) Bright field TEM micrograph showing microstructure around crack tip. There are areas of dislocation activity, but no gradient in the dislocation density as function away from the crack tip. b) Bright field micrograph showing higher magnification view of crack tip. [228]
In the case of T91 embrittled by LBE, the crack network is similarly complex, and the cracks also clearly followed martensite lath boundaries, Figure 4.81. In the case of LBE, the FIB milling did not preferentially mill the LBE, leaving the filled cracks intact. Also, due to the expansion of the LBE upon cooling by 2-3%, the cracks have widened. The crack path, however, is still evident along the martensite lath boundaries. Again, plasticity was observed surrounding the crack, but was evenly distributed. Also, voids or fine cracks were not observed ahead of the crack tip.

Figure 4.80. Bright field micrograph and corresponding elemental maps for chromium, indium, carbon and vanadium around arrested crack tip. Crack followed martensite lath boundary before being halted at a chromium carbide. Image courtesy of T. Auger. [228]

Figure 4.81. Bright field micrographs of LBE filled crack in T91. a) Cracking between martensite lath boundaries. Parallel lath boundaries visible on the right of the crack. b) High magnification TEM of crack tip showing microstructure around the filled crack. [228]
4.4.2 Armco Iron in Contact with Liquid Indium

The commercially pure Armco iron is polygonal ferrite with a mean grain size of 25 μm, Figure 4.82. There is a low density of inclusions visible on the fracture surface. Chemical analysis revealed that these are predominantly aluminum oxides. The dislocation density is low, Figure 4.83a, with a few areas showing tangles, Figure 4.83b, suggesting that the material is not well annealed. The grain boundaries appear clean, without large strains or secondary phases decorating them, Figure 4.83c.

Figure 4.82. SEM micrograph showing grain size and shape for Armco iron used for liquid metal embrittlement tests.
4.4.2.1 Intergranular Failure

The exposed fracture surface shows predominantly intergranular failure, Figure 4.84. The exposed grains appear elongated in shape; the original microstructure suggested polygonal ferrite grains. There is a mixture of smooth and rough facets. The rough facets suggest rumpling or shearing of the surface. The smooth facets are typically very clean, without evidence of abundant slip traces, though occasionally, steps (Figure 4.84b) or “pits” (Figure 4.84c) may be evident on the surface. There is the occasional inclusion evident on the fracture surface, Figure 4.84b. While there is pitting around the inclusion, it is still buried within the grain and there is little evidence to suggest that its presence greatly impacted the fracture path. The fracture facets become rougher along the sides of the CCT sample, Figure 4.85. There are also some features which may be transgranular. Previous studies have shown that the crack propagates faster in the middle of the CCT sample than towards the edges [224]. This suggests that these grains
probably failed later than adjacent grains towards the center of the sample. The failure of these grains may be influenced by the change in constraints towards the edge of the sample, and the necessity for final tearing of the sample.

Figure 4.84. SEM fractographs showing fracture surface of indium-embrittled iron with the indium removed. a) SEM micrograph showing intergranular features. b) SEM micrograph showing closer view of intergranular facets and an exposed inclusion. c) SEM micrograph showing texture of intergranular facets.
TEM samples were extracted by FIB machining from the tip of a liquid metal filled crack. The sample location was chosen to intersect the crack tip approximately 4 microns from the cut surface. The indium in the sample was milled more quickly by the ion beam than the iron, leaving large empty cracks where indium had been previously, Figure 4.86a. These cracks appear to follow grain boundaries, which is consistent with the fracture surface observed. A layer of indium still remains as a coating along the crack edges which can be observed in the dark-field image formed by using the first ring of the indium polycrystalline pattern, Figure 4.86b. The bright spots within the rings suggest that fine crystals of indium have formed upon cooling, and that certain orientations are preferred.

To more clearly observe the microstructure immediately beneath the fracture surface, a FIB sample was extracted from an intergranular facet, Figure 4.84c. The microstructure consists of fine dislocation cells approximately 500 nm in diameter, Figure 4.87. This microstructure continues unabated for several microns from the fracture surface; the limit of this measure is the extent of the sample size, not an indication that the microstructure ends at this depth.
Figure 4.86. a) Bright-field TEM micrograph of indium embrittled iron showing grain boundary cracking. b) Dark-field TEM micrograph of indium embrittled iron showing indium coating the grain boundary (fracture surface). Inset shows corresponding electron diffraction pattern of the nanocrystalline indium.
Figure 4.87.  a) TEM micrograph of dislocation cells immediately beneath intergranular fracture (dotted line) caused by indium embrittlement of iron. b) Dislocation cells just below fracture surface at lower magnification. c) Higher magnification TEM micrograph of microstructure approximately 5 μm from intergranular fracture surface.
4.4.2.2 Transgranular Failure

At the edges of the notch where cracking initiated, the fracture mode is transgranular, Figure 4.88. The transgranular failure is typically one grain deep before changing to intergranular failure, though there are examples where a couple of grains failed in a coplanar manner, extending the transgranular failure two to three grains deep, Figure 4.88b. Most of the transgranular features show river patterns parallel to the crack propagation direction, Figure 4.88a, though a few showed a limited numbers of lines, Figure 4.88b. By tilting the sample, it becomes evident that the river patterns consist of steps on the fracture surface, Figure 4.89. On some features, these steps are nearly identical in height with a step size around 0.5-1 μm, Figure 4.89a; in others, there can be a large discrepancy in height with large steps on the order of 2.5 μm and smaller steps on the order of 200 nm, Figure 4.89b. There is also a variation in the separation between steps, with some features having them evenly spaced and others having large variations. The steps themselves are relatively smooth on top, but very rough along the sides, Figure 4.89c. It is also suggested by the images in Figure 4.89 that the planes are not all parallel, as the step height changes along the length of the step. This would suggest that the steps are not caused by cleavage failure of parallel cleavage planes.

![Figure 4.88. SEM fractographs showing transgranular failure features at the crack initiation. a) Transgranular feature showing distinct "river pattern". b) Transgranular feature showing smoother surface, and extending coplanarly through second grain.](image)
To attempt to confirm this, stereographic reconstructions of the fracture features were made, Figure 4.90. As can be seen in Figure 4.90a, the reconstruction accurately reproduces the topography of the fracture surface, compare with Figure 4.89a. In order to determine the angle between the different steps, a line scan was taken across the steps, Figure 4.90b. To reduce the noise, the line scan was averaged across a width of 5 μm. The planes were found to belong to two sets of parallel planes with an angle of 18° between them, which would support these not all being parallel cleavage planes.

Figure 4.89. SEM micrographs of transgranular failure features at 52° sample tilt. a) Feature imaged in crack growth direction showing steps of varying height. b) Feature imaged perpendicular to crack propagation direction (crack initiation on left) showing one large step and many smaller. c) Close-up view of feature in a) showing details of steps.
Samples were extracted by FIB both parallel and perpendicular to these steps. Beneath the fracture surface, the microstructure is heavily dislocated, with some areas showing a clearer dislocation cell structure than others, Figure 4.91 and Figure 4.92. Diffraction pattern analysis was used to determine the likely fracture plane; ambiguity will likely remain due to images being projections. Two examples are shown in Figure 4.93, one from a sample taken perpendicular to the steps and one from a sample taken parallel to the steps. In Figure 4.93a, the fracture surface was found to be close to the (10\bar{1}) plane, which is a slip plane in the BCC system. Parts of the steps closely follow other slip planes. Similarly, in Figure 4.93b, two slip planes, (112) and (211), which are within 4 degrees of each other at this angle of projection, closely match two closely separated parts of the fracture surface at a slightly different orientation. Based on this experimental evidence, it is likely that the fracture surface is following slip planes. In one location measured, slip planes and cleavage planes were parallel in projection, and closely

Figure 4.90. a) Stereographic reconstruction of stepped feature due to indium embrittlement of iron. b) Line scan across steps of fracture surface, averaged over width of 5 \(\mu\)m.
matched the fracture plane, making the assignment of a distinct fracture plane type impossible. It is therefore possible that part of the fracture occurred along a cleavage plane, but the majority appears to follow slip planes.

