THE MECHANISM OF HYDROGEN BLISTERING

IN ALPHA-IRON

By

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ABSTRACT

Investigations to determine hydrogen entry and hydrogen blistering in alpha-iron were carried out. From the results of these investigations, a model for hydrogen blistering in alpha-iron has been developed.

The effects of impurity additions in plating baths was also investigated and it was determined that certain impurities enhanced blistering while others retarded blistering.
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INTRODUCTION

Hydrogen embrittlement has long been a problem in the iron and steel industry. Pressure vessels, pipes, electroplated and acid cleaned parts often fail catastrophically because of the presence of hydrogen in the part.

Literature is unclear as to the actual mechanism of how hydrogen enters and diffuses into the iron to form hydrogen blisters. Investigations were made to clarify the mechanism.
LITERATURE SURVEY

Characteristics of Hydrogen Embrittlement

Many mechanical properties of iron and steel are altered by the presence of hydrogen in the metal. Investigators generally agree on the following list of hydrogen embrittlement characteristics:

1. The ultimate tensile strength is often lowered as the hydrogen concentration increases. Groeneveld et al.\(^4\) write that some high strength steels have their ultimate tensile strengths lowered to as little as 17 percent of the original value while some lower strength steels show little change in ultimate tensile strength due to the presence of hydrogen.

2. The variables of ductility, reduction of area and elongation, show a very significant change with hydrogen concentration. Hofman and Rauls\(^5\) observed that there is a proportional decrease in reduction of area as the hydrogen content increases until reduction of area approaches zero. The particular behavior of a given sample is also a function of the history of the metal.
3. Dieter\textsuperscript{(6)} indicates that hydrogen embrittlement is most severe at intermediate temperatures. Farrell\textsuperscript{(7)} feels that this phenomenon exists because the diffusion rate of hydrogen below -100°C is slow and that hydrogen is highly soluble in the lattice above 100°C. Rogers\textsuperscript{(8)} says that the diffusion rate of hydrogen in iron is very rapid even at room temperature. Oriani\textsuperscript{(17)} reviewed the existing data and stated that a value of $D=10^{-5} \text{ cm}^2/\text{sec}$ is the most reliable value.

4. Failure by hydrogen embrittlement is strain rate dependent at low hydrogen concentrations. But, Groeneveld et al\textsuperscript{(14)} says that the strain rate dependence is different from most other forms of embrittlement. In impact tests, hydrogen generally does not change the behavior of steel. Some specimens containing hydrogen maintain ductility in standard tensile tests. The big change in behavior appears at very low strain rates or under static load conditions. Under these conditions, severe embrittlement may appear after long periods of time. Consequently, hydrogen-stress cracking is termed low-strain-rate embrittlement. Triano\textsuperscript{(18)} describes some detailed studies of how hydrogen adsorption on crack surfaces and how hydrogen pressures in cracks act together to propagate cracks, leading to an eventual metal failure.
5. Little change has been noted on the compressive properties of metals that contain hydrogen.

6. Groeneveld et al.\(^{14}\) points out that if hydrogen can be removed from steel before permanent damage occurs, the material may be used in a high stress environment with no hydrogen stress cracking, assuming that no hydrogen is introduced into the metal during use. The restoration of full mechanical properties with hydrogen removal shows why it is standard practice to bake hydrogen out of metal after cleaning and electroplating processes. Removal of hydrogen may be difficult if the electroplated metal is too dense and acts as a barrier to hydrogen escape.

**Current Density and Blister Formation**

Preliminary data on the relationship between current density and blister formation time was presented by Rodriguez\(^{11}\). Electrolytic bath composition was held constant while current density changed. It was discovered that blistering time is not a linear function of current density.

**Effect of Impurities in Charging Bath**

It has long been realized that minor concentrations of some elements in plating baths can make a major difference in the amount of hydrogen absorbed. For example,
Groeneveld et al (10) showed how hydrogen absorption varies with arsenic concentration. This study shows two effects that impurities may have. At low concentrations, the kinetics of hydrogen discharge are evidently altered. While at high concentrations, a barrier layer inhibits the passage of hydrogen into the iron.

