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The effect of shot peening on hydrogen entry into and hydrogen embrittlement of AISI 4130 steels

Chattoraj, Indranil, Ph.D.

The Ohio State University, 1991
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THE EFFECT OF SHOT PEENING ON HYDROGEN ENTRY INTO AND
HYDROGEN EMBRITTLEMENT OF AISI 4130 STEELS

DISSERTATION

Presented in partial fulfillment of the requirements for the Degree of Doctor
of Philosophy in the Graduate School of The Ohio State University

By
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The Ohio State University
1991

Dissertation Committee:
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Approved by
B. E. Wilde
Advisor
Department of Metallurgical Engineering
...But then they sent me away to teach me how to be sensible,
Logical, responsible, practical.
And they showed me a world where I could be so dependable,
Clinical, intellectual, cynical.

There are times when all the world's asleep,
The questions run too deep
For such a simple man.
Won't you please, please tell me what we've learned
I know it sounds absurd
But please tell me who I am.

...........

(From "The logical song" by Supertramp)
To the memory of my beloved brother
To my dear parents and my dear sister
To my grandfather, a grand man
ACKNOWLEDGEMENTS

I would like to thank Dr. Bryan E. Wilde for his guidance and for being a friend and mentor at all times. Thanks are due to Drs. Paul G. Shewmon and Susan Smialowska for their helpful suggestions. The assistance and advice provided by Clare McDonald, Jay Ellis and the late Don Murfield, and Rita Rokhlin of the Department of Physics is very appreciated. I am grateful to The General Motors Corporation and The Sandia National Laboratories for providing funds for this project. The technical assistance and advice provided by Jeff Meister of The Metals Improvement Company, Cincinnati, in the matters pertaining to shot peening are gratefully acknowledged.

I wish to thank my many friends, who are too numerous to acknowledge individually. I am indebted to my family and relatives for their love and support, which helped me through trying times.
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CHAPTER 1

INTRODUCTION

Hydrogen evolution on an iron surface by cathodic charging was first observed by Faraday in 1858 \(^1\). Since then, over a span of more than a century, many researchers have tried to characterize the hydrogen evolution reaction on the technologically significant metals \(^2,3,4,5\). Johnson \(^6\) was the first to observe hydrogen embrittlement (HE) in 1873 and a great deal of research on hydrogen entry and embrittlement has been justified because of the industrial importance of the problem of metal and alloy embrittlement by hydrogen.

The evolution of hydrogen occurs frequently due to cathodic reduction of H\(^+\) ions in aqueous corroding solutions, or hydrogen may be absorbed due to the use of high pressure hydrogen gas in the environment. In addition, the material itself may have hydrogen retained from the process of ore reduction (steelmaking for example). Hydrogen either absorbed from the environment or present in the material can lead to unpredictable catastrophic failure if the material is exposed to a tensile stress in service. This is evident in the various failures in the oil and gas industry, aircraft and automotive industries.
Because of the hazards of material destruction as well as man-hours and production time lost, numerous researches on ways of preventing HE, especially in steels have been undertaken. The belief that HE occurs only in relatively harder materials and that materials with hardnesses less than Rockwell hardness (HR) C 22 are immune to HE has been refuted by Turn, Wilde and Troianos \(^{(7)}\), who observed HE in materials of hardness HRB 66.

The various approaches adopted to tackle this problem can be broadly classified as:

a) those that involve bulk metallurgical modifications \((8,9,10)\)

b) those that introduce changes in the environment

c) those that introduce surface modifications \((8,11,12)\).

The problem with bulk metallurgical modifications brought about by alloying or heat treatment is that the consequent changes in the engineering properties may be unacceptable for application. For example, after seventy years of research, we cannot guarantee resistance to HE in low alloy steels in presence of hydrogen evolution. Altering the environment is most often done by inhibitor injection so as to reduce hydrogen absorption into the material. This approach is however always susceptible to an accidental stoppage of inhibitor supply. Moreover the inhibitor injection process is an additional burden in terms of material cost, design and supervision.
Surface modification processes are possibly the best approaches since once modified, the material doesn't require constant monitoring nor does it cause changes in the bulk properties of the material. Whereas bulk modifications attempt to change the hydrogen diffusivity, the type and distribution of trap densities in the material and the cracking kinetics of the material, surface modifications try to eliminate the problem by reducing the hydrogen entry through the surface. The work of Wilde and Shimada (11), has demonstrated a number of surface modification methods that are successful in reducing hydrogen entry into steels.

The present work was motivated by the discovery of Wilde and Shimada that shot peening successfully reduces the hydrogen ingress rate. One objective of the present work was to characterize the benefits as regards hydrogen permeation into steels by quantifying the various parameters involved in the surface reaction of hydrogen evolution and absorption, and by doing a comparison of these parameters for different degrees of peening. The present research was conducted on high strength AISI 4130 steels typical of those used in automotive fasteners. Such fasteners when exposed to water containing road salt often corrode with the liberation of hydrogen as the cathodic reaction and ultimately fail due to HE.

Another objective was to attempt to correlate the hydrogen entry process with the embrittlement severity and to demonstrate that reductions in hydrogen ingress translate to reductions of embrittlement in accelerated tests. The importance of determining the kinetic parameters of the hydrogen entry process is that they are direct proofs of the efficacy of any
surface modification process. The relative magnitudes of these parameters as compared to that of an untreated surface provide insight into the mechanism affecting the hydrogen adsorption and absorption process which is of significance both for theoretical understanding and for practical implementation.

It is well known that the process of peening introduces surface compressive stresses, a phenomenon associated with reduction in crack propagation in stress corrosion cracking and also fatigue crack initiation. It was predicted \(^{(13)}\) and proven \(^{(14)}\) that compressive stresses are beneficial from the point of view of hydrogen entry into steels. No systematic investigation has been conducted however on the influence of such stresses on the various steps leading to HE, namely hydrogen entry, hydrogen transport and eventual fracture. This research quantifies the parametric changes brought about by different intensity peening and provides explanations for the changes observed in the permeation and embrittlement response of the steel on peening.
CHAPTER II

LITERATURE REVIEW

The problem of hydrogen embrittlement of any material necessitates the step by step study of the various mechanisms which finally lead to embrittlement. The steps can be broadly classified as follows:

1. Hydrogen adsorption at the metal / alloy surface.
2. Hydrogen evolution at the metal / alloy surface.
3. Absorption of some of the adsorbed hydrogen into the bulk of the metal.
4. Transport of absorbed hydrogen to normal lattice sites as well as potential sites for cracking, under the influence of a naturally existing or externally applied chemical potential gradient.
5. Accumulation of hydrogen at the crack sites leading to catastrophic failure.

Various schematics have been proposed for the reaction sequence mentioned above. McBreen and Genshaw (4) proposed a simple scheme for the evolution and entry reaction and over the years it has served as a
satisfactory basis for iron and steels and is included here in Figure 1.

As a result of the sequential nature of the overall process, the study of HE of steels in aqueous environments can be divided into electrochemical aspects and the study of hydrogen transport; that is the study of the surface reactions and the study of hydrogen in the bulk of the material. In keeping with this loose classification, the following is a review of work done in the two related fields and their implication on HE.

1. HYDROGEN EVOLUTION AND ABSORPTION

The overall reaction of hydrogen evolution in solutions are as follows:

\[ 2 \text{H}_3\text{O}^+ + 2e^- = \text{H}_2 + 2\text{H}_2\text{O} \quad \text{(in acid solutions)} \quad \ldots \ldots \quad 1 \]

\[ 2\text{H}_2\text{O} + 2e^- = \text{H}_2 + 2\text{OH}^- \quad \text{(in alkaline solutions)} \quad \ldots \ldots \quad 2 \]

The overall reaction can proceed by two mechanisms namely:

a. **The recombination mechanism** which involves chemical recombination of adsorbed hydrogen atoms as follows:

i. \[ \text{M} + \text{H}^+ + e^- = \text{MH}_{\text{ads}} \quad \ldots \ldots \quad 3 \]

ii. \[ \text{MH}_{\text{ads}} + \text{MH}_{\text{ads}} = \text{H}_2 + 2\text{M} \quad \ldots \ldots \quad 4 \]

b. **The electrochemical desorption mechanism** which involves the following electrochemical steps:

i. \[ \text{M} + \text{H}^+ + e^- = \text{MH}_{\text{ads}} \quad \ldots \ldots \quad 3 \]

ii. \[ \text{MH}_{\text{ads}} + \text{H}^+ + e^- = \text{H}_2 + \text{M} \quad \ldots \ldots \quad 5 \]

As a result of the need for multiple steps, it is obvious that one of the reaction steps can become rate controlling in the overall reaction path. By
Figure 1. Hydrogen evolution and entry scheme. (REF 4)
considering different combinations of reaction steps, with one or more of them being rate controlling, McBreen et al (4) were able to derive relationships between the overpotential, hydrogen evolution charging current and permeation current during hydrogen charging experiments (Table 1).

Studies carried out on iron and steels (12,15,16) suggest a coupled discharge recombination mechanism for the hydrogen evolution reaction, (HER). This author also reached similar conclusions in his research with AISI 4130 steels. Thus it is necessary to discuss in more detail this mechanism as done in the following sections.

Coupled discharge recombination mechanism

In this mechanism of hydrogen evolution, the hydrogen discharge step and the chemical combination of adsorbed hydrogen atoms occur at rates comparable in magnitude, so that there is no single rate limiting step. The reaction steps are restated here:

\[ \text{H}^+ + M + e^- = \text{MH}_{\text{ads}} \] ........................................ 3

\[ \text{MH}_{\text{ads}} + \text{MH}_{\text{ads}} = \text{H}_2 + M \] ........................................ 4

If hydrogen charging is carried out at potentials significantly negative to the reversible potential for the overall reaction, the backward reaction in step (3) can be neglected and the hydrogen evolution current density can be expressed as

\[ i = FK_fC_{\text{H}^+}(1 - \theta)\exp(-\alpha\eta F/RT) \] ............ 6
Table 1. Variation of polarization parameters and steady state hydrogen flux with the rate controlling mechanism for hydrogen evolution reaction.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>$-\delta V/\delta \log i$</th>
<th>$-\delta V/\delta \log J_\infty$</th>
<th>$J = f(n(i)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow discharge-fast recombination</td>
<td>$2RT/F$</td>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>Slow discharge-fast electrochemical</td>
<td>$2RT/F$</td>
<td>$RT/F$</td>
<td>$i^2$</td>
</tr>
<tr>
<td>Fast discharge-slow recombination</td>
<td>$RT/2F$</td>
<td>$RT/F$</td>
<td>$i$</td>
</tr>
<tr>
<td>Fast discharge-slow electrochemical</td>
<td>$2RT/3F$</td>
<td>$RT/F$</td>
<td>$i^{2/3}$</td>
</tr>
<tr>
<td>Coupled discharge-recombination</td>
<td>$2RT/F$</td>
<td>$4RT/F$</td>
<td>$i^{1/2}$</td>
</tr>
<tr>
<td>Coupled discharge-electrochemical</td>
<td>$2RT/F$</td>
<td>0</td>
<td>--</td>
</tr>
</tbody>
</table>

$i = \text{charging current}$  
$J_\infty = \text{steady state hydrogen flux}$
where $C_{H^+}$ is the concentration of hydrogen ions in the solution, $K_f$ is the forward reaction rate constant for the adsorption reaction, $\theta$ is the fractional coverage of metal surface by adsorbed hydrogen, $\alpha$ is the transfer coefficient, $\eta$ is the overpotential, $F$ is the Faraday's constant and $R$ the gas constant.

The current density can also be expressed in terms of the recombination reaction as:

$$i_r = K_3\theta^2 \quad \text{........................7}$$

where $K_3$ is the recombination rate constant. At low values of $\theta$, from (A) and (B), the following equation evolves

$$\theta = \frac{K_f}{K_3}(C_{H^+})^{0.5} \exp\left\{-\frac{\alpha\eta F}{RT}\right\} \quad \text{..............8}$$

Therefore $d\eta/d\ln \theta = -2RT/\alpha F$ and $d\eta/d\ln i = -RT/\alpha F$. Iyer, Pickering and Zamanzadeh (17), with the help of suitable assumptions have developed means of calculating the hydrogen surface coverage and the various kinetic parameters for coupled discharge recombination mechanism.

It was earlier believed (18, 19) that hydrogen entered into the metal without forming an intermediate adsorbed state. The entry of hydrogen into the lattice was believed to be independent of the process of hydrogen discharge. This belief was refuted by Bockris et al (15) who showed that such a mechanism would predict that the permeation current vary as square of the charging current, a relationship which is not substantiated by
experimental findings. It is widely accepted now that hydrogen before entering into the metal lattice forms an adsorbed intermediate which acts as a precursor to both the recombination and the absorption of hydrogen. Thus the entry of hydrogen into metal is by means of series-parallel reaction mechanism.

The absorption of hydrogen into metal can be expressed by the equation

\[ K_{\text{abs}} \theta = K_{\text{des}} C_0 \]  

where \( C_0 \) is the subsurface hydrogen concentration, \( K_{\text{abs}} \) and \( K_{\text{des}} \) are the absorption and desorption rate constants. The above relationship is valid for low hydrogen coverage on the surface. Hydrogen permeation occurs in response to a concentration gradient with the surface concentration \( C_0 \) as the upper concentration limit in most cases. The importance of determination of surface coverage is evident.

**2. HYDROGEN PERMEATION**

The absorbed hydrogen atom moves down a concentration gradient in the metal or alloy thus producing a hydrogen flux at the exit surface. The permeation flux of hydrogen is an important quantity, which assists in the measurement of diffusivity, surface coverage, semi-quantitative calculation of trap density and distribution of trap types and is an important indicator of HE susceptibility.

The diffusion of hydrogen through a material is influenced by the presence of reversible and irreversible traps, application of stress and the
presence of oxide films on the surface. The permeation flux is essentially a product of the solubility of hydrogen in the material and the hydrogen diffusivity. The effect of the various variables mentioned above on both parameters have been the subject of extensive research and will be reviewed here.

Darken and Smith \(^{20}\) were among the first to experimentally record hydrogen permeation. They used a gas charging technique. The various methods used to study hydrogen permeation have been compiled by Subramanyan \(^{21}\). In spite of the numerous sophisticated methods, the permeation technique due to Devanathan and Stachursky \(^{22}\), which is very simple in design but provides very accurate data, is most commonly employed.

In the text that follows, the various methods of interpreting the permeation data and the effects of certain variables on the permeation flux of hydrogen through metals and alloys with special emphasis on hydrogen diffusion through steels, will be discussed.