Figure 4.91. TEM micrograph showing dislocation structure immediately beneath fracture surface. Sample was taken perpendicular to steps, one of which is visible on the right side of the micrograph, indicated by arrows.

Figure 4.92. TEM micrograph showing dislocation structure immediately beneath fracture surface. Sample was taken parallel to steps. a) Dislocation structure immediately beneath the fracture surface. b) Dislocation structure approximately 5 μm from fracture surface.
Figure 4.93. TEM micrographs of FIB samples taken a) perpendicular and b) parallel to the fracture surface steps. Labeled associated diffraction patterns are inset to each image. The best fit plane projections for the fracture surface are marked.
CHAPTER 5
DISCUSSION\textsuperscript{2}

5.1 Pipeline Steel Failure in Hydrogen
A detailed fractographic and microstructural study of pipeline steels loaded in compact tension has shown that the deformation processes leading to failure depend upon environmental conditions. The developing microstructure is instrumental in determining the fracture path through the material. While different microstructures led to different fracture morphologies, in the case of failure in a hydrogen environment, the microstructure immediately beneath the fracture surface is not what was expected based upon classical interpretations of the fractography. In the following sections, possible explanations for the formation of the microstructures are presented.

5.1.1 “Quasi-cleavage” Failure
SEM examination of the fracture surfaces of the hydrogen-failed sample and of foils of different metals deformed to failure \textit{in situ} in the TEM showed similar characteristics in the form of saw-teeth (ligaments). The \textit{in situ} TEM studies showed the ligaments formed in initially thick, electron opaque material that had undergone significant deformation such that a small volume was thinned to electron transparency. Final separation in this region occurred by dislocation slip followed by crack propagation along the active slip systems \cite{240}. From the similarity of these features in the two cases, it is proposed that the saw-teeth on the ridges are the result of final separation of the thinned volume that connects two ridges. Although this final stage of failure involves extreme plastic processes, which may be accelerated by the presence of hydrogen, the formation of the saw-teeth is not central to the overall hydrogen degradation and fracture of this steel. However, the presence of these features provides important evidence as to the separation process, which is similar to the final failure mechanism put forth by Beachem and Pelloux \cite{241}.

\textsuperscript{2} Portions of the discussions present herein have been previously published. Pipeline steel results were published in Martin, Fenske, Liu, Sofronis and Robertson, \textit{Acta Materialia} \textbf{59} (2011) 1601-1606 and Martin, Robertson and Sofronis, \textit{Acta Materialia} \textbf{59} (2011) 3680-3687. Nickel results were published in a paper in Martin, Somerday, Ritchie, Sofronis and Robertson, \textit{Acta Materialia} \textbf{60} (2012), 2739-2756. Liquid metal results were published in Martin, Auger, Johnson and Robertson, \textit{Journal of Nuclear Materials} \textbf{426} (2012), 71-77. Reprinted with permission of the publisher.
From topographical maps of the fracture surface along with characterization of the subsurface microstructure, it has been shown that the surface ridges are associated with failure along slip bands which have experienced intense and localized deformation. The localization of the deformation as well as the accompanying reduction in cross-slip is consistent with the localized plasticity associated with the shielding model of hydrogen embrittlement [50].

In our proposed model, void or microcrack formation is assumed to occur at and along some slip band intersections as a consequence of the strain discontinuities at such points as well as the local hydrogen concentration, Figure 5.1. A similar proposal was put forth by Nibur et al. [242] to explain the fracture surface produced in an 21Cr–6Ni–9Mn austenitic stainless steel. In that study, the void initiation sites were at points of intersection between the deformation bands with other obstacles such as other deformation bands, ferrite stringers and grain boundaries. Void nucleation along slip-band intersections was also proposed to explain flutes (elongated voids) in hexagonal-close packed metals with limited slip systems such as magnesium [243]. In the present work, it is envisioned that the initial voids form at the intersection of slip bands and extend along this intersection. These voids widen through dislocation processes until they intersect another similarly growing void. The volume between these intersecting voids forms the ridges, which gives a natural mechanism for the formation of the ridges and saw-teeth. In addition, this formation and growth process supports the observation that failure does not occur on every intersecting slip band as the distance between the ridges is greater than the separation distance between the intersecting slip bands.

This case allowed the direct correlation between fracture surface features and the microstructure underneath. The dislocation density was higher than would be expected based upon either traditional fractographic analysis or purely decohesion based hydrogen embrittlement mechanisms.
5.1.2 “Flat” Failure

It has been shown that the fracture surface feature, which appears at low resolution to be relatively flat and often attributed to the Decohesion mechanism, is actually undulating and covered with small dimples or hillocks. The microstructure immediately beneath this surface consists of a high density of dislocation lines and loops, the density of which remains constant and unchanged over distances of micrometers from the fracture surface. It also continues through several grains from the fracture surface. This observation, along with the identification of slip bands as playing a prominent role in the formation of river markings decorating hydrogen-induced “quasi-cleavage” fracture surfaces, raises questions about interpreting the relationship between the deformation processes and failure mechanisms and the topology of fracture surfaces without knowledge of the actual microstructure.

According to the HELP mechanism, the dislocation interactions and reactions are similar in the presence and in the absence of hydrogen, but occur at lower stresses when hydrogen is present. Since hydrogen is attached to and transported with the dislocations, locally high hydrogen concentrations should exist in regions of high dislocation density. It is posited that the dislocation structure, which is established well in advance of the crack with the aid of the hydrogen enhanced plasticity mechanism, and the local hydrogen concentration associated with the dislocations are central to establishing the fracture instability. This concept is supported by density functional theory calculations which show that the surface energy is reduced by the presence of hydrogen and that the dependence between the concentration and the magnitude of the reduction may be non-linear [162]. Thus, the dislocation structure established with the assistance of the hydrogen enhanced plasticity mechanism along with the hydrogen concentration would establish the local conditions that would promote fracture. Although the details of the atomistic process of separation responsible for creating the dimpled ‘flat’ surface remain elusive, the observations along with the hydrogen-induced reduction in the surface energy suggests that hydrogen influences the instability of interface fracture. The undulations, dimples or hillocks, are most likely a consequence of near surface relaxations associated with the formation of new surfaces, along with being evidence of the final failure process. Alternatively, these features could indicate the path is associated with the underlying dislocation structure, which would favor regions of high hydrogen concentration and dislocation density.
It has been proposed [215] that these features may be caused by the coalescence of nanometer sized voids. In this case, it would be expected that voids would be created throughout the grain ahead of the crack tip; it is difficult to envision a driving force to cause the congregation of nanovoids into a single plane. Furthermore, evidence of these voids is lacking. Although FIB damage may obscure smaller voids, those on the order of 100 nm should be evident. Additionally, a likely nucleation location would be at carbides or other precipitates and inclusions. No evidence of voids was found at these locations, even in close proximity to the fracture surface. The evidence in Neeraj et al. [215] is similar to what was found in this work, and does not strongly suggest this “nanovoid” mechanism compared to the current work. The matching fracture surfaces that they claim to have observed may be due to local final separation causing tearing between the two fracture halves. Whether these are dimples or mounds is debatable as the resolution of both the SEM and the AFM make the size and evidence of these features clear, but the character of it debatable. The structures observed could be due to the final separation by local tearing forming these “nano-dimple” features. This final separation is not likely to be greatly affected by the presence of hydrogen, nor is it likely to be the determining characteristic of the failure.