Metal coatings have been plated on steels in an effort to eliminate hydrogen embrittlement. According to Uhlig and Matsushima (9), the coatings act to alter the kinetics of hydrogen ion discharge. For this reason, continuous coatings are not necessary. Altering the kinetics results in less occlusion of hydrogen into the iron electrode. The authors felt that a change in hydrogen overvoltage played an important role in the alteration of the kinetics of hydrogen absorption.

**Mechanism**

Hydrogen embrittlement is initiated by hydrogen diffusing into the metal matrix. Fontana and Greene (1) give an example of a tank containing an electrolyte. Figure 1 shows a typical cross-section of this tank. Due to a corrosion reaction or cathodic protection, hydrogen is evolved at the electrolyte-tank interface. Because hydrogen is present in the electrolyte in the form, $H^+$, there is always a concentration of hydrogen present at the metal
surface. Some hydrogen ions at the metal surface, pick-up an electron from the metal, diffuse on the metal surface to a hydrogen ion in a similar state and combine to form a molecule of hydrogen gas. Hydrogen in this state then bubbles off the metal surface.

Other hydrogen ions adsorbed on the surface can move into the metal. There has been discussion as to whether the hydrogen ion remains as an ion or picks-up an electron and moves in as a hydrogen atom. Oriani\textsuperscript{17} points out that even if it is an ion, it is well-screened and there-
fore behaves essentially as an atom.

The most popular explanation of the formation of cracks due to large concentrations of hydrogen is summarized by Fast(3). In this mechanism, hydrogen diffuses into the steel and the lattice concentration in a given area is increased. Any "void" in this area (such as inclusions, grain boundaries, etc.) may collect molecular hydrogen by the simple means of hydrogen desorption from the void surface. Using Sievert's Law with modifications for non-ideality of the gas at high pressures, the molecular hydrogen pressure in the void can be related to the lattice concentration. As lattice concentration increases, void pressure is thought to increase until it reaches a point where plastic deformation in the surrounding area may occur.

Fast claims that grain boundaries are voids in which molecular hydrogen can collect. Rodriguez(11) showed that cracks in the grain boundary area of Ferrovac "E" iron are usually at an angle to the grain boundary and do not lie in the grain boundary itself. This suggests that the cracking originates in intense slip bands instead of the grain boundary.

Work performed by Darken and Smith(12) shows that due to cold work the solubility of hydrogen in iron is greatly increased while the permeability remains fairly constant. Annealing specimens and exposing them to hydrogen apparent-
ly decreases the permeability by a factor of about five while only slightly affecting the solubility.

Bockris et al\textsuperscript{(13)} carried out similar investigations by applying stress to iron and steel and measuring permeation rates. They found permeation rates increased with increased stress. It was also shown that diffusivity, $D$, was independent of stress. To show that grain boundaries probably were not important to permeation, these people obtained similar results from polycrystalline and single crystal iron specimens. Similar results were obtained for zone-refined iron. Bockris continues by saying "The point of crack nucleation must then be an aggregate of dislocations; a conclusion consistent with the fact that no blister formation occurs in iron whiskers." The above work shows the importance of dislocations to any hydrogen embrittlement mechanism.

Proof is given for the attraction of hydrogen to dislocations by Gibala\textsuperscript{(14)}. By internal friction measurements, he showed that the binding energy of hydrogen atoms to a dislocation is about $-6400$ cal/mole.
PROCEDURE

Specimen Preparation

Ferrovac "E" iron specimens were cut to approximately 1- by \( \frac{1}{2} \)-in. rectangles. Each specimen was mechanically polished in stages through a 0.05 micron alumina in distilled water slurry.

AISI 4130 steel specimens were cut to about 4- by \( \frac{1}{2} \)-in. strips. The thickness was 0.080-in. To obtain a hardness of Rockwell C 40, the hardness required for hydrogen cracking in static load bend tests, the steel was heat treated. Heat treatment consisted of austenitizing at 1550°F for 30 min, oil quenching, tempering at 850°F for 2 hr, and air cooling. With these steps in initial preparation, the specimens were ready for investigation.