2.1 Diffusivity Measurements

In the absence of trapping or stress gradients, that is when the chemical potential gradient is solely due to a difference in concentration, the Fick's laws of diffusion apply.

\[
\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta x^2} \quad \text{.....10} \quad \text{and} \quad J = D \frac{\delta C}{\delta x} \quad \text{.........11}
\]

where C is the hydrogen concentration at a distance x from the input surface at time t. J is the permeation flux and D the diffusivity of hydrogen.
at x. If permeation experiments are conducted under the condition of a constant concentration at the input surface and zero concentration at the output surface at all times (Figure 2), the permeation transient can be expressed by the infinite series

\[
\frac{J(t)}{J_\infty} = \frac{2}{(\pi \tau)^{0.5}} \sum \exp \left\{ -(2n + 1)^2 / 4 \tau \right\} \quad \ldots \quad 12
\]

By suitable approximations of this infinite series solution, various equations for diffusivity have been deduced. Devanathan and Stachursky \(^{23}\) used the breakthrough time \(t_b\) and the lag time \(t_l\), which are explained in Figure 3, in their expressions for diffusivity:

a.) \(D = \frac{L^2}{15.3 t_b} \ldots \quad 13\) \quad and \quad b.) \(D = \frac{L^2}{6 t_l} \ldots \quad 14\)

By applying Fourier transformation, the approximate first term solution to the infinite series is

c.) \(\frac{J(t)}{J_\infty} = 1 - 2 \exp \left\{ -\pi^2 D t / L^2 \right\} \quad \ldots \quad 15\)

this is valid for \(J/J_\infty \geq 0.3\). Similarly the first term solution due to Laplace is

d.) \(\frac{J}{J_\infty} = (2/\pi^{0.5}) \left( \frac{L}{(D t)^{0.5}} \right) \exp \left\{ -L^2/4Dt \right\} \quad \ldots \quad 16\)

Subramanyan \(^{21}\) and Turnbull, et al. \(^{24}\) have compiled these relationships. These equations are for the rise or buildup transient. Similar treatments have been prescribed for the decay transients. However one assumption needed in the development of the equation for the decay transient does not seem valid. This is the assumption that the input surface on switching off charging current, is impenetrable, that is no hydrogen
Figure 2. Concentration profile in a hydrogen charged membrane
Figure 3. Typical permeation curve.
flux passes through the plane $x = 0$. Nanis and Namboodhiri (25) showed that two-thirds of the hydrogen present in a membrane diffused out through the entry surface on switching off current. The alternate assumption of a zero concentration at the input surface, is also doubtful as this would require the hydrogen recombination reaction to be extremely fast. Subramanyan (21) had pointed out that even if recombination was instantaneous, the lowest hydrogen concentration at the input surface would be that which is in equilibrium with the pressure of evolving hydrogen gas.

The solution due to Laplace can be expanded to provide the following relationships:

**Decay:** \[ \log [J_\infty - J(t)] t^{0.5} = \log 2FCD^{0.5}/\pi^{0.5} - (L^2\log (e)/4D)*1/t \] .... 17

**Buildup:** \[ \log J(t) t^{0.5} = \log 2FCD^{0.5}/\pi^{0.5} - (L^2\log (e)/4D)*1/t \] .... 18

where $C$ is the input surface concentration of hydrogen during charging and $J_\infty$ is the steady state permeation current. Zakroczymski (26) compared diffusivity values from buildup and decay transients to show that H transport through metal was the rate limiting step in permeation. It should be pointed out that presence of an oxide film at the input surface, change in diffusivity with concentration and trapping will cause the diffusivity measured from buildup transient to be different from that due to decay transient. Darken and Smith (20) observed that the evolution rate of hydrogen was different from the absorption rate in their gas charging permeation experiments. This made them conclude that the diffusivity of hydrogen could not be assumed independent of concentration. In case of
reversible trapping, the effective diffusivity calculated from buildup transient will be lower due to hydrogen lost to traps. On switching off the charging current, these traps in an effort to equilibrate with decreasing lattice concentration, lose hydrogen to the lattice thus yielding a different decay transient from that which would be observed for a membrane without traps.

2.2 Trapping

Darken and Smith \(^{(20)}\) were the first to observe that hydrogen diffusion in steels was affected by imperfections in the lattice. Johnson and Hill \(^{(27)}\) coined the term "residual hydrogen" for hydrogen trapped irreversibly at imperfections. They observed a decrease in hydrogen diffusivity at low temperatures and a dependence of hydrogen diffusivity on concentration in \(\alpha\)-iron. The first formalism for trapping in steels was developed by McNabb and Foster \(^{(28)}\). They suggested a trapping and detrapping parameter and they came up with a mathematical formulation based on the assumption of local equilibrium between trapped and normal lattice sites. Their formalism considered only the reversible traps; irreversible traps were considered not to influence the diffusion as they represented sinks with hydrogen essentially removed from the permeation system. The salient points of their theory are discussed below.

If \(N\) is the density of reversible traps and \(n\) is the fraction of traps occupied, the rate of increase of trapped hydrogen is given as

\[
\frac{dn}{dt} = kC (1-n) - pn
\]
where $k$ is the trapping constant and $p$ is the detrapping constant. Expressing the hydrogen concentration $C$ as $C_0u$ ($u$ essentially defines the concentration profile in the specimen), and using non-dimensional variables, two equations are obtained, the first is the Fick's equation modified for trapping.

$$\frac{du}{d\tau} + \alpha \eta \frac{d\eta}{d\tau} = D \left\{ \frac{d^2u}{dx^2} + \frac{d^2u}{dy^2} + \frac{d^2u}{dz^2} \right\} \quad \cdots \cdots \cdots \quad 20$$

$$\frac{d\eta}{d\tau} = \beta \left\{ \gamma u - \eta - \gamma \eta \right\} \quad \cdots \cdots \quad 21$$

where $\tau = Dt/a^2$, $x, y, z$ are $x/a$, $y/a$ and $z/a$ with $a$ being the linear dimension. $\alpha, \beta$ and $\gamma$ are dimensionless parameters defined as $\alpha = N/C_0$, $\beta = pa^2/D$ and $\gamma = C_0k/p$. From these definitions it is obvious that when $\alpha$ is small (i.e. $C_0 >> N$) there is negligible reversible trapping in the specimen.

Oriani (29) utilized the concept of local equilibrium between trapped and diffusible hydrogen and developed expressions for apparent diffusivity and the activation energy for trapping, for low occupation of traps. His equation relating perfect lattice diffusivity ($D_L$) to the apparent diffusivity $D$ was

$$D = D_L \frac{C_L}{C_L + C_X (1 - \theta_X)} \quad \cdots \cdots \quad 22$$

where $C_L$ and $C_X$ are concentrations of hydrogen in the normal and trapped lattice sites and $\theta_X$ is the fraction of traps occupying hydrogen. This expression clearly shows the dependence of measured hydrogen diffusivity on lattice as well as trapped hydrogen concentration.
The works of McNabb and Foster, and Oriani considered a single population of reversible traps. Pressouyre and Bernstein\(^{(30)}\) characterized the trapping behavior of different kinds of traps, both reversible and irreversible, by controlling the type and number of traps and observing their effect on permeation transient.

Johnson, Quick and Kumnick\(^{(31)}\) analyzed saturable and non-saturable traps by considering relationships between the trapped hydrogen concentration and the lattice hydrogen content and redefining effective hydrogen diffusivity in terms of these relationships. According to their theoretical development, one can predict an increase in apparent hydrogen diffusivity with lattice hydrogen content when saturable traps are present, while the reverse is true for non-saturable traps. McNabb and Foster\(^{(28)}\) had predicted that for diffusion of hydrogen through a slab with fixed input surface concentration and output surface concentration maintained at zero, the time lag measured from permeation transients would be modified by trapping so that

\[
t_t = t_1 \left[1 + 3\alpha/\beta + 6\alpha/\beta^2 - 6\alpha\{(1 + \beta) \ln (1 + \beta)\}/\beta^3\right] ............ 23
\]

where \(t_t\) and \(t_1\) are time lag for diffusion with trapping and for pure lattice respectively, and \(\alpha = N_Tk/p\) and \(\beta = C_0k/p = n/1-n\), these parameters were defined earlier in this chapter. Kumnick and Johnson\(^{(32)}\) modified this expression for the limiting cases obtaining \(t_t/t_1 = 1 + \alpha\) for the case of low occupancy of traps (i.e. \(\beta, n << 1\)) and \(t_t/t_1 = 1 + 3N_T/C_0\) for trap saturation (\(n \sim 1, \beta >> 1\)). They suggested that at low temperatures when
3NT/C0 >> 1, the effective diffusivity can be related to the steady state flux as: D_{eff} = D_L \{1 + 3 N_T/C_0\}^{-1} \sim D_L C_0/3N_T = a J_\infty/3N_T and thus trap concentration can be obtained from independent measurements of effective diffusivity and steady state flux. Furthermore in the low coverage region, \alpha can be obtained from the \tau_0/\tau_I ratio, and since \alpha can be alternately expressed as N_T/N_L \exp (E_b/RT) where E_b is the binding energy of the trap, the latter can be estimated. Hashimoto and Latanison \cite{33} used this approach in their work.

Iino \cite{34} developed a mathematical formulation for diffusion in the presence of both reversible and irreversible traps. He predicts that the effect of the presence of both kinds of traps on diffusivity is multiplicative. An interesting artifact of his theory is the presence of intermediate plateaus in the permeation transient, a phenomenon not often reported in literature but observed by this author in some permeation transients. Pressouyre and Faure \cite{35} calculated reversible and irreversible trap concentration from successive permeation experiments on the same specimen. Pound \cite{36} used a potentiostatic double pulse technique to calculate trapping constants.

To summarize, we can consider traps as either reversible or irreversible depending on the depth of the potential well they present to hydrogen diffusion. Trapping manifests itself by changing apparent diffusivity values measured from time lag data. The amount and direction of such a change from perfect lattice diffusion depends on the amount and type of traps present in the lattice. Various methods have been reported for measuring trapping constants and trap concentrations. The influence of various traps on HE will be discussed later. So far we have considered static
traps, that is a constancy of trap population during the entire duration of the experiment. Simultaneous creation of traps and their influence on hydrogen ingress, also known as dynamic trapping, occurs during straining of hydrogen charged specimen and will be discussed in the next section.

2.3 Effect of strain

Elastic and plastic straining seems to influence the amount of hydrogen absorbed and consequently the HE susceptibility. de Kazinczy \(^{37}\) observed that hydrogen permeated more through a tube stressed in tension than an unstressed tube, when subjected to the same charging current. Beck, et al. \(^{38}\) came to the conclusion that the increased permeation was a result of increased hydrogen absorption. They were the first to report that the hydrogen diffusivity did not change with stress in steel. Moreover, they found that the effect of stress was reversible in the elastic region, that is, the increase in permeation on application of stress disappeared on removing stress.

The bulk of work done on the effect of strain on hydrogen permeation, has tried to explain the increase of observed permeation flux in terms of the effect of tensile stress on hydrogen solubility, rupture of oxide film at charging surface and dynamic trapping. Beck et al \(^{38}\) suggested a change in hydrogen solubility depending on the magnitude and type of applied stress. They suggested that since the diffusivity was independent of stress in Armco iron and AISI 4340 steels, the emigration volume expressed as \(V^* = (\delta \Delta H_D/\delta \sigma)_t\), where \(\Delta H_D\) is the activation energy for diffusion, is zero.
Since emigration volume is a measure of the lattice distortion at the saddle point of the diffusion potential energy curve, this would indicate that hydrogen migration causes negligible lattice distortion and most of the energy of activation would be required to distort interstitial sites. They went on to calculate the partial molar volume of hydrogen in the metal and found that it was significantly lower than the molar volume, thus validating the idea of interstitial distortion during diffusion. Oriani (13) suggested that since the effect of stress on solubility was thermodynamic, the chemical potential of hydrogen should increase due to a compressive stress thus decreasing its solubility. Bockris et al (14) showed that such was the case, in their work with Armco iron. An interesting observation by Beck, et al. (38) was that even in the regime of elasticity, in AISI 4340 steel, the effect of stress was not reversible at stresses well below yield. The explanation provided was that the combined action of hydrogen in voids and applied tensile stresses caused internal stresses which would not relax on removing external stress and these internal stresses would sustain the permeation flux.

Plessis, et al. (39) observed no change in permeation behavior of hydrogen through nickel with stress at elevated temperatures. This is probably due to the fact that thermal energy compensates for the lattice distortion needed for hydrogen absorption, rendering stress effects insignificant.

Donovan's (40) experiments with sorption of tritium in nickel strengthened the idea of increased hydrogen solubility with tensile stress. However, he also observed a change in apparent diffusivity of tritium on
plastic deformation. The effects discussed in the earlier paragraphs were observed in the elastic region of stress. In this region, the most acceptable explanation for the observed changes would be a change in solubility as proposed by Bockris et al. On increasing stress beyond yield, dislocations are generated. They can act as traps as well as increase hydrogen mobility by carrying hydrogen in their Cottrell atmospheres, and one of these two conflicting contributions to hydrogen transport becomes dominant depending on strain rate. As stress is increased, there is a possibility of thin oxide films formed on the charging surface breaking up, thus exposing new surfaces. Donovan observed a fifteen fold increase in the amount of tritium absorbed on the surface of a nickel specimen strained to fracture, compared to an unstressed specimen. Such a huge increase cannot be attributed to lattice expansion effect on solubility alone. It was attributed to the effect of dislocation movement on the absorption kinetics.

Zakroczymski (26) observed that in Armco iron, elastic straining caused a slight increase in permeability, but after the onset of plasticity, there was a steady decrease in permeation rate with increasing plastic strain. He suggested dynamic trapping as predominant in determining hydrogen permeation and also refuted the idea of dislocation accelerated hydrogen transport.

The interrelationship of dynamic trapping and strain rate was investigated by Frankel and Latanision (41). They observed that in nickel, the permeation flux was lower for a stressed sample compared to an unstressed sample when the strain rate was high and higher when strain rate was low. They also noted an increase in passivation current with
stress. The conclusion drawn from their experiments was that trapping by newly created dislocations overshadowed any contribution of dislocation transport to the overall hydrogen flux. At high strain rates, lattice refilling is negligible during the time of the experiment, thus causing a lowering of flux. At low strain rates adequate lattice refilling from the dynamic traps occur, this coupled with the decreased specimen thickness and increased solubility lead to an increased flux. Since dislocation transport should be highest at the highest strain rates, the contribution to hydrogen flux by dislocations is insignificant. Frankel and Latanision suggested a diffusional parameter $D/e^*L^2$, where $e^*$ is the strain rate, whose magnitude would determine if lattice refilling from strain induced traps is adequate under a given strain rate. A low value of the parameter would suggest significant trapping and vice versa.

Scully and Moran (42,43) attributed the increased hydrogen solubility with tensile strain to oxide film rupture in AISI 4340 steels. They demonstrated that the hydrogen evolution kinetics are different in slightly corroded specimen as compared to one with virgin surface (Figure 4). They postulated that either the hydrogen surface coverage or the rate constant for absorption or both are increased by straining and that hydrogen diffusion was not enhanced by dislocation transport. Hashimoto and Latanision (33,44) modified McNabb and Foster's equations by considering trap density to be time dependent and showed that there was a linear increase of trap site density with plastic strain for Armco iron. They suggested that dislocation transport would become important at low lattice hydrogen concentration.
Figure 4. Relationship between charging current and steady state hydrogen flux for AISI 4340 Steel. (REF 43).
The effect of strain is thus due to three factors. In the elastic region, stress causes a change in hydrogen solubility from purely thermodynamic considerations. Dynamic trapping occurs at near yield and above yield stresses and is sensitive to the rate of straining. Oxide film rupture should take place progressively as specimen is strained. The contributions of these three factors are difficult to separate from permeation flux measurements. Similarly, in the case of dynamic trapping, dislocation enhanced hydrogen transport cannot be ruled out. The increase in flux on tensile straining would suggest an increase in hydrogen concentration at trapped sites in local equilibrium with lattice hydrogen content and this has direct bearing on hydrogen embrittlement, if crack initiation occurs at traps. The reduction of flux on compression is thus significant from a materials protection point of view. Surface modifications that induce residual compressive stresses (shot peening, ion deposition, etc.), do have the potential to stop hydrogen embrittlement.

3. DETERMINATION OF SURFACE COVERAGE

It is evident from what has been discussed so far that the hydrogen concentration profile in the material is of great importance in the embrittlement process. The surface concentration of hydrogen is one of the boundary conditions for hydrogen diffusion; this is related to the surface coverage by the absorption-desorption equilibrium reaction. The kinetics of the adsorption-desorption process as well as the absorption process, determine the amount of hydrogen in the subsurface, so the various kinetic
parameters are good quantitative indicators of a metal's susceptibility to embrittlement, along with other factors discussed earlier.