It is worth noting that the heat tint treatment does not appear to greatly affect the fracture surface. Color can be produced by a very thin oxide layer. The oxide layer was not even thick enough to be apparent in cross-section on the FIB-TEM samples.

After failure, the applied stress is relieved, and relaxation is likely to occur. Similarly, some relaxation of the microstructure is also likely to occur during the FIB lift-out process as the constraint of the bulk is removed from the thin film. Some dislocations may be removed from the sample due to image forces at the surface. As such, a question remains as to how representative of the microstructure preceding failure is the microstructure observed. The microstructure observed is a very dense and tangled net of dislocations. As such, it would be difficult for dislocations to move in response to the relieved stress or to image forces. It is believed that the structure observed likely shows some evidence of relaxation, suggesting that an even higher dislocation density existed. However due to the tangled nature of the configuration, the structure is unlikely to be greatly changed. Based upon these assumptions, it is believed that the conclusions presented herein are still applicable.
5.1.3 Difference Between ‘Flat’ and ‘Quasi-cleavage’ Features

The fracture surface is qualitatively evenly divided between the two different fracture morphologies. In some cases, as shown, there is a “flat” feature immediately beside a “quasi-cleavage” feature. While the clearest examples were shown to demonstrate the difference possible between the two features, in the samples taken across the two different features, the difference in microstructure is less evident. This may be due to sample preparation issues, such as an insufficiently good polish or the orientation of the “quasi-cleavage” portion of the sample chosen was not appropriate to clearly view the dense slip bands. However, the difference between the microstructure of the two features was evident by EBSD point scans. From point scans taken from “quasi-cleavage” features, Kikuchi band patterns could be resolved. Efforts to identify the zone axes failed, likely due to strain of the crystal, but the patterns were distinct enough to attempt identification. By contrast, point scans taken from “flat” features never resulted in discernible Kikuchi patterns, likely due to high amount of deformation beneath these features. These EBSD tests support the reported difference in dislocation density.

Given the fairly homogenous chemistry and starting microstructure of the two pipeline steels, it is unlikely that the difference is due to the local microstructure. A more likely difference is the orientation and constraint of the grains. If the grain is favorably oriented for slip on select systems, then the honeycomb microstructure can develop, leading to the formation of ridges upon final failure. If the orientation is more random allowing more slip systems to become active over the course of deformation, then the unorganized microstructure is formed, and the ‘flat’ fracture feature results. Unfortunately, as the dislocation structure under the ‘flat’ feature is constant across the grain, and often through at least the next grain, and is too high for EBSD analysis, cross-section EBSD analysis is unlikely to yield useful orientation information to compare the two features.

These results highlight the need to understand the microstructure evolution prior to crack advance. Although this appears obvious, the evolved microstructure was dismissed or neglected in previous models and attention was focused on the crack tip volume. The evolution of complex microstructures in advance of the crack tip means that the crack tip is propagating through strained material and that any plasticity generated immediately at the crack tip must interact with the existing microstructure.
5.1.4 Effect of Hydrogen on Failure

In comparing the microstructure beneath fracture features that occurred in hydrogen with the microstructure beneath the low temperature brittle fracture, it is evident that there is an appreciable difference in the dislocation density. The low dislocation density observed beneath the cleavage surface is expected for the low temperature failure, particularly that occurring at the high strain rate likely applied during overloading. The ductile to brittle transition temperature of these steel is expected to be in the -150° to -170°C range [244], which could be reached by cooling with liquid nitrogen (-196°C). Below this transition temperature, limited dislocation motion is expected to occur. The introduction of hydrogen at room temperature also introduces characteristics of a ductile to brittle transition in the mechanical properties of steel which could be interpreted to produce a similar decrease in dislocation activity. However, the results of this study demonstrate that this would be an erroneous assumption. The dislocation activity is significant and is not limited to the immediate vicinity of the fracture surface. It extends for several microns, at minimum, from the fracture surfaces and encompasses several grains, suggesting a significant plastic zone ahead of a propagating crack tip. This plasticity would contribute to failure processes, and cannot be ignored. Based on the experimental results presented herein, it can be concluded that the assumption of brittleness based upon fractographic analysis is incorrect.

An important conclusion to draw from the microstructure observed beneath the cleavage fracture surface is that the microstructure observed in the FIB-TEM samples is not caused by the FIB process. In these samples, there is a low dislocation density, with irradiation damage in the form of small loops evident at different diffraction conditions. If different dislocation structures can be observed within the same sample material, including one with a low dislocation density, it is unlikely that the FIB process is introducing massive amounts of dislocations.

The high dislocation density observed beneath flat fracture features due to hydrogen is random, unorganized, and indicative of a high level of strain. This disorganization is in contrast to the developed cell/microband structure observed beneath the ductile failure. The microstructure observed beneath the ductile voids is similar to those formed by high strains due to rolling or torsion [245-248]. The microstructure resembles the “bamboo” structure observed during Stage IV deformation [245], with no clear cell structure within the areas defined by the geometrically
necessary boundaries (GNBs). It is also at this stage where the GNBs are typically parallel to the material flow direction. It would be expected that material flow would be parallel to the void sides, which is what is observed. Additionally, microband spacing decreases with increasing strain. Though there is a lot of variation in microband spacing, the average spacing is smallest near the fracture surface. It would be expected that local strains would be highest at the fracture surface.

While from this test it is not possible to compare the strains at failure, it is likely that, given the low fracture toughness, the strain at failure with hydrogen would be notably less than in air. It would therefore be expected that the dislocation structures at failure are indicative of lower strains in the presence of hydrogen. Therefore, it might not be surprising that microband structures did not form in the presence of hydrogen, if the strains were not sufficiently high. The normal evolution of dislocation structures is from dipoles to tangles to walls to cell structures. The question is whether hydrogen affects the dislocation structures formed. With the high dislocation density present, and the associated strain, it might be expected that cell structures should begin to form, yet there is no clear evidence for cell walls.

According to Bay et al. [248], crystals with significantly dissociated dislocations (such as with low SFE), do not form cell structures but Taylor lattices. Examples include crystals in which solute interactions increase friction stress and promote planar glide. As hydrogen does (slightly) reduce the stacking fault energy, and promotes planar glide by inhibiting cross-slip, even though it decreases the friction stress, it may be possible to form Taylor lattices, or at least suppress (to a certain extent) the formation of cell structures. Additionally, as hydrogen has been shown to decrease the stand-off distance between dislocations, this would allow tighter packing of dislocations creating the dislocation structure observed which may not exist in the absence of hydrogen.

Similarly, in the case of the microstructure underneath the “quasi-cleavage” features, the effect of hydrogen on dislocation motion may have influenced the development of the microstructure. If only certain slip systems are initially active in a grain, hydrogen will help maintain these systems by limiting cross-slip. As the dislocations cannot cross-slip onto other systems, the honeycomb structure develops, leading to the “quasi-cleavage” fracture mode.
Based on these results, it is proposed that the effect of the environment on the developing microstructure determines the fracture path through the material. Neither the “brittle” macroscopic nature of the fracture features nor the fine ductile features on the surface lead to a correct interpretation of the deformation processes. I propose that the two different fracture features caused by hydrogen are due to a difference in the microstructure developed as influenced by the solute hydrogen in the material. This has the impact of evolving the microstructure and altering the distribution of hydrogen.