Cathodic Charging with Constant Bath Composition

A polished Ferrovac "E" iron specimen was placed horizontally in a sample holder that exposed a constant specimen surface area to the electrolyte. The electrolytic cell was designed so that the specimen was the cathode.
Initial investigations dealt with cathodic charging in constant composition electrolyte baths. Baths contained 1 percent by volume $H_2SO_4$ in distilled water and 10 mg $As_2O_3$ per liter. The $As_2O_3$ acted as a cathode poison to induce hydrogen blistering. The variables in the investigation were current density and time. Curves of time for blister formation versus current density were plotted.

Subsequent investigations were performed in which current density was held constant while blister formation time was observed versus the total time the specimen was in the bath. The specimen was not cathodically charged for the total time in the bath.

In a related experiment, the effects of bath agitation were observed.

**Effect of Impurity Concentration**

Investigations were carried out with bath composition as the variable to observe changes in blistering time. Acid content remained constant at 1 percent by volume $H_2SO_4$. Current density was maintained at 1.3 amps per cm$^2$.

So that comparisons could be made relative to the effect of 10 mg $As_2O_3$ per liter, impurity oxides were added to the electrolyte in 10 mg per liter quantities. Continuous
charging was carried out to determine the time for blister formation.

Microscopic Work to Develop a Model

Following blister formation time studies, an investigation was made into the mechanism by which hydrogen enters the metal. The mechanism would be used to help construct a model of hydrogen entering iron. A polished specimen was observed under a Leitz Metallux microscope. The specimen had previously been subjected to a potassium ferrocyanide treatment to delineate the anodic areas. Then it was repolished so that only the anodes were visible.

Magnified pictures were taken indicating the location of the anodic areas. Without moving the sample, a few drops of 1 percent H₂SO₄ were placed in the same area. Pictures were again taken to determine the position of the hydrogen-gas bubble seats relative to the anodic areas.

Application of Results

To determine the industrial usefulness of the results derived from the investigations, it was decided to clean and plate some steel and observe the results. AISI 4130 steel specimens were exposed to standard acid pickling and chrome plating solutions, and compared to results for similar solutions with additives. The standard solutions
were a 15 percent H₂SO₄ by volume pickling bath and a chrome plating bath containing 250 g Cr₂O₃ and 2.5 g SO₄²⁻ per liter distilled water. The plating was done for 8 min at 0.15 amp cm⁻².

Immediately after plating, each specimen was placed in a static load bend test with a stress of 2500 psi. The stress was maintained until the sample failed from hydrogen cracking or until 10 days elapsed.
RESULTS

Charging in Constant Composition Bath

Figure 2 shows the effect of current density on alpha-iron blister formation time in 10 mg As₂O₃/liter 1 percent H₂SO₄. No blisters were detected at comparable times in 1 percent H₂SO₄. Blisters were noticed at comparable times in 10 percent H₂SO₄.

![Figure 2. Current density vs. blister formation time](image)
It was noted that the data was reproducible as long as there was no delay time between placing the sample in the bath and commencing the charge.

To investigate the effect of immersion in the bath prior to charging a separate set of experiments were conducted which related blistering times to total time in the bath.

Table 1 gives a characteristic comparison of blister formation time for continually charged samples and for those immersed and charged samples.

Table 1

<table>
<thead>
<tr>
<th>Continual Charge Time</th>
<th>Charge No Charge Time (Immersed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95 sec</td>
<td>80 sec</td>
</tr>
<tr>
<td>10 sec</td>
<td></td>
</tr>
<tr>
<td>Total: 95 sec</td>
<td>90 sec</td>
</tr>
</tbody>
</table>

In all cases, some charging time was necessary for blister formation but the applied voltage was not necessary for the entire blistering time. (See Table 1)

The effect of electrolyte agitation was also investigated in constant composition baths. Stirring of the bath produced more blisters in the same time when compared
to the unagitated solution.