Various methods of surface coverage (θ) determination have evolved with time. Bowden originated the method of galvanostatic charging which can be used for noble metals. The disadvantage of this method is that it can only be used if there is considerable difference between the potential corresponding to the completion of hydrogen dissolution and the start of the next anodic process, a condition existing only for noble metals. Bockris and co-workers developed a method using compensation curves to apply to non-noble metals. Presented below are two methods of θ and kinetic parameter determination. The first is a direct experimental determination of said parameters and the second is an indirect theoretical determination process that utilizes the polarization and permeation data.

3.1. Double charging method

This method developed by Bockris and co-workers compensates for the contribution to the anodic transient from processes other than hydrogen dissolution. The experimental procedure involves cathodic polarization of the material under consideration to a known overpotential value so that a steady cathodic current is imposed on the specimen. This current is switched off and a constant anodic current (i_a) is applied immediately. Under these conditions the potential of the double layer (V) changes with time according to

\[ C_V \frac{\delta V}{\delta t}_N = i_a - i_H - i_{an} (1 - \theta) \]

24
where $C_Y$ is the double layer capacitance, $i_H$ is the hydrogen dissolution current, $i_{an}(1 - \theta)$ is the current due to other anodic processes.

The next step involves letting the electrode lose all the adsorbed hydrogen by holding it at slightly anodic potentials and then applying the constant anodic current. Under such conditions, a compensating curve is obtained for the electrode according to

$$C_Y (\delta V/\delta t)_C = i_a - i_{an} \quad \text{........... 25}$$

From 24 and 25

$$C_Y [(\delta V/\delta t)_C - (\delta V/\delta t)_N] = i_H - i_{an} \theta \quad \text{........... 26}$$

The value of the capacitance is calculated from the compensating curve at low anodic overpotentials ($i_{an} \ll i_a$) and $C_Y = i_a/(\delta V/\delta t)$. The values for $(i_H - i_{an} \theta)$ obtained from the normal and compensating curves at various potentials are plotted against times required to reach those potentials for the normal curve. This is shown in Figure 5. The area under the curve is given as

$$A = \int i_{H,\theta}(1 - i_{an}\theta/i_{H,\theta}) \, dt \quad \text{........... 27}$$

Bockris et al. (45) showed that the error involved in neglecting the term $i_{an}\theta/H$ is very small and thus the area under the curve gives the amount of hydrogen adsorbed by the electrode ($A = \int i_{H,\theta} \, dt$) or conversely the amount of charge required to dissolve all the adsorbed hydrogen. The ratio of this value to the theoretically calculated value of charge required to
Figure 5.1 Galvanostatic anodic charging curves. A: Normal curve. B: Compensation curve. (REF 46)

Figure 5.2 \((i_H - i_{an0})\) calculated from 5.1. (REF 46)
dissolve a monolayer of adsorbed hydrogen covering the entire electrode surface, gives the surface coverage. Devanathan and Selvaratnam\(^{(46)}\) applied this method successfully to determine surface coverage on nickel in alkaline solutions. However in body centered metals, the high hydrogen diffusivity results in an error term. Kim and Wilde\(^{(47)}\) modified the theoretical development stated earlier, by including a compensation for diffused hydrogen. The hydrogen that diffuses into the metal during cathodic charging contributes to the anodic transient on switching off cathodic current, in addition to the adsorbed hydrogen. They suggested that this contribution can be calculated by considering the solution of the diffusion equation for the electrode geometry. Kim and Wilde also used steady state permeation data along with experimentally calculated \(\theta\) values to obtain the absorption constant \(k_{\text{abs}}\) according to the equation

\[
\frac{1}{J_\infty} = \frac{L}{D\theta} \left( \frac{k_{\text{des}}}{k_{\text{abs}}} \right) + \frac{1}{k_{\text{abs}} \theta} \quad \text{........... 28}
\]

where \(k_{\text{des}}\) is the desorption rate constant. The intercept of the straight line plot \(1/J_\infty\) against \(L\), the specimen thickness, is \(1/k_{\text{abs}}\theta\) and since \(\theta\) is experimentally determined, the absorption constant can be calculated.

3.2. I-P-Z Method

Iyer, Pickering and Zamanzadeh\(^{(17)}\) developed a method of determining surface coverage and related kinetic parameters from permeation and polarization data. Their method is suitable for materials in which the hydrogen evolution reaction follows a coupled discharge-
recombination mechanism, often encountered in hydrogen evolution studies on iron and steels. The assumptions necessary for this model are:

1. Coupled discharge-recombination mechanism is operative and the system under investigation is at sufficiently cathodic overpotentials so that the backward reaction of hydrogen oxidation can be neglected.

2. The intermediate adsorption-absorption reaction is in local equilibrium so that diffusion through membrane is rate controlling in hydrogen permeation.

3. The charging current \( i_c \) is the sum of the hydrogen recombination current \( i_r \) and the steady state permeation current \( i_\infty \). Steady state conditions are imposed to eliminate trapping effects.

The charging current according to the first assumption is given by

\[
 i_c = F K_1^0 a_{H^+} \exp\left( -\alpha E^{eq} F \frac{RT}{a} \right) \left( 1 - \theta \right) \exp\left( -\alpha \eta \frac{F}{RT} \right) \quad \text{...... 29}
\]

where \( K_1^0 \) is the rate constant for the forward reaction, \( \alpha \) is the transfer coefficient and \( a_{H^+} \) is the hydrogen ion concentration in the solution, \( E^{eq} \) is the equilibrium potential for the hydrogen evolution reaction, other symbols have usual meanings. This can be alternately written as

\[
 i_c = i_0' \left( 1 - \theta \right) \exp\left( -\alpha \eta a \right) \quad \text{...... 30}
\]

where \( a = \frac{F}{RT} \) and \( i_0' \) includes all the constants not explicit in this modified expression for (29). The recombination and the steady state permeation current can be expressed as

\[
 i_r = FK_3^0 \theta^2 \quad \text{...... 31} \]
\[
 i_\infty = F(D/L)C_0 \quad \text{...... 32}
\]
where $K_3$ is the recombination rate constant and $C_0$ is the subsurface hydrogen concentration. Since the adsorption-absorption reaction is in local equilibrium, $i_\infty$ can also be expressed as

$$i_\infty = F(k_{abs}\theta - k_{ads}C_0) \quad \ldots \ldots \quad 33$$

Substituting from (32) \quad $\theta = C_0/K'' \quad \ldots \ldots \quad (34)$

where $K'' = k_{abs}/(k_{ads} + D/L)$. From (31), (32), (33) and (34)

$$i_\infty = K'' \left[b/(FK_3)^{0.5}\right]^{-1} (i_\text{p})^{0.5} \quad \ldots \ldots \quad (35)$$

where \quad $b = L/FD$. Also rearranging (30)

$$i_c \exp \{\alpha \eta a\} = -(bi_0'/K'')i_\infty + i_0' \quad \ldots \ldots \quad (36)$$

Thus, if a plot of the L.H.S of equation (36) against $i_\infty$ yields a straight line, $i_0'$ and $K''$ can be calculated since $b$ is known from permeation data. Using the calculated $K''$ value, $K_3$ can be evaluated from equation (35) and $\theta$ from equation (34). An extrapolation of the plot of $\theta$ against $\eta$, to $\eta = 0$ would provide the equilibrium hydrogen surface coverage. The transfer coefficient is determined from the equation involving slopes of the cathodic polarization curves

$$\alpha^2 + [(2S_c - S_\infty)/a] \alpha + [S_c(S_c - S_\infty)/a^2] = 0 \quad \ldots \ldots \quad (37)$$

where $S_c = d\ln i_c/d\eta$ and $S_\infty = d\ln i_\infty/d\eta$.

Iyer et al, used this model to determine the surface coverage on iron and nickel electrodes. Their model predicts that the steady state permeation current ($i_\infty$) should vary as the square root of the recombination current
(ir), a phenomenon often observed in iron and steels. However there is documentation of experiments in which plots of $i_\infty$ versus $i_r^{0.5}$ have non zero intercepts \(^{(15)}\), contrary to this theory. Iyer et al rationalized this by assuming a selvedge type reaction for hydrogen such that the near surface hydrogen concentration profile is not the same as that in the bulk metal, as shown in FIG 6. This leads to modifications of the equations (35) and (36)

\[
i_\infty = K'' \left( b(FK_0)^{0.5} \right)^{-1} i_r^{0.5} + \frac{C_g}{b} \quad \text{(38)}
\]

and

\[
i_c \exp(\alpha \eta \alpha) = - \frac{(b_i'/K'')}{i_\infty - \frac{C_g}{b}} + i_0' \quad \text{(39)}
\]

The new term $C_g$ is defined as $C_g = C_i - C_s$, where $C_i$ and $C_s$ are explained in Figure 6. Such a rationalization in the absence of any direct evidence of selvedge reaction is quite arbitrary and one of the weaknesses of the I-P-Z model.

4. HYDROGEN EMBRITTLEMENT

The role of absorbed hydrogen in embrittlement can be understood by first comprehending the effects of hydrogen on the mechanical properties of iron and steel. Hirth \(^{(48)}\) summarized the deleterious effects of hydrogen on iron and steels. Oriani and Josephic \(^{(49)}\) listed the physical degradation brought about by hydrogen in medium carbon steels. It is obvious from the volume of data on hydrogen effects that contradictory results are often encountered. The most common controversy is the question as to whether hydrogen softens or hardens steels. Oriani and Josephic \(^{(49)}\) reported a hardening effect for 1045 steels. Similar findings were reported for a variety of low and medium carbon steels \(^{(50, 51)}\). A facilitation of yielding with
Figure 6. Different concentration profiles for hydrogen charged membranes (with and without selvedge). (REF 17)
increased charging of hydrogen have been reported by Lee, et al. (52), Cracknell and Petch (53) and Rogers (54). The hardening effects have been attributed to the impediment of cross slip due to presence of hydrogen or to the reduction of the generation of dislocations at the grain boundary due to hydrogen absorption at the grain boundary (49). Hirth (48) suggests that hydrogen being present in the dislocation cores could make dislocation interactions difficult; also hydrogen could be trapped in vacancies thus retarding recovery processes. Hirth and Oriani concur that at high charging currents, softening effects observed are due to microvoid production in the material. Such microvoid production can be viewed as an effective reduction in the cross section of the specimen. The fact that softening effects are observed at high charging currents and high strains lends credibility to this argument.

According to Oriani, the role of hydrogen is to pin dislocations by attractive interactions as a result of which glide initiation is more difficult and moving dislocations are slowed down by the drag force of hydrogen atoms. These would cause an increase in yield strength, rate of hardening and strain aging. Oriani rationalizes the increase in stress relaxation rate observed in steels on hydrogen injection by proposing a lowering of internal stress field due to nucleation of microvoids.

The effect of hydrogen on the fracture phenomena is a reduction in the ductility of the steel. This reduction is proportional to the hydrogen content and thus to the hydrogen charging current. Hydrogen has been found to enhance void nucleation, growth and coalescence in low strength steels. In low strength steels hydrogen tends to reduce ductility (as
measured by reduction in area) without changing the microstructural mode of fracture. In high strength steels, quasicleavage or cleavage fracture is more common. In the presence of hydrogen, crack nucleation is facilitated and crack propagation can occur at low hydrogen gas pressures (< 1 atmosphere ) as shown by Hancock and Johnson (55).

The synergistic effects of hydrogen and stress were studied by Troiano and coworkers (56,57,58), Oriani (59) and others. Troiano observed delayed fracture in high strength steels in hydrogen environments. The fracture time was found to be a function of applied stress and hydrogen content in steel as shown in Figure 7. The results show a lower limit for stress similar to the endurance limit in fatigue, below which no fracture is observed. The increase in lower critical stress with decreasing hydrogen content led Troiano to suggest that crack initiation is controlled by the dual effects of hydrogen and stress. The concept that hydrogen interacts with lattice atoms at the position of maximum triaxial stress state was postulated by Troiano. This theory of HE is one of the many theories suggested by various authors, all involving varying degrees of experimental substantiation and hypothetical deductions. The more popular concepts of hydrogen embrittlement are discussed below.

4.1. Decohesion Theory

This theory was developed by Troiano to explain the synergistic effects of hydrogen on material degradation. The work of Mortlet, Johnson and Troiano (57) tried to explain the variation of ductility of prestrained and precharged AISI 4340 steels with aging time, as shown in Figure 8. The
Figure 7. Variation of incubation period for cracking of Sharp notch specimens with applied stress and hydrogen concentration corresponding to different baking times at 300°F. (REF 56)
Figure 8. Ageing curves at 1500 F for prestrained and hydrogenated specimens. (REF 57)
curve shows a maxima and a minima, the relative magnitudes of which depend on the amount of prestrain. Troiano refuted the pressure theory and various surface adsorption theories for embrittlement, as these would predict an initial loss in ductility, in variance with experimental observations. Troiano et al proposed that the degree of embrittlement would vary as the hydrogen concentration in the region of maximum triaxiality in the lattice. Whereas the other theories were concerned with hydrogen content in cracks and voids, this theory renders hydrogen in voids harmless entities, and only hydrogen in special lattice positions as significant in embrittlement. The role of voids and cracks is to act as stress raisers, so that the region of maximum triaxiality is generally near such imperfections. The shape of the aging curve is then due to the variation of hydrogen concentration in near void regions of the lattice as governed by the diffusion of hydrogen to these positions. The disappearance of hydrogen embrittlement at low temperatures can be explained by the decrease of hydrogen diffusivity and at high temperatures by the conflicting effects of stress induced diffusion and increased homogenization.

Troiano \(^{(56)}\), made the observation that crack initiation and propagation in HE occurs in three distinct stages: (a) incubation, (b) slow crack growth and (c) catastrophic failure. From fractographic observations, Troiano concluded that the third stage of catastrophic failure was essentially overload failure and there was no effect of hydrogen in this stage. The incubation period according to Troiano was the time required for hydrogen to reach a critical concentration in the region of maximum triaxiality. The slow crack growth in the second stage
is essentially the rate of hydrogen diffusion to regions in front of the crack tip, thus implying discontinuous cracking.

Troiano suggested a decrease in cohesive strength of the lattice due to presence of hydrogen; this coupled with the observation that hydrogen accumulates at regions of high triaxial stresses near imperfections, explained embrittlement phenomena. Troiano's original speculation was that hydrogen atoms in solution in transition metals donate their electrons to the d band of the metallic core, thus increasing the repulsion of metallic cores. This theory predicted that addition of copper to nickel would increase embrittlement initially and then decrease it as the 3 d band in nickel is progressively filled; this prediction was substantiated by experimental findings.

Tetelman and Robertson (60) observed that crack growth due to hydrogen charging occurred discontinuously. Oriani and Josephic (61,62) demonstrated the existence of a threshold stress at a given hydrogen fugacity and conversely a threshold fugacity at a given stress intensity, below which crack growth did not occur in steels. They observed that the threshold values for deuterium was consistently higher than for hydrogen. This observation can only be reconciled with the decohesion theory; deuterium has a lower molal volume than hydrogen in α-iron, thus it is less effective in concentrating at triaxiality sites due to stress induced diffusion. According to Oriani, decohesion due to hydrogen is manifested in high strength steels by an increase in cleavage fracture and in low strength steels by an enhancement of microvoid nucleation. Stress relaxation studies (63) on AISI 1045 steels were explained by suggesting that since hydrogen
causes decohesion, it favors microvoid generation over relaxation by dislocation activity. Oriani and Josephic (49) also proposed that reduction of Peierl's stress and reduction of screw dislocation cross slip in bcc iron are due to reduced cohesive strength in the presence of hydrogen.