5.2 Nickel Intergranular Failure

A distinct and fine dislocation cell structure exists immediately beneath and well beyond the hydrogen-induced intergranular facets, including beneath those with only one set of steps evident on it. The complex dislocation structure underneath the nickel intergranular facets is unexpected based upon classical interpretation. In particular, the single set of slip steps on the surface of many facets suggests that planar slip is active within the grain. At first sight, this latter comment might appear inconsistent with the formation of a dislocation cell structure. However, dislocation-grain boundary interactions are complex, with a one-to-one correlation between incoming dislocation systems and outgoing dislocation systems being rare [249-251]. Slip can be either completely accommodated by the grain boundary or reemitted into the original grain as well as being transmitted. It is important to appreciate that, apart from a few special cases, dislocations will be accommodated in the grain boundary and new dislocations will be emitted into either adjoining grain, and that many dislocations may be accommodated prior to a single dislocation being emitted from the boundary. Additionally, even with multiple slips systems active, not all systems will intersect the failed grain boundary. Other facets show evidence of dislocation activity on multiple systems, which can be easily envisioned to generate a cell structure beneath it. However, it is noteworthy that a one-to-one correspondence does not exist between the cell size and the slip traces, which reinforces the difficulty of interpreting dislocation processes from features on fracture surfaces. The steps are likely caused by the sudden and rapid ejection of dislocations from the boundary after a high arrival and accommodation rate, resulting in shearing of the grain boundary plane.
With a yield strength of 55 MPa and a failure strain of 13%, it is reasonable to expect a certain degree of plasticity within the sample at failure. There was a reduction in area with hydrogen (6-29%), which, although significantly less than without hydrogen (74-86%) [36], would suggest some plasticity. Previous studies had observed that considerable plastic flow can occur prior to crack propagation (evidenced by the stress-strain behavior), but crack initiation can be rapidly followed by failure without any further significant plastic deformation [38, 44]. In particular, plasticity has been observed around the grain boundaries prior to failure, or around subsidiary cracks [44]. The microstructure associated with plasticity varies as a function of applied strain. Studies of nickel microstructure as a function of strain (without hydrogen) show a clear progression from dipoles, tangles and walls at low strains, to walls and cell structures, with cell size decreasing with increasing strain, Figure 5.2 [252]. The shrinkage of all deformation elements as a function of strain is expected in FCC metals [248]. A strain of 13% should result in a dislocation structure with a cell size on the order of 1.2 μm [252]. The actual cell size of 200-500 nm would correspond more to a strain of 40%. The difference in the strain needed to produce similar cell sizes with and without hydrogen suggests that hydrogen enhances and accelerates the dislocation processes.

The calculated effective strain of 40% based upon a 200-500 nm cell size assumes the behavior observed by Keller et al. continues with increasing strain, and that a transition to a new cell configuration does not occur. Without hydrogen, the cell structures tend to organize into groups of cell blocks or microbands at high strains [245-248]. New wall structures, geometrically necessary boundaries, form to divide areas of larger rotation, allowing the accommodation of larger strains. At a strain of 40% in nickel, the microstructure is quite likely to resemble that in Figure 5.3 [246], which is not what was observed. In the presence of hydrogen, a refinement of the cell size occurred, possibly due to the closer packing of dislocations in the presence of hydrogen, but not a true acceleration to an equivalent strain of 40%, as no transition in the

![Figure 5.2. Evolution of dislocation cell size as a function of strain. Adapted from [252].](image)
microstructure was observed. This suggests that hydrogen may delay the transition to the next microstructural stage.

The HELP mechanism \([35, 120, 195]\) can explain the acceleration of the dislocation processes. The hydrogen atmospheres surrounding the dislocations allow the dislocations to move at lower stresses than in the absence of hydrogen. The faster dislocation motion at lower stresses will lead to the more rapid development of dislocation structures at lower strains. Another effect of the stress-field shielding due to the hydrogen atmosphere is the reduction in the stand-off distance between dislocations. This will allow closer packing of dislocations allowing smaller cell size. It may also be able to account for the delay of transition to the next microstructural stage. Hydrogen has been shown to delay the transition between Stage I and Stage II deformation in single crystal experiments by the inhibition of cross-slip \([253]\). The accessibility to given dislocation cell configuration depends upon the applied stress, but also the slip systems that are available and the dislocation mobility within these systems \([248]\). If hydrogen, by limiting cross-slip and altering dislocation mobility and spacing, can limit the cell configurations available, it may delay or prevent transitions to Stage III or IV microstructures consisting of microbands. As hydrogen allows closer packing of dislocations, microstructures that could not exist without hydrogen may occur, and the microstructure observed beneath the nickel intergranular facets may be an example of this.

The global effect of the solute hydrogen due to the HELP mechanism would also account for the high dislocation density observed in the bulk. Even millimeters away from the fracture surface, a dislocation cell structure with cell sizes of 400-800 nm exists, suggesting an effective strain of 25% \([252]\). This is a significant refinement from the cell structure expected for the 13% strain to failure measured. The extent of the plasticity suggests that it occurs along the gage length, and that the dislocation structures formed prior to the initiation of failure, which would concentrate

![Figure 5.3. High strain microstructure in nickel created by cold rolling to 40% strain. Adapted from [246].](image)
stress to the cracked region, hence the higher strain microstructure observed near the fracture surface. The establishment of the microstructure is essential to the fracture process.

That a sufficiently high concentration of hydrogen is necessary to cause a transition from transgranular to intergranular failure in nickel was shown by Lassila et al. [67, 77, 254]. If a sufficiently high bulk concentration was introduced to the sample, a high percentage of intergranular failure would occur. However, if sufficient aging was allowed prior to loading, a lower bulk concentration was needed to cause intergranular failure. This suggests that hydrogen segregated to the grain boundary during aging and this produced sufficiently high concentrations at the grain boundaries. Without this concentration of hydrogen at the grain boundary, intergranular failure will not occur.

In the case of external hydrogen embrittlement, loading generally begins before sufficient aging has occurred to segregate hydrogen to the grain boundaries. And yet, intergranular failure will still occur. By conventional wisdom, hydrogen would be expected to accumulate at the maximum stress ahead of the crack tip. McMahon [8] states that while solid mechanics describes the maximum stress ahead of a crack as $3\sigma_y$, and $C_H \propto exp(\sigma_H)$, the resulting lattice concentration is far lower than needed to be deleterious, and that there is no evidence that hydrogen would segregate to the grain boundaries to a large enough degree to explain intergranular fracture. This has led to the argument that other segregants, such as sulfur, are needed to sufficiently lower the cohesive energy of the grain boundary. It has even been suggested that segregants such as sulfur may attract hydrogen to the grain boundary [77]. Recent studies have shown that hydrogen is sufficient by itself in high purity steels [79] and in Ni [67, 195, 219], though there has still been concern about how to achieve the high hydrogen concentration necessary.