**Effect of Impurity Concentrations**

The presence of small amounts of arsenic in the 1 percent $\text{H}_2\text{SO}_4$ solutions greatly increased the tendency for iron to blister. A standard $\text{As}_2\text{O}_3$ concentration of 10 mg per liter 1 percent $\text{H}_2\text{SO}_4$ and current density of 1.3 amps per cm$^2$ was used. Similar impurity concentrations and current density were used in the investigations of the effect of other impurities except where noted. Table 2 compares the results.

Table 2

Comparison of blister formation time using impurities in the electrolyte.

<table>
<thead>
<tr>
<th>impurity</th>
<th>charge time</th>
<th>result</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>20 min</td>
<td>many blisters</td>
</tr>
<tr>
<td>MgO</td>
<td>30 min</td>
<td>no blisters</td>
</tr>
<tr>
<td>BaO</td>
<td>45 min</td>
<td>no blisters</td>
</tr>
<tr>
<td>$\text{P}_2\text{O}_5$</td>
<td>570 sec</td>
<td>blisters</td>
</tr>
<tr>
<td>$\text{As}_2\text{O}_3$</td>
<td>95 sec</td>
<td>blisters</td>
</tr>
<tr>
<td>$\text{Sb}_2\text{O}_3$</td>
<td>15 sec</td>
<td>blisters</td>
</tr>
<tr>
<td>$\text{Bi}_2\text{O}_3$</td>
<td>50 sec</td>
<td>blisters</td>
</tr>
<tr>
<td>ZnO</td>
<td>12 min</td>
<td>no blisters</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>10 min</td>
<td>no blisters</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>10 min</td>
<td>few blisters</td>
</tr>
<tr>
<td>Zn(OH)$_2$</td>
<td>5 min</td>
<td>few blisters</td>
</tr>
<tr>
<td>Fe(OH)$_3$</td>
<td>5 min</td>
<td>blisters</td>
</tr>
<tr>
<td>$\text{Ag}_2\text{O}$</td>
<td>5 min</td>
<td>blisters</td>
</tr>
<tr>
<td>TeO$_2$</td>
<td>2 min</td>
<td>many blisters</td>
</tr>
<tr>
<td>$\text{K}_2\text{SO}_4$</td>
<td>210 sec</td>
<td>no blisters 5.8 amp/cm$^2$</td>
</tr>
<tr>
<td>$\text{Na}_2\text{SO}_4$</td>
<td>180 sec</td>
<td>no blisters</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>14 min</td>
<td>no blisters 5.8 amp/cm$^2$</td>
</tr>
</tbody>
</table>
Figure 3 shows iron samples charged with MoO₃ and As₂O₃ in sulfuric acid for the above investigations.

Fig. 3. Samples charged in sulfuric acid containing As₂O₃ (top) and MoO₃.

Microscopic Work

Figure 4 shows anodes decorated by potassium ferro-cyanide. Figure 5 shows the same area exposed to sulfuric acid. The hydrogen bubbles can be seen to emerge from areas immediately adjacent to the anode areas.
Fig. 4. Anodes in Ferrovac "E" delineated by potassium ferrocyanide.

Fig. 5. Hydrogen bubbles on the surface shown in figure 4.
Application of Results

Investigations were made to see the effect of desirable impurities on AISI 4130 steel. Figure 6 shows a MoO₃ charged specimen after the bend test. Figure 7 shows a specimen that failed after 8 hrs in the bend test. It was charged in baths containing no MoO₃.

Fig. 6. AISI 4130 steel charged in sulfuric acid containing MoO₃, 10 days in bend test.
Fig. 7. AISI 4130 steel charged in 15% sulfuric acid, 8 hrs in bend test.
DISCUSSION

Blistering Time Versus Current Density Curve

The prevailing idea of the blistering mechanism is the one in which hydrogen diffuses in from the outer surface and precipitates in a "void" until enough pressure has built up to cause plastic deformation. If this model is correct, then the curve shown in figure 2 can be theoretically derived.