Birnbaum's (64) objection to this concept of lowering of cohesive strength is that such a reduction should also manifest itself in the reduction of atomic force constants and elastic constants. In the case of fcc metals a decrease in these constants is indeed observed in presence of hydrogen. However in Vb metals like niobium, even at very high hydrogen charging, there is significant increase in $C_{11}$ and bulk modulus values (65). The other criticism of this theory is in the appearance of fractures. Decohesion theory predicts that intergranular fracture surface should show the morphology of grain interface whereas actual observations with high resolution microscopes reveal fracture along slip planes near grain boundaries, often crossing over into adjacent grains along slip planes (66).

In spite of these criticisms, decohesion theory is one of the more popular theories of HE. Calculations based on embedded atom model (67) and cluster variation method (68) do suggest that hydrogen would indeed cause decohesion, thus vindicating this theory.

4.2. Internal Pressure Theory

A theory of hydrogen embrittlement based on hydrogen accumulation at voids was proposed by Zapffe and Sims (69). According to these authors hydrogen atoms accumulate at voids until an equilibrium pressure is attained. When this pressure attains a value close to the elastic strength of
the metal, the metal embrittles. de Kazinczy \(^{(70)}\) elaborated on this concept by suggesting that crack growth is facilitated by the energy released by expanding hydrogen gas in cracks. de Kazinczy utilized Griffith's theory of brittle fracture, which states that for a stable crack to grow, the system must undergo a total decrease in the energy content. He suggested that part of the total energy of the material charged with hydrogen is due to the energy content of hydrogen gas in the cracks and voids. On crack propagation, the gas expands releasing energy and thus the energy due to strain required to meet Griffith's criterion is reduced, that is, the strain at which crack propagates is lower. This model however requires that the material have pre-existing cracks in it. However Bilby and Hewitt \(^{(71)}\) and Garofalo et al \(^{(72)}\) proposed that crack initiation could be due to dislocation pile up under the influence of external stress. Bastien and Azou \(^{(73)}\) suggested that hydrogen is concentrated in Cottrell atmospheres of dislocations and is transported along with dislocations to the cavities. This dislocation enhanced diffusion of hydrogen would account for the incubation time and temperature effects of embrittlement.

Bockris and Subramanyan \(^{(74)}\) developed relationships for the hydrogen fugacity in microcracks and voids as a function of overpotential, in electrochemical charging of hydrogen. Based on theoretical calculations, they predicted which rate controlling mechanisms for hydrogen evolution would cause embrittlement when pressure theory was valid (Table 2). Beck et al \(^{(38)}\) suggested that blister formation due to high internal pressure of hydrogen in cavities would lead to plastic deformation in the vicinity of
Table 2. Variation of hydrogen fugacity as a function of rate controlling mechanism for hydrogen evolution reaction. (REF 74).

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Fugacity($f_{H_2}$)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast discharge-slow recombination</td>
<td>$\exp(-2\eta F/RT)$</td>
<td>Could be embrittling</td>
</tr>
<tr>
<td>Slow discharge-fast recombination</td>
<td>1</td>
<td>Non-embrittling</td>
</tr>
<tr>
<td>Fast discharge-slow electrochemical</td>
<td>$\exp(-2\eta F/RT)$</td>
<td>Could be embrittling</td>
</tr>
<tr>
<td>Slow discharge-fast electrochemical</td>
<td>$\exp(2\eta F/RT)$</td>
<td>Non-embrittling</td>
</tr>
<tr>
<td>Coupled discharge-recombination</td>
<td>$10^{1.5}\exp(-\eta F/RT)$</td>
<td>Could be embrittling</td>
</tr>
<tr>
<td>Coupled discharge-electrochemical</td>
<td>$\exp(-2\eta^* F/RT)$</td>
<td>----</td>
</tr>
</tbody>
</table>

$\eta$ = overpotential
blisters. This was supposed to increase the dislocation density near blisters, which would act as crack initiation sites.

There are two criticisms to this theory. Johnson and Hirth (75) showed that hydrogen supersaturations obtainable at dislocations were greatly overestimated in literature, and dislocation transport, even if it was effective, could not account for large internal pressures required by this theory. The findings of Hancock and Johnson (55), that crack propagation occurs even at very low hydrogen pressure environments, also contradicts the internal pressure mechanism of embrittlement. Such a mechanism might be effective in high fugacity environments (76) but it cannot be accepted as a general theory.

4.3. Slip Softening Theory

Beachem (77) observed that in low alloy steels, crack tip growth in hydrogen assisted cracking occurred by microscopic deformation processes, and this deformation decreased as the stress intensity factor increased. Based on these observations, he proposed that hydrogen enhances plasticity at a microscopic level, of the crack tip. At high stress intensity (K) values, since the plastic zone is proportional to K^2, there is a significant plastically deformed region in front of the crack tip, containing void nuclei. The fracture process in this case would be by microvoid coalescence. As K decreases, there is a gradual change over in the fracture mode from microvoid coalescence to quasicleavage and eventually to intergranular fracture. The seeming contradiction of enhanced plasticity and enhanced brittleness occurring simultaneously was explained by
Beachem by pointing out the facts that: a) crack growth is much faster than diffusion of hydrogen into rest of the lattice so enhanced plasticity due to hydrogen is very localized, b) hydrogen tends to concentrate near crack tips since these are regions of maximum triaxiality and maximum trap density. Beachem's model considered hydrogen as an enhancer of dislocation motion, quite in contrast to other theories.

Birnbaum and co-workers (78,79) observed increased dislocation activity in presence of hydrogen and its cessation on removal of hydrogen, in a variety of materials. The effect of hydrogen was found to be the reduction of stress for dislocation motion. Birnbaum suggested that this was due to elastic interaction between dislocation and hydrogen solutes. The enhanced dislocation motion due to hydrogen was postulated to be due to elastic shielding of dislocations by hydrogen atmospheres (64). Hydrogen being extremely mobile can move along with dislocations and participate in interactions between dislocations and other elastic defects. Hydrogen decreases short range elastic interactions of defects with no effect on long range interactions since the spatial variation of hydrogen effects is proportional to $1/r^2$, while dislocation stress fields vary as $1/r$.

Lynch (80) views the phenomenon of enhanced plasticity as a surface effect. He observed similarities between embrittlement caused by hydrogen and liquid metal embrittlement (LME). Since there is virtually no diffusion of embrittling atoms in LME, Lynch suggested that this was due to surface adsorption of embrittling atoms at crack tips, which caused weakening of interatomic bonds facilitating dislocation nucleation and promoting crack growth by localized plastic flow. By analogy, he proposed that HE followed
the same pattern of events. Lynch assumed that ductile crack growth occurred when dislocations exited at the crack tip. Thus facilitating dislocation nucleation from crack tip would increase the total number of dislocations available for crack advance.

Lynch's view differs from that of Birnbaum in that dislocation enhanced hydrogen motion is not considered significant in the overall fracture process. He argues that the initial velocity of dislocations injected from rapidly growing cracks is too high for hydrogen atmospheres to accumulate around them; and even if hydrogen transport did occur by dislocations, such movement would be along slip planes steeply inclined to crack planes resulting in hydrogen transport away from crack tip front. Lynch's observation of dimpled fracture surfaces strengthened Beacham's localized plasticity theory.

The drawback of this theory is that it does not propose a mechanism of crack initiation due to hydrogen. The increased dislocation nucleation in the presence of hydrogen was attributed by Lynch to decohesion due to adsorbed atoms. Birnbaum's suggestion of enhanced hydrogen diffusion due to dislocations would not explain HE, it would provide one means of hydrogen transport to potential crack sites. Oriani (81,82) pointed out that observations of increase in flow stress required to nucleate and propagate Luder's band, and increases in flow stress and reduced plastic deformation in the presence of hydrogen are inconsistent with this theory. However if localized plasticity is in regions too small to discern with low resolution tools, the inconsistency is resolved. Observations from stress relaxation experiments, where hydrogen introduction causes increased
relaxation can be explained by hydrogen enhanced dislocation activity, but the observation of relaxation enhancement on cessation of hydrogen charging cannot.

4.4. Surface Adsorption Theory

Petch and Stables\(^{(83)}\) based their model on Orowan's\(^{(84)}\) suggestion that adsorption of atoms on surface Griffith's cracks lowered the fracture stress and produced delayed fracture effects. Hydrogen adsorption was proposed to lower the surface energy of the surfaces created in crack propagations resulting in lowered work of fracture. Petch\(^{(85)}\) developed the following relationship for the lowering of surface energy due to the presence of a diatomic adsorbate that dissociates on adsorption

\[
\gamma - \gamma_1 = 2 \Gamma_s K T \ln \left[1 + (AP)^{0.5} \right] \quad \ldots \quad 40
\]

where \(\gamma_1\) and \(\gamma\) are surface energies with and without adsorbed atoms on the surface respectively, \(\Gamma_s\) is the number of adsorbed atoms per unit area at saturation, \(A\) is a constant, \(K\) is the Boltzmann's constant and \(T\) and \(P\) have usual meanings. If a very mobile solute such as hydrogen was present, then the cracks could form with the adsorbed solute on them and crack propagation could occur at much lower stresses.

One argument against this theory is that it underestimates the work of fracture and that it cannot explain the reversibility of fracture. However Thompson\(^{(86)}\) has shown that brittle crack tip advancement can occur when a sharp crack tip is screened, so that small elastic stress
concentration is present at the crack tip. The fracture process in such cases is nearly reversible.

The strong criticisms against this theory are that it cannot explain the specificity of the adsorbate nor is it able to explain reversibility of the failure process with regards to stress application. Oxygen, although having a higher heat of adsorption, is found to inhibit cracking. These arguments rule out a completely brittle surface energy controlled cracking process; it can only be a complement to other processes.

4.5. Other Theories

Gilman (87), in contrast to Lynch's theory of localized plasticity due to adsorption, suggested that strong chemisorption of hydrogen would tend to prevent dislocation emission at crack tips and thus favor brittle cracking.

One theory, definitely not applicable to iron and steels, but quite valid for a variety of materials is the hydrogen related phase change mechanism. The basic premise of this theory is that a brittle phase be stabilized in the presence of hydrogen and stress. Under the presence of stress, the chemical potential of solute hydrogen and hydride is reduced at tensile stress concentrations such as at crack tips (64). Since these hydrides are brittle, the stress intensity for crack propagation is reduced. This mechanism can explain the observance of a temperature range in which embrittlement occurs, decreased embrittlement at high strain rates and presence of hydrides on the fracture surfaces. It has been argued that not only hydrides but some martensitic phases which are stabilized by hydrogen and stress can also cause embrittlement.
4.6. Overview

It is evident that there is no consensus regarding embrittling mechanism. Brittle hydride formation is the undisputed mechanism of hydrogen embrittlement in Group Vb metals, zirconium and titanium, and their alloys. For the other metals and alloys there are a number of theories, none of which are above criticism. The overlap of ideas among various theories is obvious and reconciliation between the various theories have been attempted. Thus Oriani (81), a proponent of the decohesion model, viewed Lynch's mechanism as essentially decohesion along the shear plane induced by hydrogen, a variation of the idea of decohesion along the tensile axis. Most authors also concur on the subject of hydrogen concentration at regions of high triaxiality as proposed by Troiano. The internal pressure theory, can be excluded to be of general validity, and might be applicable only at very high hydrogen fugacities. Similarly surface energy reduction theory is ruled out as a prominent mechanism. Atomistic calculations and very high resolution experiments are needed to resolve the dispute between the several theories. It is quite possible that a combination of these mechanisms could be operative for a given system. As Hirth (48) pointed out, except for the competition between brittle crack tip propagation and dislocation emission, and between reversible and irreversible events occurring at the crack tip, an overall cracking process is conceivable with all the mechanisms contributing to some extent.
5. SURFACE MODIFICATIONS

The earlier sections give an insight into the various steps involved in embrittlement due to hydrogen. The easy availability of hydrogen ions in aqueous and other solutions, the small atomic radii and high diffusivity of hydrogen atoms, all contribute to the widespread occurrence of HE. It is evident that in the right environment, HE is inevitable and can be catastrophic.

Several methods to combat HE have been proposed over the years. These methods can be broadly classified as those that introduce bulk modifications and those that modify the surface. The aim of bulk modification is to cause one or more of the following alterations:

1. Change the hydrogen diffusivity in the material so that hydrogen transport to potential crack sites is slowed down.

2. Reduce the number and distribution of harmful traps.

3. Change the kinetics of hydrogen absorption and the surface coverage of hydrogen by suitable alloy addition.

Grobner, et al. (9) showed alloy additions could reduce embrittlement. Heat treatment was also found effective in this respect (10). Bockris and coworkers (88, 89) reduced hydrogen diffusivity in iron by Ni and Cr alloying. Noble metal additions was found effective in reducing HE in AISI 4130 steels by Wilde et al (8, 90, 91). They found that addition of Pd and Pt at concentrations in excess of 0.5 weight percent improved resistance to HE,
and postulated that the effect was due to the influence of these solutes on the hydrogen discharge kinetics as well as due to the preferential distribution of these solutes near second phase non-metallic inclusion interfaces. The latter causes retardation of hydrogen gas precipitation at these potential cracking sites.

The limited success in combating HE by bulk modifications has made researchers look at other options. Surface modifications are attractive solutions since they cause no change in the bulk engineering properties of the material while reducing hydrogen entry. The success of noble metal alloying led to the study of ion beam deposition and ion beam mixing of these metals on the surface of steels to prevent HE \(^{(8,11)}\). Many researchers tried electrodepositing various metals on the surface of the material to be protected, to reduce hydrogen entry either by changing the electrochemical reaction mechanism or by reducing hydrogen diffusivity through the surface layers \(^{(92,93)}\). The various surface modification techniques that have been found to reduce HE or hydrogen entry are discussed below.

5.1. Surface deposition

Electrodeposition of Ni, Cu, Cr, Pb, Co, Sn and Pt \(^{(92-96)}\) on the surface of materials prone to HE, enabled reduction of hydrogen entry. These metals are effective due to the much lower diffusivity of hydrogen through these metals, so that even a very thin surface layer significantly affects hydrogen permeation. Ion implantation has been utilized by Zamanzadeh et al \(^{(12)}\) and Wilde and coworkers \(^{(8,11)}\). Zamanzadeh et al observed that Pt ion implantation reduced hydrogen permeation through
iron membranes. Similar reductions were observed by Pd ion implantation of AISI 1018 steels $^{(11)}$ and AISI 4135 steels $^{(8)}$. Ion implantation of Ar $^{(97)}$ has no effect, but Cr and Pb implanted on the surfaces of steels $^{(98,99)}$ change the polarization behavior of steels.

The effect of ion implantation was explained by Zamanzadeh, et al. as due to the catalysis of the hydrogen evolution reaction so that most of the hydrogen discharge occurred on the Pt. As a result the steel surface was exposed to very low surface coverage of hydrogen. Shimada and Wilde$^{(100)}$ suggested that Pd implantation altered the polarization behavior of the steel surface. While Pd surfaces have a fast discharge-slow recombination mechanism for hydrogen evolution, on steel surfaces it is coupled. According to these authors both of these mechanisms are operative on a steel surface thus reducing hydrogen surface coverage.

Amorphous layer deposition on steels either by chemical vapor deposition or by electrodeposition have been attempted to reduce HE $^{(11,100,101)}$. The results of Shimada and Wilde$^{(11,100)}$ however are inconclusive at the present time although Wilde and Henderson$^{(101)}$ have found a marked beneficial effect of Ni/P alloy layers. More work needs to be done before amorphous alloy deposition is unambiguously accepted as a method for reducing hydrogen entry.