The large amounts of plasticity observed in this study can account for the discrepancy between the presumed required hydrogen concentration and the achievable hydrogen concentration. Hydrogen dissolved in the nickel would accelerate plastic processes. This will harden the grain interior, as well as raise local stresses. This would presumably raise the stress needed for ductile failure. As the dislocations move, the hydrogen atmospheres are dragged with them, presuming the correct strain rate range. As the temperature was higher and the strain rate lower than that at
which serrated yielding is generally observed, it can be presumed that the hydrogen was likely dragged along with the dislocations. This condition would be different from those proposed previously where dislocation transportation of hydrogen was deemed unimportant [55]. As dislocations intersect grain boundaries, and are accommodated, it is presumed that hydrogen will be deposited in the grain boundary, which would act as a sink due to its large capacity for hydrogen. Although as dislocations are emitted, it is presumed that some of the hydrogen would also be removed from the grain boundary, as more dislocations are accommodated than are emitted, there would be a net accumulation of hydrogen in the grain boundary, lowering the cohesive strength. Concurrently, the grain boundary is being deformed and, consequently, further weakened. Supposing sufficient hydrogen in the system, there would be a point where the weakening of the grain boundaries, due both to deformation and to the presence of hydrogen, would cause the stress needed for grain boundary failure to be lower than the stress needed for ductile failure, which is raised due to the accelerated hardening. The hardening of the matrix lowers the cohesive strength drop needed for intergranular failure, and the deformation of the grain boundary adds to the reduction in cohesive strength in addition to the direct effect of hydrogen.

Applied to Lassila and Birnbaum’s results [254], the trends can be explained by this new interpretation. If there is insufficient hydrogen in the system, the cohesive strength of the boundaries can never be low enough for intergranular failure to be favored over ductile processes. Given sufficient aging time for the hydrogen to segregate to the grain boundaries, the starting cohesive strength of the grain boundaries will be lower than without the aging. This means less strain hardening is needed, and less dislocation-mediated hydrogen segregation is needed. This would account for why intergranular failure can occur at a lower bulk hydrogen concentration than without aging.

Knowing the underlying microstructure beneath the intergranular facets allows a new understanding of the fracture process. Classical interpretation of intergranular failure would be that hydrogen causes a sufficient reduction in cohesive strength of the grain boundaries such that grain boundary decohesion is favored over ductile failure through the matrix. Plasticity is thought to be insignificant, with grain boundary failure occurring prior to extensive plastic deformation. However, in steels, the onset of intergranular failure has long been associated to be
a function of the yield stress, but was associated with blocked plasticity [8]. In the new understanding, the yield stress of the material would help determine the stress (though lower with hydrogen) at which the dislocation structures formed to sufficiently harden the material and transport the hydrogen.

The presence of hydrogen during the loading of nickel results in intergranular failure and in an unexpected microstructure that is indicative of higher strains than was applied prior to failure. This microstructure points to a dislocation mediated mechanism for intergranular failure. The hydrogen-accelerated plasticity results in strain hardening and locally high hydrogen concentrations which together determine the fracture path.

5.3 Fatigue of Stainless Steels

As expected, hydrogen caused a reduction in the fatigue life of the stainless steels. Concurrently, there was a change in the fracture surface features. In the work reported herein, striation spacing and height decreased with the presence of hydrogen during loading. This result is contrary to previous findings in which the distance between striations increased in the presence of hydrogen [61, 62, 220]. This result was interpreted and validated as being indicative of greater cyclic crack advance in the presence of hydrogen. Of course, the magnitude of the striation spacing depended on the distance from the fracture origin, but was always larger in the presence of hydrogen [63]. Although every effort was made to extract samples from the same distance from the crack, it is possible that variations in the spacing reflect this difference. However, assuming this is not the case, the striation spacing in the presence of hydrogen may reflect a difference in mechanism, with crack advance in ambient conditions being related to the classical mechanism and the striation spacing associated with cyclic crack advance, whereas in hydrogen, crack advance and the formation of striations may be controlled by the need to develop a critical stress first.

The microstructure evolution as a function of depth beneath fatigue striations and flat regions on the fracture surfaces of uncharged and hydrogen-charged 304 and 316 stainless steel have been compared. The evolved microstructure is dependent on the steel and on the presence or absence of hydrogen, although it is unclear that internal versus external hydrogen has a significant effect.
From the observations of the hydrogen-induced microstructure ahead of arrested fatigue cracks, the deformation mechanism is seen to be predominantly due to dislocations, although in 304 stainless steel, as the crack is approached, there is evidence for the formation of strain-induced \(\alpha\)'-martensite plates. The volume transformed to martensite decreases with the presence of hydrogen, such that the transformed martensitic volume beneath striations in the uncharged material is replaced with martensite laths in an austenite matrix in the presence of hydrogen. The martensite plates form sequentially, as evidenced by the displacement of some plates due to the formation and extension of another variant. This microstructure, however, is different from that observed immediately beneath the fracture surface, which contains the refined sub-grain microstructure. This raises an interesting question of what drives the transition from a microstructure of dislocations with martensite plates to a refined sub-grain structure in which there is no evidence of martensite. Here, the difference between the microstructure evolution in 304 stainless steel in the presence and absence of hydrogen is not considered, as the primary difference is related to the transformation to martensite. Similarly, in 316 stainless steel, testing in the presence of internal hydrogen results in the formation of the sub-grain layer and deformation twinning whereas, in the absence of hydrogen, a complicated banded structure exists.

This is not the first report of such grain refinement under fatigue loading. It has been observed by atomic force microscopy measurements around a crack of a 0.47% C steel that underwent fully reversed Mode II fatigue [255]. It has also been observed in a Haynes 230 Ni alloy that had undergone fatigue loading with a load ratio of 0.05 [256]. From the study of Haynes 230 nickel, it has been revealed that the grain refinement occurs immediately ahead of the crack tip. As such, rubbing during the compression portion of the cycle, which would be less in the Haynes 230 system than in the system studied here, is not likely to be the principal cause of this grain refinement. This suggests that the grain refinement is formed either during the process of crack advance or by energy minimization processes associated with the formation of low energy dislocation structures. In both of these cases, it would imply that hydrogen influences the evolving microstructural processes, considering the differences between the samples with and without hydrogen. The formation of a fine grain structure can be the result of high strain processing, and has been observed due to equiangular channel extrusion [257], torsion [258, 259], and by wear [227, 260, 261], with wear also having a component of rubbing. The
refinement may be ubiquitous to fatigue, as even the 316 stainless steel fatigued in air showed evidence of refinement, though combined with the formation of high strain microband structures.

The hydrogen-evolved microstructure under the flat regions is different from that under the main striations with no evidence for the formation of sub-grains. Indeed, the microstructure is similar to that found in regions on the sample surface in close proximity to the arrested fatigue crack. This might indicate that such regions are generated rapidly, linking regions showing striations. One possible fast crack path could be a grain boundary or martensite lath boundary weakened by hydrogen. This possibility is supported by the case where the fracture appears intergranular.

In 304 stainless steel, the influence of hydrogen is more profound as it suppresses the wide-scale transformation to martensite. This is consistent with previous observations and has been attributed to hydrogen causing a narrowing of the plastic zone [9]. It is worth noting that the change from a wide-scale transformation to thin laths suggests a difference in the microstructural response in the presence of hydrogen, rather than simply a narrower zone of martensite transformation. The thinness of the laths suggests that they are formed due to local slip processes. The increased dislocation activity along certain slip systems leads to increased local deformation, which may in turn lead to local martensitic transformations. This localization of the plasticity to a narrower region may prevent a large-scale transformation.

