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THE PROCESS OF BLISTER FORMATION
ON ELECTROGALVANIZED SHEET STEELS

by

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Submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

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January 1995
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THE PROCESS OF BLISTER FORMATION ON ELECTROGALVANIZED SHEET STEELS

Abstract

by

PAUL JANAVICIUS

Electrogalvanized sheet steels are the base material in the production of automobile bodies and appliances. The coated sheet steels act as substrate materials to complex coating systems. When small defects known as blisters form at the zinc steel interface the coating integrity can be adversely effected. The formation and growth of blisters on electrogalvanized sheet steels was examined in this study.

Blister growth was examined by evaluating models of the zinc-steel system, analyzing the internal gases in blisters, monitoring the growth of blisters, and evaluating the amount of hydrogen absorbed by the preplating electroprocesses.

The plate model was found to best describe the zinc-steel system. The gases within the blisters were found to be hydrogen and methane. The methane is the reaction of hydrogen with interfacial carbon. Blister growth
monitoring demonstrated that blisters do not grow once they have formed. The zinc coating was seen to deform via a grain boundary sliding mechanism. It was found that the permeation of hydrogen through a steel membrane is reduced by 90% by pulsing between cathodic and anodic states. It was also determined that the sequence of pulsing has an effect on the amount of hydrogen absorbed.

The formation of blisters can be summarized in the following manner. The presence of areas of poor adhesion at the zinc steel interface act as initiation sites for blister growth. Hydrogen which is injected into the steel during the plating process will diffuse into the initiation site. If carbon is present at the initiation site the formation of methane is favored. When the internal gas pressure builds up the coating is deformed. Plastic deformation can occur by flow or grain boundary sliding. Deformation will continue until the pressure is relieved by a void or a crack in the coating.
I would like to take this opportunity to thank the people that have helped me throughout this whole undertaking. First a great deal of thanks is extended to my advisors Prof. Joe Payer and Prof. Gary Michal. Prof. Payer’s prodding kept me thinking and directed. Prof. Michal was always willing to go over the problems which I thought complicated and make them seem simple.

I would like to thank LTV Steel Co. for their support with my education. The personal support of the LTV Fellowship and the support of the research in general. I would particularly like to thank George Eierman of LTV Laboratories for his support of my research. I would also like to thank Paul Luke, George Themolis, and Gene Staib for their help with specific measurements and processes. In addition I would like to thank Ron Miner and Jack Butler for realizing the usefulness of university research in helping industrial problems. I would also like to acknowledge the financial support of the State of Ohio Steel Futures Program in sponsoring the project.

The corrosion group at Case Western Reserve University deserves a great deal of thanks. In particular I would like to acknowledge the help of
Steve Amey and Greg Shaw who were responsible for the other aspects of the research in this project. I would also like to thank Klaus Fink for his friendship and help. Dr. Inho Song and Dr. Don Gervasio deserve much thanks for their help in answering many questions. Brett Ricket, Gail Ball and Brenda Trautman who helped me on occasions too numerous to count.

Finally I would like to thank my family for supporting me during my extended education. My brother Luke for his support in solving numerous problems, his wife Jackie and daughter Josie for bringing a smile. My sister Vilija for numerous dinners. I would also like to thank my father for his support during all my education. Sadly I acknowledge my grandmother who recently passed away who always supported me with food and love.
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1.1 Statement of Problem

Electrogalvanized sheet steels are used in the automotive and appliance industries to provide a more corrosion resistant product. The coated sheet steel acts as a substrate for a multilayer paint system. The paint system includes phosphate layer, electrocoated primer, base coat, and clear coat. A defect in a sublayer can result in a unacceptable top layer. A small defect known as a blister can form at the zinc-steel interface during paint bake cycles which hold the material at 163° C (325° F) for 20 minutes. Although these defects are small (5-200 μm dia.), they disrupt the quality of the final finish. Therefore, the occurrence of blisters must be minimized.