5.2. Laser surface modification

Wilde and Shimada $^{(11)}$ employed laser glazing to change the surface characteristics of AISI 1018 steels. The observed reduction in hydrogen permeation was attributed to either the refinement of surface grains to near
amorphous character or to the presence of impressed residual stress at the fine grain/normal grain interface. Manohar and Wilde\textsuperscript{16} provided further evidence of the effectiveness of laser surface modification. Their work on laser surface melting of AISI 4135 steels established that the surface kinetics of hydrogen evolution was affected by the treatment and reduced hydrogen coverage resulted in improved resistance to embrittlement. The effect of laser surface melting was attributed to change in surface microstructure due to rapid solidification as well as to the presence of a narrow residual compressive stress layer near the laser melted region. One interesting observation made by Manohar was that increased laser power level caused increased hydrogen permeation; this was postulated to be due to increased pipe diffusion of hydrogen through the heat affected zone.

The combined benefits of laser melting and noble metal additions can be obtained by laser surface alloying. Manohar and Wilde\textsuperscript{16} observed large decreases in hydrogen flux on laser surface alloying AISI 4135 steels with Pt, Pd and Au. In addition to the above mentioned effects due to laser melting, it was postulated that the electronic distribution in these metals affected the kinetic parameters for hydrogen adsorption and absorption. Neither laser surface melting nor laser surface alloying was found to affect the effective diffusivity of hydrogen in the steel. The reduction observed in hydrogen permeation experiments were substantiated by improved resistance to HE in slow strain rate environmental cracking experiments.
5.3. Shot peening

Shot peening is possibly the most widely used and cheapest of all the surface modification processes discussed in this review. The beneficial effects of peening on varied mechanical and metallurgical properties are well documented in literature \((100, 102-104)\). There are two effects of shot peening that make it beneficial in a number of industrial applications. The process of bombarding the material surface causes plastic deformation. The material immediately underneath this cold worked layer is highly compressed. Peening is employed to work harden metals like titanium which are work hardenable. The cold work effect is also utilized to reduce intergranular corrosion and improve surface texture. Since a compressive stress hinders crack propagation, peening increases fatigue, corrosion fatigue and stress corrosion cracking resistance. The effect of peening on fatigue strength is demonstrated in Figure 9, taken from the work of Tarazov and Grover \((102)\). Similarly peening prior to chrome or electroless nickel plating counteracts residual tensile stress and improves fatigue life \((103)\) as shown in Figure 10. Peening is supposed to improve resistance to intergranular corrosion in stainless steels due to the cold work effect. Peening done prior to sensitization, provides nucleation sites for chromium carbide precipitation in the form of dislocations, slip planes, etc., thus preventing preferential precipitation along grain boundaries \((104)\).

The effect of peening on HE had surprisingly received little attention. Wilde and Shimada \((11)\) observed significant decrease in permeation of hydrogen through AISI 1018 steels on peening. Shimada \((100)\) attributed it to
Figure 9. Improvement of fatigue life of ground parts on peening. (REF 102)
Figure 10. Improvement of fatigue life of chrome plated parts on peening (REF 103).
a change in the transfer coefficient ($\alpha$) for the hydrogen evolution reaction. The effect of peening on HE can be due to one or more of the following factors:

1. Change in hydrogen adsorption and/or absorption kinetics due to the presence of a surface compressive layer and/or a cold worked layer.

2. Decrease in hydrogen diffusivity through the surface layer.

3. Inhibition of crack propagation due to the impressed compressive layer.

The ease of application, the diversity of shapes and sizes that can be peened and the low cost of the process, all make peening very attractive as a modification method. It is also one of the few surface modification methods that do not alter the composition nor the microstructure of the material. This research was motivated by these latter qualities of peening as well as the actual benefits observed in permeation flux reduction by Wilde and coworkers at the Fontana corrosion center of the Ohio State University.
CHAPTER III

EXPERIMENTAL DETAILS

**Materials:**

AISI 4130 Steels with chemical composition as shown in Table 3 were used for this study. Steels of this category are used in automotive fasteners and have been found to fail in service by HE. The steel was heat treated to achieve a 0.2% offset yield strength of 180 ksi. The heat treatment given to the various specimens was as follows. They were austenitized at 870° C for one hour in an inert atmosphere maintained by flowing argon gas through the furnace, followed by oil quench. Subsequently the specimens were tempered at 425° C for one half hour; the resulting microstructure was tempered martensite as shown in Figure 11.

Shot peening of specimens were done by Metals Improvement Company. The different amounts of shot peening on different specimens were designated according to the industrially accepted nomenclature devised by Almen and discussed here\(^\text{(105)}\). The energy imparted by the shot stream is a function of the media size, material, hardness, velocity and impingement angle. J.O. Almen of General Motors research laboratories devised the method of calibration of peen energy using SAE 1070 spring
Table 3. Chemical composition of steel used in this study

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.31</td>
<td>0.52</td>
<td>0.012</td>
<td>0.006</td>
<td>0.28</td>
<td>0.02</td>
<td>0.87</td>
<td>0.19</td>
<td>REST</td>
</tr>
</tbody>
</table>

Magnification: 1000X

Figure 11. Microstructure of heat treated AISI4130 steel - tempered martensite
steel specimens of specific dimensions also called Almen strips. These strips are fastened to a steel block and impinged with shots for a given period of time. The strips after exposure to the shots curve due to surface deformation with the peened side convex. The resulting arc height is measured with a standard Almen gauge. The stepwise process is demonstrated in Figure 12. The variation of the arc height with different exposure times is shown in Figure 13, also known as the saturation curve. The time for saturation (T) is defined as the earliest point in the curve where doubling the exposure time produces no more than a 10% increase in the arc height. It should be understood that the saturation curve is material specific, however it is cumbersome to develop saturation curves for all materials. Hence once the Almen intensity is specified for a material along with shot size, the part is peened with that combination of nozzle size, velocity and the distance of nozzle from the part, which would produce the desired arc height in an Almen strip.

It is also desired to attain total surface coverage on the peened part and the time required to cover the entire part with the peened dimples will depend on the hardness of the part relative to the Almen strip. To ensure complete coverage of the part the PEENSCAN process was used. The Almen strip used for calibrating in this study was the standard Almen A strip with dimensions of 3.0" x 0.75" x 0.051".

The shot peening beads or shots were made of steel and different bead sizes were employed to produce the desired Almen intensity on a given specimen. In this study all shot peened specimens will be referred to by a code consisting of two numbers each consisting of three numerals, the first
Figure 12. Schematics of the peening system and the Almen intensity determination (REF 105)
Figure 13. Saturation curve in Peening (REF 105)
three indicating the bead size and the last three indicating the Almen intensity. For example SP 330/012 would be a specimen that has been shot peened with shots of 0.033" average diameter to produce 12 Almen intensity. The relative sizes of the shot peening indentations on the specimens are illustrated in Figure 14.

All the specimens, after heat treatment, were polished to a 600 grit finish. Shot peening was done on heat treated and polished specimens. The permeation specimens were Palladium coated on one side (the anodic side) by sputtering process using a Veeco instruments Microetch systems. This produced a layer of palladium about 2400 Å thick. The conditions under which sputtering was done are listed below. The sputtering time was short enough to render annealing of specimens during sputtering negligible.

Sputtering condition:

- Operating pressure: $8 \times 10^{-5}$ Torr
- Arc discharge: 1A/30V
- Cathode: 20A/8V
- Magnet: 0.8A/28V
- Suppresor: 6mA/200V
- Accleration: 65mA/1KV

**Permeation and polarization set-up**

The well known Devanathan-Stachursky cell, shown schematically in Figure 15 was used for electrolytic charging experiments. The electrolyte was prepared from reagent grade sodium hydroxide pellets and demineralized double distilled water. In all the experiments high purity nitrogen gas was bubbled through the electrolyte for the duration of the
Figure 14. Indentations due to two different peening conditions.
1. Working electrode
2. Pt counter electrode
3. Calomel reference electrode

Figure 15. Schematics of Permeation cell due to Devanathan and Stachursky (REF 23)
experiment to reduce oxide formation on the specimens. All experiments, unless specified otherwise, were conducted at ambient temperatures.

The permeation experiments were conducted as follows. The half cell in contact with the Palladium coated side of the specimen, was filled with the electrolyte and an anodic potential of 100 mV with respect to a standard calomel electrode was applied to the specimen. This caused hydrogen atoms present at the metal surface to oxidize resulting in an oxidation current which was monitored by the recorder. Before charging was started at the opposite side of the membrane, the applied anodic potential caused the residual hydrogen in the steel to efflux and a decay transient was obtained. This decay transient reached a very low steady state value after 10-15 hours of degassing, once all the residual hydrogen had evolved. Hydrogen impregnation on the opposite side of the membrane was initiated by filling up the other cell with enough solution such that only a very small, lower region of the steel membrane was in contact with the solution. The charging current was impressed galvanostatically and the rest of the cell filled with the electrolyte to expose the entire circular section of the membrane to the current. This procedure ensured that most of the charging side of the membrane was cathodic prior to commencement of charging. The overpotential of the charging side of the membrane with respect to a standard calomel electrode, was monitored frequently. This simultaneously provided permeation as well as polarization data. The reverse charging experiments were conducted with the same set up, the only difference was that the shot peened side was coated with palladium and made the anodic side while hydrogen was charged galvanostatically on
the non peened side.

**Slow strain rate test**

Tensile bars were machined to dimensions shown in Figure 16 and the schematic for the slow strain rate test is shown in Figure 17. The threads of the tensile specimens were masked off with an insulating paint so that only the gauge lengths of the specimens were exposed to the electrolyte. Care was taken to ensure that the samples were cathodic prior to commencement of charging. In situ hydrogen charging, with different charging current densities, was started simultaneously with the start of tensile loading and the samples were all loaded to failure. After the samples fractured, they were examined under an SEM.

**Permeation under compression**

A cylindrical cell was designed (Figure 18) for measuring permeation flux while the steel was subjected to different compressive loads. This cell is conceptually the same as the Devanathan cell mentioned earlier. The maximum stress under which this experiment was conducted was less than the yield stress of the material. Both permeation as well as polarization data were obtained for different elastic compressive loads.

The interior of the cylinder was filled with the electrolyte and the cylinder was slowly loaded to the desired load. The outer teflon cell was then filled with electrolyte and hydrogen charging was initiated. The charging current density and the applied compressive load were maintained at constant values until the permeation transient reached a
Figure 16. Tensile bar

Figure 17. Schematic of the slow strain rate test set up
Figure 18. Schematic of Compression cell used for permeation and polarization.
steady state. This ensured that hydrogen atoms diffused from the exterior surface to the interior surface of the cylinder, the latter had zero concentration of hydrogen due to the application of an anodic potential of 100 mV SCE. The cylinder wall was thin enough to justify one dimensional diffusion as the mode of hydrogen transport.
CHAPTER IV

RESULTS

Results will be presented in a sequence more or less in keeping with the chronological order of the experiments. It has been subdivided into the following sections:

1. Preliminary Results: results of the investigation of the effect of peening on permeation, polarization and slow strain rate tests to establish the benefits of peening as well as investigation of the effect of solution concentration and strain rate on HE to establish conditions for more extensive investigation.

2. Effect of compressive loading on permeation and polarization: results of the investigation of the effect of uniform compressive stress on permeation and polarization.

3. Effect of shot peening at different intensities: demonstration of the effects of different surface stress gradients present in different intensity peening on HER kinetics by considering the permeation and polarization data and utilizing the I-P-Z analysis, and on HE resistance.

4. Reverse charging experiments: demonstration of the surface stress gradient as the single most important factor in the determination of the surface coverage of hydrogen in peened samples.
1. Preliminary Results

1.1. Permeation:

The first indications that shot peening may be beneficial in countering hydrogen embrittlement were obtained from permeation data. Reduced hydrogen absorption as demonstrated by permeation results are qualitative indicators of increased resistance to HE. Untreated base steel membranes and shot peened membranes, peened for different durations, were charged with hydrogen electrolytically and the ensuing hydrogen flux observed. The shapes of the permeation fluxes for three different specimens charged with the same current density are shown in Figure 19. The surface coverage for shot peened specimens can be understood in the following way. The surface to be shot peened is covered with a colored dye, with peening the dye disappears from the surface and after a certain duration of time is totally removed. A 100% SP is one that is peened for this duration, a 200% SP peened for double the duration, and so on. The figure clearly indicates a higher steady state hydrogen flux for the untreated steel, as much as twice that for the shot peened membranes. Figure 20 shows that at all charging currents the hydrogen absorption is much higher for the untreated steel membrane compared to the peened membranes. The square root variation of steady state flux with charging current density for all the specimens is indicative of a rate process identified earlier as the coupled discharge-recombination mechanism. The various parameters obtained from the permeation experiments are summarized in Table 4. The hydrogen diffusivities in different specimens are obtained from the slope of the straight line plots of log J*Square root (t) against 1/t (Figure21). It is evident
Figure 19. Hydrogen permeation flux for different specimens in 1 N NaOH

Figure 20. Variation of Steady state flux with charging current
Table 4. PERMEATION RESULTS

<table>
<thead>
<tr>
<th>Condition</th>
<th>$J_\infty$ $(\mu A/cm^2)$</th>
<th>$C_0$ gatom/cm$^3$</th>
<th>$D$ cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASE STEEL</td>
<td>.55</td>
<td>2.34*10$^{-6}$</td>
<td>4.07*10$^{-7}$</td>
</tr>
<tr>
<td>100%SP</td>
<td>.26</td>
<td>9.78*10$^{-7}$</td>
<td>4.6*10$^{-7}$</td>
</tr>
<tr>
<td>200%SP</td>
<td>.3</td>
<td>1.37*10$^{-6}$</td>
<td>3.78*10$^{-7}$</td>
</tr>
<tr>
<td>300%SP</td>
<td>.23</td>
<td>9.34*10$^{-7}$</td>
<td>4.26*10$^{-7}$</td>
</tr>
<tr>
<td>400%SP</td>
<td>.31</td>
<td>1.38*10$^{-6}$</td>
<td>3.89*10$^{-7}$</td>
</tr>
</tbody>
</table>

1 N NaOH, $I_C = 200 \mu A/cm^2$

Figure 21. Diffusion calculations for permeation in 1 N NaOH
that the lowered hydrogen absorption (or $J_\infty$) due to peening is not a result
of change in bulk diffusivity of hydrogen but due to change of the sub-
surface solubility of hydrogen ($C_0$).

1.2. Slow strain rate tests

Slow strain rate tests conducted under hydrogen charging conditions
($I_c = 200\text{mA/cm}^2$) complement the findings from permeation tests. The
fractographs shown in Figures 22 through 24 clearly indicate that at the
above mentioned charging condition, base steel samples fractured in a
brittle manner, evident from the presence of intergranular cracks and low
reduction in area after fracture. The shot peened specimens on the other
hand underwent ductile fracture, the fracture mode being microvoid
coalescence as opposed to quasi cleavage for the base steel. It is interesting
to note that only a small fraction of the fractograph for the brittle fracture
show intergranular cracking with the remainder exhibiting microvoid
coalescence. The ductile fracture surfaces were devoid of any intergranular
cracks. The effects of various parameters on slow strain rate fracture of
AISI 4130 steel were investigated and the results are listed below.

a. Effect of strain rate:

The base steel was evaluated at two different strain rates ($2 \times 10^{-6}$ and
$5 \times 10^{-6}$ s$^{-1}$), and exposed to different amounts of hydrogen charging currents
at both strain rates. This was done to establish a threshold charging
current value above which the material is brittle. The changeover from
ductile to brittle fracture with increasing charging current is evident in the
fractographs shown in Figure 25. The various parameters pertaining to
Figure 22.1 Fractograph of base steel specimen charged in 1 N NaOH at 200 $\mu$A/cm$^2$ at a strain rate of $2 \times 10^{-6}$ s$^{-1}$.