It is clear that the presence of hydrogen changes the deformation processes accompanying fatigue loading and crack advance. The enhancement of the deformation processes and acceleration of the evolved microstructure by hydrogen can be ascribed to the hydrogen-enhanced localized plasticity (HELP) mechanism [50, 262-264]. Due to the shielding effect of the hydrogen atmospheres, the dislocation velocity is increased, or, alternatively, the same velocity is reached at a lower shear stress, and the equilibrium distance between dislocation decreases. Previous attempts to show that the presence of hydrogen accelerated the evolution of the dislocation density or the microstructure yielded mixed results. For example, prior attempts to find differences in dislocation density and distribution in Ni were inconclusive as no statistically significant differences were found between behavior in a hydrogen versus an inert gas environment [28, 265]. In contrast, Matsui et al. reported an increase in dislocation density in Fe cathodically charged at 200 K and deformed in tension [266]. One result which confirms
the effect of hydrogen increasing the effective strain is the effect of hydrogen on the bulk microstructure of a low alloy steel [149]. The microstructure after 100,000 cycles with hydrogen was more developed than that in vacuum: a doubling of the strain amplitude in vacuum produced a similar microstructure. The results in this thesis, in which the hydrogen concentration was significantly greater than in previous studies, have shown a discernible difference in the dislocation density and evolved microstructure. Here it is suggested that hydrogen enhances and accelerates the plastic processes in both 304 and 316 stainless steel. A consequence of this, irrespective of when and how the dislocations are generated, is that there is significant dislocation generation such that the pre-existing microstructure is destroyed and replaced with a refined sub-grain structure that extends up to 1 μm from the fracture surface. The extent of the refinement simply reflects the degree of deformation that has occurred.

The complicated nature of fatigue creates ambiguity in relating microstructural features with performance, but the effect of hydrogen on the microstructure is evident. While further tests varying the parameters of fatigue are needed for full understanding, the complicated microstructure that is produced suggests that current models of fatigue are too simplistic.

5.4 Liquid Metal Embrittlement

As in the case of hydrogen embrittlement, the mechanical properties of metals are often reduced when in contact with liquid metals. Liquid-metal embrittlement (LME) is a ductile-to-brittle transition induced by the intimate contact of a liquid metal on a metallic solid while applying mechanical stress. The severity of the embrittlement depends upon the metal/liquid metal system, with intergranular failure occurring by liquid metal penetration along the grain boundaries in certain systems [223, 267-272], and brittle cleavage occurring in others [273]. Several mechanisms have been proposed [70, 274-277], but the field remains under dispute, much like the field of hydrogen embrittlement. The similarities between hydrogen embrittlement and liquid metal embrittlement have been noted and it has been suggested that similar mechanisms are operating in both cases [70, 208]. The results shown herein suggest that, while there are similarities between the two cases of environmental embrittlement, the mechanisms are not what have been proposed previously.
5.4.1 T91 Martensitic Steel with Lead-Bismuth Eutectic or Liquid Indium

These results provide strong evidence that intergranular cracking is the main fracture mode in the liquid metal embrittlement of T91 steel rather than the previously claimed quasi-cleavage fracture mode [228]. Because the specimens were taken from typical areas of the fracture surface, this fracture mode is undoubtedly ubiquitous, and naturally explains the complex crack pattern observed, as the martensitic microstructure is intricate. The potential crack path is therefore determined by the interplay between the microstructure, the stress loading state and the competition between grain boundary cracking and plastic deformation. It is posited that for T91 liquid-metal-induced cracking proceeds as follows: plastic deformation produces an elongated microstructure, and, in plane stress, grain rotation proceeds until a shear texture is formed. Beyond some threshold, intergranular cracking occurs by the two available paths, namely, general grain boundaries and martensite lath boundaries. Because of the shear texture, the “river-like” appearance of the fracture surface is explained as the result of an intergranular crack finding its way in a heavily deformed and textured martensitic microstructure.

The occurrence of intergranular cracking in the case of steels, especially at martensite lath boundaries, calls for a re-assessment of the previous LME observations. Given the complexity of the microstructure of most high-performance steels used in the study of LME, it is likely that intergranular cracking is potentially the major fracture mode and not quasi-cleavage as claimed in previous studies [222, 278-280]. Crack arrest is due to the crack tip encountering a grain boundary carbide. This arrest mechanism adds to the complexity of the interpretation as the crack propagation would potentially depend strongly on the precipitation state of the alloy. Consequently, the sensitivity to LME and the severity of embrittlement would depend on the thermo-mechanical treatment, corresponding to previous results [281].

Having established that the fracture path is along the boundaries, it is necessary to consider what processes occur in the grain boundary in association with the uptake and diffusion of the liquid-metal species. Two notable effects occur: (1) the introduction of the impurity can cause a change in the grain boundary composition and, hence, in the cohesive strength; and (2) the impurity can cause structural changes in the boundary. Luo et al. [282] suggested that these two effects together, which can cause a change in the boundary even to the extent of producing another phase, are responsible for LME. Although no information on an impurity-induced change was
obtained, the magnitude of change in the cohesive strength can be estimated for Fe-9%Cr by using known parameters for pure Fe.

Grain boundary wetting in the Fe/Pb system has been studied by mechanical alloying [283]. Samples of Fe and Pb were produced by ball milling followed by sintering at 700°C under hydrogen and observed using TEM. These observations revealed that the grain boundaries are not wetted by Pb and the measured grain-boundary wetting angle \( \theta_{S-L} \) of Pb is 135°±10°. Therefore, assuming there is no segregation of Pb to the grain boundary, i.e. grain-boundary wetting by Pb is not favored thermodynamically, the equilibrium of surface energies at the grain boundary leads to the following relationship between grain-boundary energy \( \gamma_{GB}^{Fe} \) and solid-liquid iron surface energy \( \gamma_{S-L}^{Fe} \):

\[
\frac{\gamma_{GB}^{Fe}}{\gamma_{S-L}^{Fe}} \approx 2 \cos \left( \frac{\theta_{S-L}^{Fe}}{2} \right) \quad (5.1)
\]

Notably, inserting the mean value of grain-boundary energy measured in zero-creep experiments in terms of the surface energy of Fe in eq. (1) yields \( \gamma_{GB}^{Fe}/\gamma_{surf}^{Fe} \approx 0.37 ± 0.05 [284] \). The surface energy of iron, typically measured near melting and independent of surface type, is \( \gamma_{surf}^{Fe} \approx 2.5J/m^2 [284] \). The solid-liquid surface energy reduction becomes

\[
\frac{\gamma_{S-L}^{Fe}}{\gamma_{surf}^{Fe}} = \frac{0.37 ±0.05}{2 \cos(\theta_{S-L}^{Fe}/2)} \approx 0.483 \approx \frac{1}{2} \quad (5.2)
\]

This factor of two reduction is insufficient in itself to explain cracking.

Using this viewpoint, the thermodynamic work of separation, S, compares the surface energies of the initial state (with a liquid-metal wetted grain boundary) to the final state (with two liquid-metal wetted free surfaces) and is

\[
S = \gamma_{GB}^{Fe} - 2\gamma_{S-L}^{Fe} \quad (5.3)
\]

Grain-boundary wetting and spontaneous cracking would be observed if S is positive in equation (3), i.e., the wetted free surface is favored in energy. Indeed, using the observed wetting angle yields \( S \approx -0.62\gamma_{surf}^{Fe} \), which is negative (i.e., favors the grain boundary over free surface generation). Therefore, although the presence of liquid metal on the grain boundary lowers the energy barrier for intergranular failure, it is not, in and of itself, sufficient to cause intergranular failure and an additional driving force must be supplied. While extensive diffusion along the
boundaries may be favored in certain systems, which may form bilayers of liquid metal with weak bonding between them, effectively reducing cohesion without invoking interfacial energy changes [223], there is a question of the time required to diffuse along the grain boundaries to form these systems. Given the time scales of the mechanical testing, it is unlikely that this is the dominant effect in question. Here, it is the mechanical loading or the consequences of it that provides the additional driving force. Thus far it has been assumed that the boundary is free of other segregants. This situation is unlikely, but the presence of other segregants, which also impact the boundary energy [285], is not central to this interpretation as the effect would be additive in either a positive or negative sense.