The assumption is made that the void pressure necessary to cause blistering deformation is approximately the nominal yield stress of the metal. This yield stress is about 2000 atm. Using Vibrans(18) calculations, the lattice concentration of hydrogen in equilibrium with a pressure of 2000 atm is approximately $3 \times 10^{-2} \text{ cm}^2 \text{ H/100 g Fe}$ or $1.2 \times 10^{17} \text{ atoms H/ cm}^3$.

Knowing the concentration at a distance $X$ from the surface, which is necessary to cause blister formation and by assuming a surface concentration, it is possible to determine blistering times by applying the diffusion equation for a semi-infinite solid with zero initial concen-
tation. Since the experimental results show a current density dependence on blistering time, it is interesting to speculate how the current density affects the effective surface concentration.

Effective surface concentration may be estimated as follows. A current density of 1 amp cm\(^{-2}\) will be used for the calculation with the assumption that 2 out of every 3 hydrogen atoms are absorbed. Therefore, about \(4 \times 10^{18}\) atoms of H would be absorbed during any second. It is next assumed that the surface concentration is that concentration in the first unit cell layer which has interstitial sites as noted in figure 8.

![Fig. 8. BCC unit cell with interstitials](image)
By assuming that each of the atoms moves into the lattice cell and then jumps at random, an estimate can be made of the average length of stay of each atom in the first unit cell layer. For example, the first jump is from a \( y_1 \) or \( z_1 \) site to a \( z_2 \) or \( y_2 \) site. The probability of an atom leaving the first unit cell layer in one jump is therefore zero. By cataloging the possible second jumps, it can be shown that there are eight possible positions for an atom to be after two jumps, only two of which are in the third layer. So, the probability of an atom leaving the first unit cell after two jumps is \( \frac{2}{8} = 0.250 \). The same analysis for four jumps gives 104 possible positions of which 44 are outside the first unit cell. The probability has increased to 0.423 after four jumps. Likewise, the probability goes to 0.540 after six jumps. Continuing like this, it is possible to estimate that the average atom jumps about ten times within the first unit cell layer. Using this figure, an average time of stay can be calculated. Taking

\[
D = \frac{1}{6} d^2 \tau \quad \text{(1)}
\]

where \( D \) is the diffusivity, \( d \) is the jump distance, the jump frequency, \( \tau \), can be calculated

\[
\tau = \frac{6D}{d^2} = \frac{6 \times 10^{-5}}{(1.4 \times 10^{-8})^2} = 3 \times 10^{11} \text{ jumps/sec} \quad \text{(2)}
\]
The average time per jump is then \((3 \times 10^{11} \text{ sec})^{-1}\).

The average time spent by an atom in the first unit cell layer is then

\[
\frac{10}{3 \times 10^{11}} \approx 3.3 \times 10^{-11} \text{ sec.} \tag{3}
\]

Since \(4 \times 10^{18}\) atoms pass through this layer per second, the average population of this layer is

\[
4 \times 10^{18} \cdot 3.3 \times 10^{-11} = 1.3 \times 10^8 \text{ atoms.} \tag{4}
\]

The volume of this layer is

\[
1 \text{ cm}^2 \cdot 2.8 \times 10^{-8} \text{ cm} = 2.8 \times 10^{-8} \text{ cm}^3. \tag{5}
\]

The concentration of the layer is then

\[
c = \frac{1.3 \times 10^8 \text{ atoms}}{2.8 \times 10^{-8} \text{ cm}^3} = 0.46 \times 10^{16} \approx 5 \times 10^{15} \text{ atoms/cm}^3. \tag{6}
\]

This is lower than the concentration estimated above required for blistering in the vicinity of the void. This surprising result suggests that the "void" blistering mechanism does not operate because it is not possible to build up the required lattice concentration in the vicinity of the void to equalize with large enough pressure to cause blistering. A model must then be developed which allows for greater hydrogen concentration in localized regions.