Figure 22.2 Fractograph of base steel specimen charged in 1 N NaOH at 200 $\mu$A/cm$^2$ at a strain rate of $2 \times 10^{-6}$ s$^{-1}$.
Figure 23.1 Fractograph of 100% shot peened specimen charged in 1 N NaOH at 200 $\mu$A/cm$^2$ at a strain rate of $2 \times 10^{-6}$ s$^{-1}$.

Figure 23.2 Fractograph of 100% shot peened specimen charged in 1 N NaOH at 200 $\mu$A/cm$^2$ at a strain rate of $2 \times 10^{-6}$ s$^{-1}$.
Figure 24.1 Fractograph of 300% shot peened specimen charged in 1 N NaOH at 200 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.

Figure 24.2 Fractograph of 300% shot peened specimen charged in 1 N NaOH at 200 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.
ductility are listed in Table 5.

It is evident that embrittlement is very sensitive to the strain rates. The explanation for this behavior is dynamic trapping discussed earlier. At faster strain rates there is a proliferation of dislocations. The dislocations can either trap the hydrogen and effectively reduce the flux or they can increase the diffusivity of hydrogen by dislocation transport. In permeation experiments done at different strain rates \(^{(41)}\), it was observed that the flux decreased with increased strain rates. This would suggest that increased dynamic trapping dominates over increased dislocation mobility. The consequence of this is that the effective lattice hydrogen concentration is reduced. Since dislocations are less harmful as traps as regards embrittlement, and since the concentration of harmful traps like second phase interfaces, voids and carbide-matrix interfaces are not affected by strain rates, there is less hydrogen available for embrittlement. Another possible effect of strain rate is its influence on the surface entry kinetics of hydrogen and on the creation of active sites for hydrogen adsorption. Unfortunately no reported work investigating this effect could be found in literature and merits future study.

b. Effect of solution concentration:

The effect of different solution concentration on slow strain rate fracture is illustrated in Table 6. The higher susceptibility to hydrogen embrittlement in less alkaline (lower pH) solution is in agreement with the higher hydrogen fluxes observed in such solutions. The severity of the less
Figure 25.1 Fractograph of base steel specimen charged in 1 N NaOH at 100 μA/cm² at a strain rate of $5 \times 10^{-6}$ s⁻¹.

Figure 25.2 Fractograph of base steel specimen charged in 1 N NaOH at 200 μA/cm² at a strain rate of $5 \times 10^{-6}$ s⁻¹.
Figure 25.3 Fractograph of base steel specimen charged in 1 N NaOH at 300 μA/cm² at a strain rate of 5 x 10⁻⁶ s⁻¹.

Figure 25.4 Fractograph of base steel specimen charged in 1 N NaOH at 400 μA/cm² at a strain rate of 5 x 10⁻⁶ s⁻¹.
<table>
<thead>
<tr>
<th>Strain rate</th>
<th>$I_C$</th>
<th>Fracture mode</th>
<th>$\sigma_f$</th>
<th>Reduction in area</th>
</tr>
</thead>
<tbody>
<tr>
<td>mA/cm²</td>
<td>Ksi</td>
<td>%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2X10^{-6}</td>
<td>50</td>
<td>MC</td>
<td>230</td>
<td>30.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>IGC</td>
<td>224</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>IGC</td>
<td>208</td>
<td>12.1</td>
</tr>
<tr>
<td>5X10^{-6}</td>
<td>100</td>
<td>MC</td>
<td>280</td>
<td>50.5</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>MC</td>
<td>280</td>
<td>48.6</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>IGC</td>
<td>202</td>
<td>15.8</td>
</tr>
</tbody>
</table>

1 N NaOH

$\sigma_f$ = Fracture stress
MC: Microvoid coalescence
IGC: Intergranular fracture

<table>
<thead>
<tr>
<th>Solution conc.</th>
<th>$I_c$</th>
<th>Fracture mode</th>
<th>$\sigma_f$</th>
<th>Reduction in area</th>
</tr>
</thead>
<tbody>
<tr>
<td>µA/cm²</td>
<td>Ksi</td>
<td>%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1 N</td>
<td>50</td>
<td>IGC</td>
<td>241</td>
<td>11.4</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>IGC</td>
<td>226</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>IGC</td>
<td>218</td>
<td>5.1</td>
</tr>
<tr>
<td>1 N</td>
<td>50</td>
<td>MC</td>
<td>230</td>
<td>30.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>IGC</td>
<td>224</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>IGC</td>
<td>208</td>
<td>12.1</td>
</tr>
</tbody>
</table>
alkaline solution is demonstrated in Figure 26, it shows that the alloy is brittle at all charging current densities employed.

The effect of solution concentration (or pH) on hydrogen embrittlement is well documented in literature (106,107,108). The increase in HER kinetics with decreasing pH is believed to result in increased hydrogen permeation and thus increased embrittlement susceptibility at lower pH values.

2. Effect of Compressive loading

Base steel hollow cylinders were subjected to charging such that the hydrogen flux travelled from the outside surface to the inside surface of the cylinder. The cylinders were subjected to different compressive stresses, none of which exceeded the elastic stress limit of the material. The aim of these experiments was to isolate the effect of compressive uniform stress per se on permeation from other effects prevalent in shot peening, like surface cold work, presence of a stress gradient, etc. Due to experimental constraints it was not possible to charge all the specimens with exactly the same charging currents and hence \( C_0 \) comparisons at the same charging condition was not possible.

The diffusivities of hydrogen in the different samples stressed at different levels, were calculated from the permeation transients and are listed in Table 7. The diffusivity values for all the specimens are comparable and show no particular trend. The diffusivity values are somewhat lower
Figure 26.1 Fractograph of base steel specimen charged in 0.1 N NaOH at 50 μA/cm² at a strain rate of \(2 \times 10^{-6}\) s⁻¹.

Figure 26.2 Fractograph of base steel specimen charged in 0.1 N NaOH at 50 μA/cm² at a strain rate of \(2 \times 10^{-6}\) s⁻¹.
Figure 26.3 Fractograph of base steel specimen charged in 0.1 N NaOH at 100 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.

Figure 26.4 Fractograph of base steel specimen charged in 0.1 N NaOH at 100 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.
Figure 26.5 Fractograph of base steel specimen charged in 0.1 N NaOH at 200 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.

Figure 26.6 Fractograph of base steel specimen charged in 0.1 N NaOH at 200 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.
than that for base steel unstressed membranes. It is apparent from these calculations that compressive stress does not affect hydrogen diffusivity through this material.

The variation of $C_0$ with charging current for different stresses is shown in Figure 27. The square root variation is observed by the data points as if they were obtained from the same material. The implication of this along with the finding that the Tafel slopes for the different specimens are the same, is that the bulk compressive stress does not alter the surface entry reaction mechanism nor the kinetic parameters involved in such a reaction scheme. Beck $^{(38)}$ had suggested that diffusivity was not affected by uniform stress. Such was indeed found to be the case in the present studies. Bockris et al $^{(14)}$ had observed a decreased permeation flux with compressive stress in Armco iron, but their results for AISI 4340 steel were ambiguous in that they did not observe a reversible stress effect on hydrogen permeation in the elastic regime. The results reported here do suggest that in AISI 4130 steel, bulk compressive stresses do not alter the permeation characteristics of the material.

3. Effect of shot peening at different intensities

It was quite conclusive from the experiments conducted in 1N NaOH that shot peening markedly improved the HE resistance of the alloy. The permeation results indicated that peening did affect the surface kinetics of the hydrogen entry process. The lowered steady state permeation flux after peening did not appear to be a cold work effect on bulk diffusivity, which is
### Table 7. EFFECT OF COMPRESSIVE LOADING

<table>
<thead>
<tr>
<th>Compressive stress (Ksi)</th>
<th>dη/dlog I (mV/decade)</th>
<th>Diffusivity (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>105</td>
<td>2.19E-7</td>
</tr>
<tr>
<td>45</td>
<td>95</td>
<td>1.86E-7</td>
</tr>
<tr>
<td>100</td>
<td>96</td>
<td>2.53E-7</td>
</tr>
<tr>
<td>150</td>
<td>96</td>
<td>2.5E-7</td>
</tr>
</tbody>
</table>

1 N NaOH

**Figure 27.** Hydrogen flux variation with charging current in compressed AISI 4130 cylinders
evident from the similarities of the apparent diffusivity values for the various peened and unpeened specimens. An increase in trap density causing a low apparent flux can thus be ruled out as the mechanism. The improvement in HE resistance can be attributed to the lowered hydrogen flux into the specimen as well as to the presence of a residual surface compressive stress. The latter is believed to hinder mode I cracking by compensating the applied tensile stress.

The aim of investigating different intensities of peening was to investigate the effect of different degrees of cold work and residual compressive stresses on the surface kinetics of hydrogen entry. However these features are not mutually exclusive in a peened sample and any benefit that accrues from peening is due to their combined contribution. From a practical point of view, we desired to establish the optimum conditions for peening. The results in this section are for the more severe 0.1 N NaOH environment.

3.1. Permeation and polarization

McBreen and Genshaw \(^4\) have provided the means for identifying the rate controlling step in the hydrogen entry process. The first query was whether shot peening had altered the rate controlling step. The three parameters required to identify the rate controlling steps are (i) \(J_\infty\) as a function of \(I_c\) (ii) the Tafel slope \((d\eta/d \log I_c)\) and (iii) \(d\eta/d \log J_\infty\). The various relationships involving the above parameters are illustrated in Figures 28 through 33 and the results summarized in Table 8. It is obvious from the results that in 0.1 N NaOH the rate controlling step for hydrogen
Figure 28.1 **Base steel**: Cathodic polarization

Figure 28.2 **Base steel** Variation of Steady state flux with charging current
Figure 29.1 SP170/007: Cathodic polarization

Figure 29.2 SP170/007 Variation of Steady state flux with charging current
Figure 30.1 SP170/012: Cathodic polarization

Figure 30.2 SP170/012 Variation of Steady state flux with charging current
Figure 31.1 SP330/012: Cathodic polarization

Figure 31.2 SP330/012 Variation of Steady state flux with charging current
Figure 32.1 SP550/015: Cathodic polarization

Figure 32.2 SP550/015: Variation of Steady state flux with charging current
Figure 33.1 **SP550/022**: Cathodic polarization

Figure 33.2 **SP550/022**: Variation of Steady state flux with charging current
Table 8. POLARIZATION PARAMETERS

<table>
<thead>
<tr>
<th>Condition</th>
<th>$d\eta/d\log I_c$ (mV/decade)</th>
<th>$d\eta/d\log J_\infty$ (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASE STEEL</td>
<td>101</td>
<td>235</td>
</tr>
<tr>
<td>SP 170/007</td>
<td>115</td>
<td>200</td>
</tr>
<tr>
<td>SP 170/012</td>
<td>106</td>
<td>157</td>
</tr>
<tr>
<td>SP 330/012</td>
<td>108</td>
<td>226</td>
</tr>
<tr>
<td>SP 550/015</td>
<td>100</td>
<td>209</td>
</tr>
<tr>
<td>SP 550/022</td>
<td>94</td>
<td>231</td>
</tr>
</tbody>
</table>

0.1 N NaOH
entry is a coupled discharge recombination mechanism. The square root variation of $J_\infty$ with $I_c$, a value of Tafel slope of about 120 mV/decade and a value of $\frac{d\eta}{d \log J_\infty}$ of about 240 mV/decade for all the specimens conclusively indicate this mechanism. Thus the effect of shot peening is not manifested as a change in the rate controlling step but as a change in hydrogen diffusivity or a change in the kinetic parameters for hydrogen entry or both.

The permeation rise and decay transients for two shot peened specimens are illustrated in Figure 34. The diffusivities are calculated from both the rise and decay transients and are tabulated in Table 9. It is evident that the effect of peening on apparent diffusivity is not significant. The other important conclusion is that the the presence of an oxide layer is insignificant on permeation of hydrogen through all the specimens, this is inferred from the similarities of the diffusivity values obtained from the rise and the decay transients.

3.2. IPZ analysis

The results obtained so far indicate that the benefits of shot peening cannot be attributed to either a change in the surface reaction mechanism nor a change in the bulk hydrogen diffusivity. The IPZ analysis discussed earlier, was utilized to measure the important kinetic parameters of hydrogen entry. The IPZ analysis for a coupled discharge recombination mechanism of hydrogen entry, requires that plots of $J_\infty$ against square root of $I_c$, $\eta$ against $\log I_c$ and $\log J_\infty$, and the Function $F(\eta)$ against $J_\infty - C_g/b (= J')$, should be linear. Figures 28 through 33 and Figure 35 show that such
Figure 34. Permeation rise and decay transients for two different intensity peening
<table>
<thead>
<tr>
<th>Condition</th>
<th>Diffusivity (Rise)</th>
<th>Diffusivity (Decay)</th>
<th>$J_\infty$ at $I_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm²/s</td>
<td>cm²/s</td>
<td>µA/cm²</td>
</tr>
<tr>
<td>BASE STEEL</td>
<td>$4.1 \times 10^{-7}$</td>
<td>$4.3 \times 10^{-7}$</td>
<td>1.055</td>
</tr>
<tr>
<td>SP 170/007</td>
<td>$3.5 \times 10^{-7}$</td>
<td>$4.38 \times 10^{-7}$</td>
<td>0.7173</td>
</tr>
<tr>
<td>SP 170/012</td>
<td>$5.13 \times 10^{-7}$</td>
<td>$3.83 \times 10^{-7}$</td>
<td>0.5</td>
</tr>
<tr>
<td>SP 330/012</td>
<td>$3.62 \times 10^{-7}$</td>
<td>$3.8 \times 10^{-7}$</td>
<td>0.67</td>
</tr>
<tr>
<td>SP 550/015</td>
<td>$3.87 \times 10^{-7}$</td>
<td>$3.61 \times 10^{-7}$</td>
<td>0.67</td>
</tr>
<tr>
<td>SP 550/022</td>
<td>$7.6 \times 10^{-7}$</td>
<td></td>
<td>0.425</td>
</tr>
</tbody>
</table>

0.1 N NaOH
Figure 35. Variation of the parameter f(n) with compensated flux
requirements are fulfilled by all the specimens under investigation. The two equations used for determination of the various parameters are restated below:

\[ J_\infty = K'' \left( \frac{b}{(FK_3)^{0.5}} \right)^{-1} (I_\eta)^{0.5} + \frac{C_g}{b} \] ............ 38

\[ I_c \exp(\alpha \eta a) = -\left( \frac{b}{I_0'/k''} \right) (I_\alpha - \frac{C_g}{b}) + I_0' \] ............ 39

The surface coverage \( \theta \) at different charging currents can be calculated after the recombination constant (\( K_3 \)) is calculated. By extrapolation of the plot of \( \theta \) against \( \eta \), the equilibrium surface coverage \( \theta_E \) can be obtained and is illustrated in Figure 36. The various kinetic parameters of interest, namely, the transfer coefficient \( \alpha \), the recombination rate constant \( K_3 \), the adsorption-absorption constant \( K'' \), and the equilibrium surface coverage \( \theta_E \), are tabulated for the different specimens in Table 10. It is pertinent at this point to discuss the significance of the various parameters listed in Table 10.

a. \textit{Significance of} \( \alpha \)

The transfer coefficient \( \alpha \) is present in the expression for the charging current for the charge transfer reaction: \( H^+ + e^- + M = M-H_{ads} \)

\[ I_C = I_0' (1-\theta) \exp(-\alpha \eta) \] ............ 30

In the most general form the transfer coefficient in a multiple step electrochemical reaction is a combination of the symmetry factor \( \beta \), the number of steps in the reaction, the number of electrons involved, etc. The values of \( \alpha \) for the various hydrogen evolution mechanisms are 0.5, 1.5 or 2.
Figure 36. Surface coverage of hydrogen on different peened specimen
### Table 10. KINETIC PARAMETERS