5.4.2 Armco Iron with Liquid Indium

It is evident from both the fractography and the FIB-TEM of the crack tip that the primary fracture mode of this system is intergranular failure. From the TEM analysis, it is evident that the failure occurred along the boundary not parallel to it. However, the failure is not entirely brittle, since a significant amount of plasticity occurred prior to failure. This is evident from the fractography and from the FIB lift-out samples, both from ahead of the crack tip and from the fracture surface. Given the chemical similarities between the T91/In system and this system, the same mechanism is active in both. The difference in the fracture surface is due to the complexity of the martensite structure in the T91 system compared to the simple microstructure of the Armco iron.

The crack initiation at the notch is more puzzling. The fracture initiates in transgranular “quasi-cleavage” mode that in plan-view appears similar to the “quasi-cleavage” features in pipeline steels described earlier. However, as evident from higher magnification fractography at various tilts, the river patterns are due to steps on the surface, rather than ridges, suggesting a closer acquaintance with cleavage features than with the “quasi-cleavage” observed in pipeline steels. Analysis showed that the failure planes are not cleavage planes, but slip planes, and there is a correspondingly high dislocation density beneath these features. The question remains of how this failure occurred and why there was a transition from transgranular “brittle” failure to intergranular failure.
The proposed cause of this transition is the presence of a work-hardened layer at the notch due to machining damage induced during the fabrication of the sample. This work-hardened layer frequently presents itself as a layer of fine grains, which may not be completely removed by grinding and polishing. The liquid metal could penetrate through this layer and encounter the first layer of grains. Due to plastic deformation, slip traces are likely to have formed on the grain surface. These could act as crack initiation sites that allow entry of the liquid metal into the grain along the slip plane leading to slip plane failure. It may be that this process is initially more energetically favorable than grain boundary failure. This may be true if the amount of plastic deformation is insufficient to drive the grain boundary decohesion. Once fracture has initiated, it is more energetically favorable to fail along the grain boundaries as sufficient plasticity has occurred. This failure mode may be dependent upon the preparation conditions.

5.4.3 Comparing Liquid Metal and Hydrogen Embrittlement

Previously, it has been claimed that similarities in the appearance of the hydrogen-induced and LME-induced fracture surfaces indicated a similarity in mechanism [70, 208]. The current study as well as recent reports on the microstructure beneath hydrogen-induced fractures compared to low-temperature fracture surfaces [233, 234, 286, 287] have shown that similarities in the appearance of fracture surfaces cannot be taken as evidence for operation of the same mechanism.

For example, in the study by Nagao et al. of hydrogen embrittlement of a martensitic steel, “quasi-cleavage” type failure has been observed [287]. FIB-TEM analysis of these fracture surfaces revealed that the “transgranular fracture” was actually martensite lath boundary failure. Plasticity was observed for an extended area around the fracture surface, and the deformation was sufficient to disrupt the lath boundaries. As with the case of LME, the combination of an embrittling agent at the grain boundary and applied stress leading to a hardened matrix is required for failure. A key similarity between hydrogen and LME cases and the previous “transgranular fracture” claim is that now the need is for a reduction in the cohesive strength of the interface to occur concurrently with an increase in the local stress through work hardening of
the matrix. This scenario is supported by our detailed electron microscopy beneath the facets on the fracture surface, but could not be ascertained from the fracture surface morphology alone.

A comparison of the work of Nagao et al. in hydrogen embrittled martensitic steel with the liquid metal failures of T91 martensitic steels can also be made to show the differences in the mechanism. Previous studies have suggested similar processes are at work. While both show martensite boundary failures, the microstructures were different. In the hydrogen assisted failures of Nagao et al., the lath texture was similar to the original microstructure, however large amounts of plasticity disrupts the lath boundaries. This plasticity was likely locally accelerated by the presence of the hydrogen. By contrast, the microstructure of the T91 LME samples was significantly different from the original microstructure. Equiaxed grains changed into strongly textured laths. Significantly more deformation was needed prior to failure, and as this is bulk deformation, it is unlikely that the liquid metal at the crack tip significantly impacted it.

The similarity between HE and LME is that both failures occurred due to an embrittling agent at the grain boundary. In other words, the weakest path through the material failed, and the weakest paths were along the grain boundary due to the presence of the environment. Hydrogen diffused through the bulk, probably aided by dislocation activity. The liquid metal diffused along the grain boundary. Both also required plasticity to develop a work-hardened matrix and modify the local stresses in order to produce the conditions for the failure to occur. A simple calculation showed that the liquid metal by itself is insufficient to cause the boundary failure. However, the plasticity in both cases was of different magnitudes. Hydrogen accelerated the plasticity, particularly in the vicinity of the crack tip, while this did not occur in the LME case. There is, therefore, a similarity between LME and HE, however, the microstructural mechanism for each differs in the effect of plasticity.

This is in contrast to crack tip plasticity mechanisms which state that the only effect of hydrogen or the liquid metal is at the crack tip, lowering the energy needed to emit dislocations. The projected result of this mechanism is a decreasing dislocation density as function of distance away from the crack tip, and fine voids opening up ahead of the crack tip that link back to the crack tip. It is the evidence on the fracture surface produced both by hydrogen and liquid metal embrittlement that has been held as support for this mechanism. The current study allowed the
viewing of various local crack tips that are filled with liquid metal. While liquid metal was observed to diffuse along the boundaries ahead of the crack tip, voids were not observed ahead of the crack tip. The deformation was uniform with no distinct gradient from the crack tip, and no half-loops were observed extending from the crack tip supporting surface emission.

While there are similarities between liquid metal embrittlement and hydrogen embrittlement, the microstructural mechanisms are different. Liquid metals affect the surface and internal interfaces, aided by the applied stress. Hydrogen infiltrates the material, requiring diffusion or dislocation-assisted transport to reach the grain boundaries, and affects the developing microstructure due to the applied stress.

5.5 Proposed Hydrogen Embrittlement Mechanism

The results presented herein [233, 234, 286, 288] have demonstrated that plasticity processes are a fundamental part of hydrogen-assisted fracture. Although different loading conditions were applied to different materials, and different microstructures were observed in each, there is a commonality between them. Complex and unexpected dislocation structures formed, showing refinement of dislocation features. It is evident that the observed plasticity is neither a byproduct of brittle processes nor simply a surface effect, but is significant.

Hydrogen clearly accelerates the plastic deformation processes. This acceleration can be explained by the Hydrogen-Enhanced Localized Plasticity (HELP) model [35, 120, 195]. This would cause plasticity to occur at stresses lower than the expected yield strength, and to produce microstructures that are expected for higher strains or higher fatigue cycles than occur during loading. This accelerated plasticity would be limited to areas of sufficiently high hydrogen concentration. In many real situations, this would be limited to the area around cracks where hydrogen ingress is occurring (in the case of external hydrogen) or where hydrogen is concentrating due to the applied stress.

This “limited” plastic zone, according to results presented herein, likely covers tens of microns ahead of the crack tip. In many materials, this will extend through multiple grains, developing the microstructure in front of the propagating crack. This leads to strain hardening of the
material. It is important to stress that any crack that forms is not propagating through virgin material. It is propagating through highly deformed material that has different properties from its original form. Due to effect of the hydrogen, in terms of closer packing of dislocations and inhibition of cross-slip, microstructures that would not form in the absence of hydrogen may be created. This different microstructure will have a different influence on the propagation of cracks than either virgin material or microstructures developed in the absence of hydrogen.