The nature of these localized regions must be considered. Although there is always a possibility of increased impurity concentration in the vicinity of any lattice...
defect, only dislocations are available in densities great enough to attract large hydrogen concentrations. A rough calculation may be made to illustrate this point.

Assuming a slip band in alpha-iron with a modest dislocation density of one dislocation per 100 iron atoms in cross section, an average hydrogen concentration may be calculated. For purposes of the calculation, a lattice concentration of hydrogen will be assumed to be $8.5 \times 10^{16}$ hydrogen atoms per cm$^3$ of iron. This corresponds to 1 ppm or $10^{-6}$ hydrogen atoms per each iron atom.

For a lattice plane which cuts the slip band and contains $10^6$ iron atoms and $10^4$ dislocations, there will be one hydrogen atom in equilibrium with the lattice. The question is how many will be associated with the dislocations?

Using Gibala's figure of $-6400$ cal/mole for the binding free energy of the hydrogen-dislocation pair and following the analysis given by Swalin$^{19}$ it can be shown that

$$\frac{X_d}{X} \approx \exp \left[ \frac{-\Delta G_B}{RT} \right]$$

where $X_d$ is the mole fraction of hydrogen around a dislocation

$X$ is the lattice mole fraction

$G_B$ is the binding free energy

therefore $X_d \approx 5 \times 10^4 X$

or $C_d \approx 5 \times 10^4 C$

For each dislocation site therefore there are $(10^{-6})5x10^4$. 
or $5 \times 10^{-2}$ H atoms.

In the assumed array of iron atoms at equilibrium therefore, there is one lattice hydrogen atom plus $(10^{14})(5 \times 10^{-2}) = 500$ hydrogen atoms associated with the dislocations. This corresponds to a concentration in the slip band of $4 \times 10^{19}$ hydrogen atoms per cm$^3$. While the system is not expected to be at equilibrium, the above calculation does serve to show the greatly increased affinity for hydrogen atoms in a slip band.

The proposed model for hydrogen blistering therefore is as follows. Hydrogen enters the lattice and diffuses normally until it reaches a slip band. It then diffuses in the slip band to a point where its progress is disrupted such as at an intersection of two slip bands or a slip band-grain boundary intersection. The actual crack nucleation mechanism can only be speculated upon but, it seems reasonable to assume that the progress of a hydrogen atom can be temporarily retarded at a dislocation intersection, allowing another atom to catch up and join with the first to form one molecule of hydrogen. The stress associated with the distortion caused by this formation cannot be easily relieved on the slip plane because of the presence of previously piled-up dislocations on the slip planes at the intersection. This model will then explain why hydrogen cracks are generally found to form on slip planes as shown.
by Tetelman (20) and at angles to grain boundaries as shown by Rodriguez (11).

While this model explains how hydrogen blisters form, it does not yet explain why they form in some and not in other areas. Since there are obviously many more slip band intersections than blisters, there must be a mechanism that allows a greater hydrogen concentration to build up in a few intersections. It has been tacitly assumed above that the surface is homogenous and hydrogen enters all areas in equal quantities. A glance at hydrogen evolving from any cathode shows this assumption to be false and the model must be modified to account for this.

Furthermore, the investigations relating blistering times to total immersion times can only be explained by assuming that substantial amounts of hydrogen enter the iron when no external current is flowing. This strongly suggests that there is a surface mechanism by which hydrogen is being absorbed with zero current density.

One has only to consult the literature concerning the corrosion of iron in dilute acid solutions to discover an appropriate mechanism. The surface of iron is thought to contain anode areas and cathode areas and corrosion proceeds by electrochemical reactions involving these microscopic cells. For the purposes of this model, it can be assumed that these cells operate at zero external voltage and in
certain areas, therefore, hydrogen is always being evolved.

These cells were demonstrated in the microscopic work mentioned above. Figures 6 and 7 show hydrogen evolving at zero current density in the immediate vicinity of known anode areas. This implies that the effective cathodes are immediately adjacent to the anodes.