<table>
<thead>
<tr>
<th>Condition</th>
<th>$\alpha$</th>
<th>$i_0$</th>
<th>$K''$</th>
<th>$K_r$</th>
<th>$\theta_E$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\mu A/cm^2$</td>
<td>mole/cm$^2$s</td>
<td>mole/cm$^3$</td>
<td></td>
</tr>
<tr>
<td>BASE STEEL</td>
<td>0.5913</td>
<td>1.66*10^{-6}</td>
<td>1.45*10^{-5}</td>
<td>2.295*10^{-8}</td>
<td>0.0338</td>
</tr>
<tr>
<td>SP170/007</td>
<td>0.5150</td>
<td>3.14*10^{-6}</td>
<td>4.62*10^{-5}</td>
<td>3.309*10^{-7}</td>
<td>0.01401</td>
</tr>
<tr>
<td>SP170/012</td>
<td>0.5635</td>
<td>4.68*10^{-6}</td>
<td>2.15*10^{-5}</td>
<td>9.043*10^{-8}</td>
<td>0.02214</td>
</tr>
<tr>
<td>SP330/012</td>
<td>0.5512</td>
<td>1.78*10^{-6}</td>
<td>1.44*10^{-5}</td>
<td>3.093*10^{-7}</td>
<td>0.0299</td>
</tr>
<tr>
<td>SP550/015</td>
<td>0.5975</td>
<td>1.47*10^{-6}</td>
<td>3.38*10^{-5}</td>
<td>1.785*10^{-8}</td>
<td>0.0099</td>
</tr>
<tr>
<td>SP550/022</td>
<td>0.6353</td>
<td>5.09*10^{-4}</td>
<td>7.355*10^{-4}</td>
<td></td>
<td>0.000123</td>
</tr>
</tbody>
</table>

0.1 N NaOH

$\alpha$ = Transfer coefficient

$K''$ = Adsorption-Absorption constant

$K_r$ = Recombination constant

$i_0$ = Exchange current density

$\theta_E$ = Equilibrium surface coverage
In the present study we do not observe a significant deviation of $\alpha$ from 0.5 to suggest a change in the rate controlling step for hydrogen evolution. In coupled discharge recombination mechanism the value of $\alpha$ is the same as that for the symmetry factor $\beta$. The symmetry factor is explained as follows.

In an electrode polarized to any overpotential, there is an accumulation of charge on both sides of the solution-electrode interface. The movement of ions (H$^+$) from the solution to the electrode, involves climbing a potential energy barrier or an activation hill. The activation hill is essentially the envelope of the overlapping potential energy versus reaction coordinate curves for the initial and final states of the ion (Figure 37). Bockris and Reddy (109) defined $\beta$ as the fraction of the electrical energy available on polarization, that contributes towards lowering of the energy barrier for the ion jump from solution to the electrode. The symmetry factor is unaffected by the overpotential applied, for a wide range of potentials. $\beta$ thus depends on the shape of the activation curve for the polarization reaction and since the activation curve is due to the superposition of the initial and final state curves of the potential energy versus reaction coordinate, a change in $\beta$ suggests a change in the shape of either or both.

The values of $\alpha$ tabulated in Table 10 indicate that the process of shot peening has insignificant or no effect on the activation barrier for the hydrogen discharge step. Alternately this means that the potential energy curves of the final (M-H$_{ads}$) and initial (H$^+$) states are unaltered. However this doesn't preclude the possibility of a change in the concentration of the final state (M-H$_{ads}$) on the electrode surface.
Figure 37. Activation hill for hydrogen adsorption reaction
Significance of \( K_3, \theta, \theta_E \)

The recombination reaction was expressed in terms of the recombination current as: \( I_r = FK_3 \theta^2 \). The charging current is a summation of the permeation current \( (I_\infty) \) and \( I_r \). To reduce \( I_\infty \) in galvanostatic charging (\( I_c=\text{constant} \)), an increase in \( I_r \) is necessary. This would imply an increase in \( K_3 \) is desired and that this is an indicator of the effectiveness of the surface modification. An increase in \( \theta \), although it would imply an increase in the recombination reaction, is not desired since \( \theta \) also modifies the permeation current (\( I_\infty \) is proportional to \( \theta \)). However \( K_3 \) is not an independent parameter of significance, due to the very definition of \( K_3 \). It is indicative of the recombination rate process occurring on unit area of the electrode. In galvanostatic charging, the results indicate that \( \theta \) varies with shot peening. What this means then is that the 'active' regions of a unit area electrode are different for different specimens exposed to the same charging current, and the recombination process is in essence occurring on different areas of the specimens. The parameter \( K_3 \) is thus a mathematical artifact and the surface coverage \( \theta \) is of greater significance at any given charging current density.

The non-equilibrium surface coverage \( \theta \) can be used for comparison for different specimens under the same galvanostatic or potentiostatic condition. However unless the different specimens have identical polarization characteristics, such comparisons will not be under similar electrode conditions. To exclude all electroic variables, the hydrogen surface coverage at equilibrium, \( \theta_E \), is used for comparison. Conceptually
this quantity is similar to the exchange current density. This is intrinsically of no value since at equilibrium all the hydrogen that is adsorbed is desorbed back due to the equilibrium of the charge transfer reaction. However in a coupled discharge-recombination reaction the surface coverage variation follows the relationship \( \frac{d\eta}{d\log \theta} = -\frac{F}{4RT} \), so a higher \( \theta_E \) would imply a higher surface coverage at any overpotential.

The value of \( \theta_E \) was found to be much lower in all the shot peened samples compared to base steel. Also there is a trend towards decreasing \( \theta_E \) with increasing peening intensity, from which it is clear that peening alters the kinetics of the hydrogen entry process. It should be noted that at low overpotentials the value of \( \theta \) is much less than unity; thus its contribution to the charging current (\( I_C \propto 1-\theta \)) is negligible. The similarities of the Tafel curves for the different specimens is thus not contradictory.

**Significance of \( K'' \) and \( C_0 \)**

The adsorbed atom has two options: to convert to hydrogen molecule by recombination or to enter the bulk. The latter is the absorption process and involves the first jump into the bulk interstitial site. The adsorption-absorption rate constant \( K'' \) should thus be affected by the near surface diffusion characteristic of hydrogen. The results show that \( K'' \) in general is higher for the shot peened specimens compared to base steel but there is no distinctive trend with peening intensity. As mentioned earlier, the two effects of peening are the introduction of a surface stress gradient and
surface cold work. The influence of these on near surface hydrogen transfer will be discussed later.

The most important single parameter in a HE study is probably $C_0$. In permeation experiments this is the boundary condition for permeation and thus defines the gradient for hydrogen diffusion. In slow strain rate tests using cylindrical samples charged galvanostatically, the situation is more complex. For a cylindrical sample exposed to a constant charging current there is a change in the concentration profile with time as shown in Figure 38, until the whole sample volume attains a concentration of $C_0$. This value can be obtained from the permeation transient for a membrane specimen exposed to the same charging condition. However on straining, it is likely that the surface kinetics of the hydrogen entry process is altered due to the stress effects. As a result, even under constant charging current, the hydrogen concentration at the surface would possibly be a continuous function of the applied stress (or strain). Thus in straining experiments, $C_0$ would be an approximate parameter and in constant load situations $C_0$ would be a very good indicator of HE susceptibility. The values of the $C_0$ (gatom/cm$^2$) for a charging current of 200μA/cm$^2$ for the various specimens investigated are listed below

<table>
<thead>
<tr>
<th>Base steel</th>
<th>170/007</th>
<th>170/012</th>
<th>330/012</th>
<th>550/015</th>
<th>550/022</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.097</td>
<td>4.855</td>
<td>2.309</td>
<td>4.385</td>
<td>4.1</td>
</tr>
</tbody>
</table>

It is observed that $C_0$ decreases with increasing intensity of peening and is lower than base steel for all the peening intensities. The value of $C_0$ is the culmination of the effects of the various surface entry parameters.
Figure 38. Concentration profile in a cylinder of radius a at different times t with initial concentration $C_1$ and surface concentration $C_0$. The values in the figure are for $Dt/a^2$ (REF 112).
discussed earlier.

3.3. Effect of peening on SSRT

The findings from permeation transients in 0.1 N NaOH suggest that peening decreases the hydrogen adsorbed on the steel surface and decreases the flux of hydrogen into the material. At a first glance this would suggest that increased peening intensity should decrease the susceptibility to embrittlement and this is tested out in slow strain rate tests. In earlier tests where hydrogen charging was done in a 1 N NaOH environment, it was observed that low intensity peening (7 Almen) had caused enhancement of ductility. It was established earlier that a charging current density of only 50 μA/cm$^2$ was sufficient to cause embrittlement of untreated base steel specimen in 0.1 N NaOH. Specimen subjected to three different shot peening conditions were exposed to different charging currents in the slow strain rate tests (SSRTs). The objective was to obtain the threshold charging current for brittle fracture for each specimen.

The fracture micrographs at each charging current for the three peened specimen are shown in Figures 39 through 41 and the parameters pertaining to ductility tabulated in Table 11. It is evident that contrary to expectations, embrittlement occurs for the two specimens peened at higher intensities (330/015 and 170/012) at all charging currents, in essence exhibiting no improvement compared to base steel. Only the low intensity peened specimen(070/007) fails in a ductile manner at a charging current that cause embrittlement in base steel. The attainment of a threshold value for the other specimen is not feasible since that would require charging at
Figure 39.1 Fractograph of SP070/007 specimen charged in 0.1 N NaOH at 50 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.

Figure 39.2 Fractograph of SP070/007 specimen charged in 0.1 N NaOH at 50 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.
Figure 39.3 Fractograph of SP070/007 specimen charged in 0.1 N NaOH at 100 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.

Figure 39.4 Fractograph of SP070/007 specimen charged in 0.1 N NaOH at 100 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.
Figure 39.5 Fractograph of SP070/007 specimen charged in 0.1 N NaOH at 200 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.

Figure 39.6 Fractograph of SP070/007 specimen charged in 0.1 N NaOH at 200 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.
Figure 40.1 Fractograph of SP170/012 specimen charged in 0.1 N NaOH at 50 μA/cm² at a strain rate of $2 \times 10^{-6} \text{ s}^{-1}$.

Figure 40.2 Fractograph of SP170/012 specimen charged in 0.1 N NaOH at 50 μA/cm² at a strain rate of $2 \times 10^{-6} \text{ s}^{-1}$.
Figure 40.3 Fractograph of SP170/012 specimen charged in 0.1 N NaOH at 100 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.

Figure 40.4 Fractograph of SP170/012 specimen charged in 0.1 N NaOH at 100 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.
Figure 40.5 Fractograph of SP170/012 specimen charged in 0.1 N NaOH at 200 μA/cm² at a strain rate of $2 \times 10^{-6} \text{ s}^{-1}$.

Figure 40.6 Fractograph of SP170/012 specimen charged in 0.1 N NaOH at 200 μA/cm² at a strain rate of $2 \times 10^{-6} \text{ s}^{-1}$.
Figure 41.1 Fractograph of SP330/015 specimen charged in 0.1 N NaOH at 50 µA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.

Figure 41.2 Fractograph of SP330/015 specimen charged in 0.1 N NaOH at 50 µA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.
Figure 41.3 Fractograph of SP330/015 specimen charged in 0.1 N NaOH at 100 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.

Figure 41.4 Fractograph of SP330/015 specimen charged in 0.1 N NaOH at 100 μA/cm² at a strain rate of $2 \times 10^{-6}$ s⁻¹.
Figure 41.5 Fractograph of SP330/015 specimen charged in 0.1 N NaOH at 200 μA/cm² at a strain rate of 2 x 10⁻⁶ s⁻¹.

Figure 41.6 Fractograph of SP330/015 specimen charged in 0.1 N NaOH at 200 μA/cm² at a strain rate of 2 x 10⁻⁶ s⁻¹.
Table 11. EFFECT OF PEENING INTENSITY ON SSRT

<table>
<thead>
<tr>
<th>Condition</th>
<th>$I_c$ (µA/cm²)</th>
<th>$\sigma_F$ (Ksi)</th>
<th>Reduction in area</th>
</tr>
</thead>
<tbody>
<tr>
<td>330/015</td>
<td>50</td>
<td>243</td>
<td>18.8</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>215</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>210</td>
<td>4</td>
</tr>
<tr>
<td>170/012</td>
<td>50</td>
<td>257</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>214</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>211</td>
<td>3</td>
</tr>
<tr>
<td>070/007</td>
<td>50</td>
<td>240</td>
<td>52.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>200</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>210</td>
<td>5</td>
</tr>
</tbody>
</table>

0.1 N NaOH
Strain rate = 2*10^{-6}
current density values corresponding to very low overpotentials, that is at a potential too close to the reversible potential where the coupled discharge-recombination mechanism is not valid.

The apparent discrepancy arising from the SSRT results can be resolved by a consideration of the stress distribution in peened specimen as shown in Figure 42. In a free body, the introduction of a residual compressive stress is compensated by a tensile stress in the interior. It is obvious that the higher the impressed residual compressive stress at the surface, the higher the maximum value of the tensile stress in the specimen interior. It is also apparent that the thicker the sample, the more gradual the tensile stress distribution in the interior. Thus the specimen peened at high intensity, compounded with the fact that they are cylindrical and peened all around, present a steep stress gradient. Two opposing effects are at work, the surface compressive stress reduces the hydrogen entry kinetics whereas the interior residual tensile stress makes it more prone to crack initiation and propagation. In low intensity peening (070/007 in 0.1 N NaOH and 110/007 in 1 N NaOH), the beneficial effects of peening are evident and in high intensity peening the tensile effect is dominant. It should be noted that the latter effect will be evident only in actual straining experiments.

This explanation can be verified by studying the crack initiation site or the sites of first crack propagation (in case of preinitiated cracks) in specimens peened to different intensities and correlating it to the residual stress distribution in them. This was beyond the scope of the present study. One fact that is evident however is that shot peening benefits have a size
Figure 42.1 Variation of stress distribution profile with shot peening intensity

Figure 42.2 Schematic of Stress distribution profile in cylindrical samples
constraint. The specimen or the part must be thick enough to flatten out the interior stress distribution due to peening, for beneficial application with regards to HE. The slow strain rate device used in this study could not accommodate thicker specimen.

4. Reverse charging results

The results so far show that peening does not alter the apparent diffusivity significantly, but causes significant decrease in the permeation flux due to a decrease in the subsurface hydrogen concentration. These indicate that surface compressive stress is the most important beneficial factor vis-a-vis hydrogen permeation. It is logical then to assume that if hydrogen charging is done on the reverse side of a peened membrane, the permeation transient would be identical to that for a base steel membrane. This is what will be referred to as reverse charging for the rest of this section. The shot peened surface would now be the surface at which hydrogen atoms exit the membrane and enter the solution after oxidation to H⁺ ions. The exit surface was palladium coated to eliminate any effect peening might have on the desorption kinetics.

Two intensities representing the two ends of the intensity spectrum were subjected to reverse charging at different charging currents. The results are compared with the flux variation with charging current densities for base steel membranes and for direct charging on a peened specimen of the same intensity in Figures 43 and 44. The SP110/007 specimen showed J∞ versus square root of ic variation very similar to base
Figure 43 SP110/007: Variation of Steady state flux with charging current

Figure 44 SP330/022: Variation of Steady state flux with charging current
steel and very different from direct charged SP110/007. The behavior of SP330/022 specimen on reverse charging is closer to that of base steel than of a direct charged SP330/022 but there is significantly lower steady state fluxes at all charging currents compared to base steel.