Within the strain rate regime where hydrogen embrittlement occurs, the hydrogen atmosphere would be dragged along with the dislocations. The hydrogen-influenced plasticity would lead to a redistribution of hydrogen throughout the material. This must be considered since the plasticity is significant, not limited as previously assumed. The hydrogen distribution is now likely to be more complicated than the simple model with the highest concentration at the point ahead of the crack tip. In particular, locally high concentrations of hydrogen can accumulate to extent that decohesion processes start to become significant. This will lead to locally weak regions within the microstructure. By accounting for dislocation transport due to crack tip stresses, new solid mechanics models show that it is possible to dramatically change the hydrogen distribution and create locally high concentrations [289].

The combination of hardened microstructures with local weak regions due to hydrogen will determine the fracture path through the material. The weak regions will be the first to fail, possibly due to decohesion processes. The fracture surface will follow the weakest path through the material, possibly with fast ductile tearing joining these regions. If failure is too fast for hydrogen diffusion, it will have a limited effect on the process, which is probably true of ductile features on the fracture surface due to final failure. Depending upon the microstructure that has developed, the failure itself may be a very brittle process, as in intergranular failure, or a more ductile linking of brittle initiation sites, as in refined microvoid coalescence, or something in between where cracks initiated by decohesion grow locally by plastic processes, but are limited in scale such that they appear brittle, as in “quasi-cleavage” features.

This model can account for the transitions in failure mode from refinement of ductile microvoid coalescence to “brittle” transgranular and to intergranular failure with increasing hydrogen concentration. These transitions are caused by changing the balance between the different
effects of hydrogen on both the plastic processes and the cohesive strengths of the various microstructural components. In summary, fracture follows the weakest path through the material, and hydrogen determines the path through the microstructure and local concentration.

5.6 Limits of Fractography

While there have been significant advances in scanning electron microscopy, the use of the instrument for fractography of hydrogen-induced fracture surfaces remains much the same. A cursory overview to determine the mode of failure (ductile, intergranular, or “quasi-cleavage”) is generally the extent of analysis. While it is crucial to understand the fracture mode, particularly for fracture analysis (such as needing to improve grain boundary impurity levels), a problem arises when basing mechanisms of deformation processes upon these observations.

Higher resolution fractography sheds light upon the problems of pure brittle fracture interpretations placed upon these features based upon classical fractography methods. The evidence of plasticity on these features helped pioneer the field of plasticity-based hydrogen embrittlement [194, 206]. However, surface analysis does not indicate the amount or the depth of dislocation activity. In many cases, markers of plasticity can lead to erroneous interpretations. It is difficult to define the evolved microstructure from knowledge of just the fracture surface and the morphological features on it. In general, the envisioned microstructure is too simple. This raises the interesting question about the importance often attached to fine features on fracture surfaces, which are generally indicative of ductile processes, to the overall hydrogen-induced failure of the material. If they are generated in the final stages of separation of the surfaces, they are of less significance to the overall process, especially in determining any role of hydrogen on deformation processes.

The case of nickel intergranular failure is essential to proving this point. Many facets show only one set of slip traces, suggesting planar slip in the grain beneath. However, the TEM results shown here demonstrate that this is clearly not the case. Previous analysis even admitted that basing interpretations of hydrogen effects of slip on slip band observations were fraught with difficulties. One example given by Lynch [214] is that the hydrogen-influenced preferentially activity of edge dislocation components over screw due to inhibition of cross-slip and strain-
localization could result in coarser slip bands compared to in air, but could also lead to the activation of other slip systems leading to finer more complicated slip bands. Therefore, the interpretation of dislocation activity below a surface based upon surface traces is likely to be erroneous in most cases, as arguments could be made either way.

The problem of basing failure mode interpretations for “quasi-cleavage” features is particularly apt in the work of Nagao et al. [287]. Hydrogen assisted failure of martensitic steels showed similar fracture features to low temperature fractures, both of which were labeled “quasi-cleavage”. However, upon FIB-TEM analysis, it was shown that the hydrogen-assisted failures were boundary failures of the martensite laths, while low temperature fractures were cleavage failures along {001} type planes at angles to the martensite lath boundaries. Very similar fracture features were produced by two different processes. Another case is the hydrogen-assisted failure of dissimilar metal weldments where “cleavage” failure was observed in a face-centered cubic metal [192]. Only through careful analysis of the underlying microstructure was it revealed that the failure occurred along the boundaries of closely packed precipitates that were aligned along crystallographic planes. The resulting fracture closely followed the habit plane of these precipitates leading to a failure mode that resembled cleavage without any cleavage mechanism occurring.

The similarity between LME and HE described earlier is another case where fractography had been used to determine the fracture mechanism. Comparing the work of Nagao et al. with the T91 LME failures presented herein, it can be seen that both samples failed by plasticity-mediated boundary failure, leading to similar looking failures. However, the microstructure mechanism of the plasticity-mediated failure differs for both cases, with hydrogen influencing the one, and the liquid metal not affecting the other. This fundamental difference is important in understanding and modeling these failures.

While fractography can be useful in many cases, it is limited in its capabilities for understanding deformation and fracture mechanisms. While it provides crucial information for understanding these processes, it is insufficient in itself. The similarities between fracture features formed by completely different processes clearly illustrates the risk in using fractography as the sole means of extrapolating fracture mechanisms.
CHAPTER 6
CONCLUSIONS

A set of tools was developed to investigate the microstructural mechanisms of failure and was applied to cases of environmental failure. In particular, the application of focused-ion beam lift-out sample preparation allows the observation of microstructures immediately beneath fracture surfaces, and the correlation of the evolved microstructure to the fracture surface features. Applied to hydrogen embrittlement, several conclusions can be drawn from the study of different structural materials failed in different geometries and loading conditions.

An immediate result from these investigations is that the underlying microstructure cannot be determined based upon fracture surface features. High magnification fractography reveals information about the fracture path and the final separation processes. However, fracture surfaces produced by very different fracture processes can appear nearly identical. Additionally, signs of plasticity, such as slip traces or dimples, can be deceiving as to the amount of plasticity and the type of plasticity processes that have occurred. Final separation processes, while useful in determining the sequence of failure events, are not likely to be strongly impacted by environmental factors, and are more likely the inevitable result of the microstructural and fracture processes preceding final separation.

The commonalities between the various cases studied suggest that there is a common mechanism for hydrogen-enhanced failure. Hydrogen enhances the dislocation activity throughout the material. This behavior can be accounted for by the hydrogen-enhanced localized plasticity (HELP) model. This results in the creation of complex and highly strained microstructures. Two consequences result from this accelerated plasticity: the material is strain hardened, and locally high hydrogen concentrations are created within this microstructure. Local features can become weakened by the combination of strain and high hydrogen concentration. Failure of the weakest microstructural features occurs through a decohesion process, initiating either a sharp crack or a void. Fracture occurs through the weakest path of the material, as developed by the plasticity and influenced by the local hydrogen concentration.

The similarity between LME and HE is likely due to the weakest path failing: in many structural materials, the weakest paths, such as grain boundaries, are both susceptible to weakening due to
an embrittling agent. The important factor is the developing microstructure ahead of the propagating crack, which is accelerated in the presence of hydrogen, but not in the presence of liquid metals.

It is the developing microstructure that is crucial to understanding environmental embrittlement. In order to accurately predict failure, models must account for the plasticity, both in terms of the developing microstructure and the consequences on the local hydrogen distribution. By knowing this information, it may be possible to develop predictive models that can aid in the selection of materials to perform in a Hydrogen Economy.
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