Anode areas are those at which metal atoms go into solution and it is thought that these atoms are in higher than average energies within the metal lattice. Atoms associated with the intersection of a slip band with the surface would be in such energy configurations. It can therefore be assumed that the active anodes are indeed at slip bands, the larger slip bands being the more active anodes.

The fact that blistering does not occur under conditions of zero current density indicates that these microscopic cells by themselves are unable to cause hydrogen to be absorbed at rapid enough rates to concentrate it in large enough quantities to build blistering pressure. Microscopic examination of the hydrogen evolution reaction gives a hint as to why this might be. At any anode area, the initial hydrogen evolution is rapid but falls off with time. This suggests that the hydrogen concentration in the vicinity of the cathode area is being depleted. The major effect of an imposed current density, therefore is to keep a constant supply of hydrogen ions at the cathode.
areas. A secondary effect is to provide some hydrogen absorption at non-cathode areas where the hydrogen may still diffuse to the slip bands. The observation that stirring during charging leads to more blistering supports the hydrogen concentration theory.

**Impurity Concentrations in Bath**

Impurity oxide additions to the electrolytic bath alter the blister formation times with constant current densities. Uhlig (9) feels that plating of some metals on iron decreases the hydrogen overvoltage at the iron surface. This may be the action of some of the metal ions. Reliable data on hydrogen overvoltages is lacking but there are indications that the overvoltage for arsenic is greater than that for iron which in turn is greater than the molybdenum overvoltage. Arsenic and molybdenum may therefore act in opposite ways to change the hydrogen overvoltage at the cathode areas on the iron surface; the higher the hydrogen overvoltage, the more hydrogen absorbed at those sites.

**Application of Results**

Investigations reveal that the addition of molybdenum ions to acid pickling and chrome plating baths alters the kinetics of hydrogen ion discharge. Apparently the action is to lower the hydrogen overvoltage at the cathode area
of the steel surface.

The result of charging in the presence of molybdenum is a very significant lengthening of time to failure for specimens in a static load bend test. Specimens charged without molybdenum failed after a few hours. Specimens charged with molybdenum did not fail after ten days of static load.
CONCLUSIONS

The following model has been developed to explain hydrogen blistering in alpha-iron. Areas adjacent to anodes on the metal surface absorb large concentrations of hydrogen. Hydrogen diffuses into the metal and collects along slip bands. Where slip bands cross, hydrogen atoms join to form gas and create a void in the metal. With additional hydrogen, the pressure in the crack grows until plastic deformation causes a blister on the iron surface.

Metal ions plated on the iron surface act to alter hydrogen absorption kinetics. For example, arsenic acts to promote blistering while molybdenum retards blistering.
SUGGESTIONS FOR FURTHER INVESTIGATION

Plating metal ions on the iron gave some very interesting results relative to blister formation times. For instance, some ions promoted blistering while others inhibited or prevented blistering. Literature shows little data on the hydrogen-overvoltages for many important metals. Consequently, investigations should be made into the effect these ions have on the hydrogen-overvoltage at the iron surface.

Additional proof to substantiate the model could be produced if the location of anode areas relative to blisters was established.

Different approaches to the explanation of the current density versus blistering time curve should be made.

Studies should be conducted on the effect current density has on hydrogen concentration in the iron.
### APPENDIX

#### Chemical Analysis of Metals

<table>
<thead>
<tr>
<th></th>
<th>Ferrovac &quot;E&quot; Iron</th>
<th>AISI 4130 Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.007%</td>
<td>0.33%</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.002%</td>
<td>0.008%</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.01%</td>
<td>0.31%</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.01%</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.0027%</td>
<td></td>
</tr>
<tr>
<td>Tin</td>
<td>0.005%</td>
<td></td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.005%</td>
<td></td>
</tr>
<tr>
<td>Manganese</td>
<td>0.001%</td>
<td>0.60%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.006%</td>
<td>0.016%</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.004%</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>0.05%</td>
<td></td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.023%</td>
<td></td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.003%</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>0.01%</td>
<td></td>
</tr>
</tbody>
</table>
LITERATURE CITED