The diffusivities of hydrogen at both the intensities are similar to that of base steel. The apparent deviation in steady state fluxes is due to impressed stress on the reverse side. In peened specimens, the peened surface bows out due to plastic deformation with a resulting compressive stress in the subsurface. Depending on the intensity, this bowing out may be to the extent that the opposite surface assumes a configuration roughly corresponding to that of the peened surface, with less curvature. This phenomena is visually evident on specimens peened at high intensities. This would imply that a residual compressive stress is inadvertently introduced on the reverse side of a peened specimen. The effect will be more pronounced in thinner specimens and also depend on peening intensity.

The decrease in steady state flux on reverse charging can be explained as due to the effect of the surface compressive layer on hydrogen entry kinetics. The value of this compressive stress will be somewhere in between that for the peened surface and zero residual stress (base steel). and $J_\infty$ would vary accordingly. This is borne out by the results, moreover the higher intensity peening deviates more from the base steel permeation values on reverse charging than low intensity peened specimens, as predicted.
The predominant effect of shot peening is evidently the surface compressive stress. The observed results can be explained by the presence of a surface compressive stress distribution in the peened specimen. The interesting observation is that on subjecting the base steel material to uniform compressive stress does not alter permeation characteristics. The fact that a uniform compressive stress present throughout the material does not affect hydrogen entry kinetics whereas a surface compressive stress is effective, has to be accommodated in any explanation of the beneficial effects of shot peening.

The effect of stress on hydrogen permeation has been investigated by several authors and was discussed in an earlier chapter. The various schools of thought regarding stress effects have mostly concentrated on tensile stress tests. The effect of stressing has been attributed to oxide film fracture, to a change of hydrogen solubility or to accelerated trapping and detrapping. Of these, a change in solubility seems to be the most general. The oxide film rupture theory can explain why tensile stress increases hydrogen permeation by increasing the area of fresh surface available for hydrogen adsorption. But compressive stressing would also cause oxide
film rupture, so the often observed decrease in hydrogen permeation on compressive stressing is contradictory to the film rupture theory. The dynamic trapping theories suggest a competitive process between hydrogen trapping at dislocations and increased hydrogen mobility due to dislocation motion. Dislocation motion will be observed in the plastic stress regimes, hence in the elastic regime, permeation transient should be invariant, results found in literature prove otherwise. Also both compressive and tensile stresses generate dislocations and the opposite effects of these on permeation cannot be explained by any dislocation proliferation theory.

The change in solubility with stress depending on thermodynamic considerations was first proposed by Beck \(^{38}\). Oriani \(^{13}\) proposed a decrease in permeation on the application of a compressive stress and this was proved to be the case by Bockris, et al.\(^{14}\). This theory has universal validity since it does explain an increase in hydrogen flux on application of tensile stress and a decrease on application of compressive stress. There conclusion can be summarized by the following relationship:

\[
\frac{d \ln(C_{H,\sigma}/C_{H,0})}{d\sigma} = \frac{V_H}{RT} \quad 41
\]

where \(C_{H,\sigma}\) is the hydrogen solubility in the material on the application of a stress \(\sigma\), \(C_{H,0}\) is the hydrogen solubility in the absence of stress and \(V_H\) is the partial molar volume of hydrogen in the material. The variation of permeation flux with stress for ARMCO iron and for low strength AISI 4340 steel are shown in Figure 45 which is taken from the
Figure 45.1 Hydrogen permeability-stress relationship for ARMCO iron (REF 14)

Figure 45.2 Hydrogen permeability-stress relationship for AISI 4340 steel (REF. 14)
work of Bockris, et al.\textsuperscript{(14)} Two points merit special attention. The first is that in an alloy steel the stress effect on solubility is less pronounced than in a nearly pure iron as is expected from the lower partial molar volume of hydrogen in the alloy steel. The second point is that even at relatively high stresses, the change in hydrogen flux is not spectacular. For example, in AISI 4340 steel, at a stress of 100 Ksi (close to yield stress for the material tested), the change in flux compared to that in an unstressed specimen is only 17.5%.

The present results indicate that elastic compressive stresses do not cause significant change in permeation (or solubility) of hydrogen in AISI 4130 steel. The thermodynamic effect would be present but its contribution is not discernible, that is, less than the experimental error. This means that the partial molar volume of hydrogen in the tempered martensitic structure of heat treated AISI 4130 steel is low enough to reduce stress effects negligible. This leads to the conclusion that any change in the permeation flux in AISI 4130 steels cannot be explained by the change in solubility due to the thermodynamic considerations of stress application. It also leads to the observation that for the material used in this study, application of either a uniform tensile or compressive elastic stress will have negligible effect on hydrogen flux if charging is done in environments where oxide film buildup on the charging surface does not occur. The word 'uniform' needs to be emphasized, it means that the entire specimen is subjected to the same stress value, without any stress gradient present anywhere in the body. In shot peened specimen, a uniform stress does not exist throughout the sample. This important distinction is undoubtedly
significant in explaining why residual surface compressive stress retards permeation while uniform compression has no effect. Any theory used to explain the benefits of peening must address this distinction.

From the permeation results it is evident that peening can decrease permeation flux as much as 60%. The diffusivity values for all the specimens are comparable. The presence of a surface compressive stress does not affect diffusivity. Bockris (14) and Beck (38) have showed that elastic stress will not change hydrogen diffusivity. The similarities of the diffusivity values calculated from rise and decay transients also eliminate the possibility of oxide film presence playing a role in hydrogen permeation. Typically in peening, the maximum compressive stress introduced is about 50% of the yield stress of the material. In the absence of any data on the partial molar volume of hydrogen in AISI 4130 steels, the exact correlation between stress and solubility is not possible. However the permeation transients for compressed cylinders had shown such effect to be negligible. The IPZ analysis of the various specimens show that the reduction in $C_0$ or subsurface solubility is primarily due to a reduction in the surface hydrogen coverage, that is, the number of adsorbed hydrogen atoms. This requires a theory that can not only explain the reduction in surface coverage on peening but also explain the effect of peening intensity on adsorption. It should be pointed out that increasing peening intensity does not change the maximum compressive stress impressed in the material, it however increases the region in the material having residual compressive stress as shown schematically in Figure 42. This observation is further proof that Bockris' theory is not valid in these specimen, since that would
need all the peened specimen have the same surface solubility of hydrogen. The hydrogen pump model proposed by Tiller and Schreiffer (110,111) seems to explain the effects of peening.

Tiller and Schreiffer (110) proposed that the average energy of electrons in a material is affected by the presence of local stress fields. Their conclusion was that the electrons would flow from a region of compression to a region of tension. We should expect then in shot peened specimens, a redistribution of the free electrons.

The various observations in the results, can be satisfactorily explained by this electron redistribution theory. In essence, a material with local stress variation, would have compressed regions that reject electrons to the tensile regions. In shot peened specimens the surface has compressive stress, so effectively the surface is 'less active' with regards to the charge transfer reaction or the adsorption process due to the lesser availability of electrons. Moreover the compressed region increases with intensity thus rendering the specimen peened at higher intensity less susceptible to adsorption. A brief discussion of the development of the electron pump model is presented here.

The average energy per electron consists of various contributions and is expressed as

\[ E(r_s) = E_0(r_s) + E_k(r_s) + E_e(r_s) + E_c(r_s) + E_{co}(r_s) \] ............ 42

where \( E_0 \) is the ground state energy, \( E_k, E_e \) and \( E_c \) are the kinetic, exchange and correlation energies of the electron respectively and \( E_{co} \) is
due to overlap repulsion and van der Waal's attraction of the ionic cores plus a coulumbic term. \( r_s \) is the dimensionless atomic radius given as \( r_s = [4/3\pi a_0^3V/N]^{1/3} = A/N^{1/3} \) where \( N \) is the number of free electrons in the volume \( V \) and where \( a_0 \) is the Bohr radius. Application of stress changes the value of \( r_s \) and thus changes the average energy of electrons. For instance the change in the kinetic energy of electrons (Fermi energy), \( \Delta E_k \) associated with a small atomic volume change \( \Delta V \) is (113) \( \Delta E_k = -2/3(\Delta V/V)E_F(0) \) where \( E_F(0) \) is the unstrained Fermi energy at 0 K. Using Winger's approximation (114) for the \( E_k, E_e \) and \( E_c \) terms, the electronic energy can be expressed as

\[
E = E_0 + 2.21/r_s^2 - 0.916/r_s - 0.88/(r_s + 7.8) + E_{co} \text{ rydbergs} \]

The total free energy of the system containing \( N \) electrons at constant \( r_s \) and 0 K is given as \( F_0 = N (E-e\Phi)_0 \), where \( \Phi \) is the electrochemical potential of the system. The chemical potential of the electrons is then expressed with respect to some standard state (\( \Phi=0 \)) as

\[
\mu_e = (\delta F_0/\delta N) = 5/3 E_k + 4/3 E_e + [1.33 - 2.6/(r_s + 7.8)] E_c \text{ rydbergs} \]

This equation can be interpreted in terms of \( r_s \) as, when there is stress the chemical potential of electrons is higher in a region of compressive stress as compared to a region under tension and electrons migrate in response to this chemical potential gradient.

The shot peened specimens would have a similar redistribution of electrons resulting in a lesser concentration of electrons at and near the surface where the material has residual compressive stress. In coupled
discharge recombination mechanism the surface coverage ($\theta$) can be deduced from either the charge transfer reaction or the recombination reaction. If we consider the charge transfer reaction $H^+ + e^- = H_{ads}$ then the concentration of $H_{ads}$ at the equilibrium or reversible potential ($\theta_E$) is proportional to $[H^+]$ which is fixed by the pH of the solution and $[e^-]$ which is the near surface electron concentration determined by the surface compressive stress. Thus the $\theta_E$ for the peened surfaces will be lower since $[e^-]$ is lower due to electron redistribution in response to the compressive stress distribution.

Under galvanostatic charging conditions, the law of mass action would again predict that the surface coverage ($\theta$) of hydrogen would be proportional to the total electron concentration available for the charge transfer reaction. Under the same charging current density, different specimens would be supplied with the same number of excess electrons, however $[e^-]$ is the summation of the impressed excess electrons and the inherent surface electrons, the latter affected by the surface treatment. This explains the lesser surface coverage of hydrogen for the peened specimens compared to untreated specimens at all charging current densities. Moreover the compressive layer increased with increasing intensity of peening, thus there are lesser number of electrons available for the hydrogen discharge reaction with increasing peening intensity.

If we consider the bulk compression results, the absence of stress variation in the specimen or the uniformity of stress values throughout the specimen prevents electron redistribution thus causing no change in the surface availability of electrons. Thus in the absence of oxide films, and
if stress effects on thermodynamic solubility is negligible, there will be no change in permeation of hydrogen through the material with increasing stress.

An alternate theory could be based on the physical impingement of shots on the specimen. It is proposed that peening would smoothe out the specimen surface by reducing the number of kinks and ledges present on the surface, thus reducing the sites for hydrogen adsorption. The increased intensity of peening would then represent increased force employed for kink and ledge breakup and thus reduce coverage ($\theta$). This theory is hypothetical and requires quantification by actual calculation of the number of kinks and ledges present on the surface of various peened and unpeened specimen. One discrepancy is the reverse charging result. The reverse side of a peened specimen doesn't undergo any physical impingement leading to reduction of active adsorption sites for hydrogen. Reverse charged specimen however show a decreased hydrogen coverage which can be correlated to the presence of a residual compressive stress at the surface. This implies that even if a smoothing effect due to peening is operative, it cannot explain the entire effect of peening on hydrogen entry.

The results of slow strain rate tests with peened specimens are very conservative. On straining, the residual compressive stress is nullified by the applied tensile stress, so that at a certain tensile stress, the peened specimen reverts to base steel at the surface. This means that as long as their is a compressive stress at the surface, the specimens will retard hydrogen entry, this effect dying out with time as the stress is increased since the surface adsorption kinetics of hydrogen changes with the change
in the residual compressive stress at the surface. As a result, the shot peened specimen allow less total hydrogen accumulation in the material, but this value is higher than if the specimen was charged with the same current density for the same duration with no load applied. The effect of compressive stress on retardation of initiation and propagation of surface cracks is another possible benefit of shot peening, but such study was not within the scope of this work. Constant load tests are better simulations of practical applications and would be a better indicator of the shot peening benefits in practical situations. However the length of duration of such tests prevent them from being practical.

The various fractographs do not indicate any change microscopically in the embrittling mechanism on peening or with different intensity peening. It should be noted that samples which fractured in a brittle fashion always had a small fraction of intergranular cracking with the remainder showing ductile microvoid coalescence. The cross sectional area which failed due to overload (the ductile region) was always much larger for the brittle specimens compared to specimens which were ductile under the same charging condition suggesting a weakening of the cohesive strength of the material due to hydrogen ingress.

The various theories of hydrogen embrittlement all require enhancement of surface hydrogen coverage (surface adsorption theory, slip softening theory) or bulk hydrogen concentration (decohesion theory, internal pressure theory). Our study doesn't invalidate any of these theories, nor was that the intent of this study. Since all the theories require critical hydrogen concentration, any reduction in the concentration is
desired for countering hydrogen embrittlement. Shot peening is obviously effective in achieving that goal. The hydrogen pump model proposed by Tiller and Schreiffer is most suitable for explaining the peening effects on hydrogen entry kinetics, with other effects making insignificant contribution.

The interpretation of surface coverage in terms of the concentration of the near surface electrons available for the charge transfer reaction opens up the possibility of viewing any surface modification technique as a means of altering the electron density near the surface. Such an alteration could be brought about by the introduction of a stress gradient as in shot peening or by chemical means (ion deposition).
CHAPTER VI

CONCLUSIONS

The conclusions based on my results are

1. Shot peening reduces the hydrogen entry into low alloy steels. Increasing intensity of peening results in a greater reduction in the hydrogen absorption flux.

2. The primary effect of peening is a reduction in the surface coverage of hydrogen or the amount of adsorbed hydrogen on the steel surface. The hydrogen surface coverage is inversely proportional to the intensity of peening.

3. An explanation for the observed reduction in surface coverage is proposed using the electron pump model in which the presence of a surface compressive stress affects the distribution of surface electrons between tensile and compressive regions. Increased intensity peening results in an increased surface layer under compressive stress which further activates the electron pump.

4. Reverse charging experiments support the conclusion that the surface coverage of hydrogen is proportional to the depth of the surface
compressive stress layer. Hydrogen permeation data obtained in the bulk compression experiments also support the above explanation.

5. The effect of change in surface diffusivity of hydrogen or reduction in the number of active sites such as kinks or ledges for hydrogen adsorption due to peening cannot be ruled out. However reverse hydrogen charging experiments indicate that such effects are minor.

6. The reduced hydrogen permeation observed with low intensity peening results in improved resistance to HE as measured in the slow strain rate tests. Under higher intensity peening conditions, the sample dimensions are not large enough to smooth out the tensile stress buildup in the interior of the samples and the effect on improving resistance to HE is nullified.
CHAPTER VII

FUTURE WORK

1. The premise of this research is that surface modification methods which affect the electron distribution at the surface due to the introduction of a compressive stress, due to chemical alteration or due to metallurgical changes will be beneficial for countering HE. It is proposed that the various surface treatments found elsewhere be evaluated from the electron pump point of view.

2. The benefits of shot peening are primarily due to the presence of a surface compressive stress. The quantitative determination of the stress profiles in peened specimens and their variation with different intensity peening are required to establish accurate correlation between intensity of peening and hydrogen surface coverage.

3. The possibility of peening affecting the surface diffusivity of hydrogen and the density of surface active sites needs to be explored.

4. The observation that peening results in a decreasing degree of coverage of hydrogen should be confirmed by an independent experimental method such as the double pulse analysis.
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