Blisters result from a combination of events. The uncoated sheet steel is subject to electrocleaning and electropickling steps prior to the plating of zinc. Electrocleaning is performed in an alkaline environment. Electropickling is performed in an acidic solution. Both processes are run at moderate temperatures (55-75°C) and at high current densities (50-500 mA/cm²). During these electroprocesses the steel is held in both cathodic and anodic conditions. While in the cathodic cycle hydrogen is generated at the steel surface. The hydrogen can either form hydrogen gas or be absorbed by the steel. The zinc
coating will act as a barrier to hydrogen escape trapping the hydrogen in the steel. Normally the trapped hydrogen is not a problem, but if areas of poor adhesion exist at the zinc-steel interface hydrogen can recombine. When sufficient pressure is built up a blister forms.

1.2 Approach

The problem of blister growth was investigated by looking at three aspects of the system. Hydrogen absorption during preplating processes, surface chemistry of the steel substrate and its effect on adhesion, and the blister formation process. It was shown that significant amounts of hydrogen were absorbed by the steel during the preplating processes\(^1\). It was found that carbonaceous species can react with the steel surface and have detrimental effects to the adhesion of zinc\(^2\).

This document is an investigation on the blister growth process. In this investigation the parameters which effect blister growth were identified by: applying models to describe the system, identifying the gas within blisters, monitoring blister growth, determining how hydrogen charging effects the steel surface, and investigating the effect of cathodic and anodic pulsing on hydrogen entry into the steel.
1.3 Dissertation Organization

This document is separated into eight chapters. Chapter 1 contains this introduction. A review of information relevant to the blistering problem is presented in Chapter 2. Experimental techniques and methods are documented in Chapter 3. In Chapter 4 the mechanical models are applied to the zinc-steel system. Chapter 5 is the analysis of the gas within blisters. Various attempts to monitor the growth of blisters in both ex-situ and in-situ modes is examined in Chapter 6. Chapter 7 documents investigations into the effects of cathodic and anodic pulses on hydrogen permeation through a steel membrane. In Chapter 8 measurements of the amount of hydrogen absorbed during simulations of preplating processes are reported. Chapter 9 draws conclusions from the various aspects of the study to present a mechanism of blister growth. Directions for future work are presented in Chapter 10.
The purpose of this section is to review the literature which will provide insight into the processes involved with the formation of blisters on electrogalvanized sheet steels. For the electrogalvanized steel system it is useful to look at all the parameters involved in producing and using the coated product.

The bare steel sheet is produced by hot rolling and cold rolling into the final thickness. After cold rolling the sheet is annealed in either a batch or continuous process. The sheet is electrocleaned, electropolished, and electroplated with zinc. After production of the steel sheet, it is then stamped into shape, painted with a multi-layer coating system, and baked. During the baking process the defects known as blisters form.

The organization of this section will be along the following lines. The substrate material, hydrogen entry during the electrogalvanization process, and properties of the zinc coating. There is an extensive amount of information and this coverage does not attempt to be all inclusive, but to highlight pertinent aspects of the literature.
2.1 Steel Substrate

The substrate material for electrogalvanized steels are typically low carbon steels (>0.05% C) or ultra-low carbon steel (>0.005% C). The steel is commonly cast into a billet by a continuous casting process. The billet is then reduced in a hot rolling process. After hot rolling the strip is pickled to remove the iron oxide scale formed during hot rolling. After pickling the strip is cold rolled to a thickness of about 0.75 mm (0.030"). Annealing is the final step in the strip process. Annealing is either performed in a batch or continuous process. In the batch process the entire coil is placed in a furnace with a hydrogen atmosphere. During a continuous anneal the coil is unwound and passed through a furnace. As the strip passes through the furnace, annealing temperatures are reached and the length of the annealing cycle can be tightly controlled as compared to a batch anneal.

2.1.1 Steel Surface

The surface of the steel strip is influence by the rolling processes. These processes reduce an approximately 30 cm billet into a steel strip that is on the order of 1 mm in thickness. Because the topography of the steel surface will influence the zinc coating a review of the rolling process is in order.
Although rolling is a very complex process there are four variables which control the deformation of the steel. These variables are: roll diameter, the metals resistance to deformation, front and back tension, and friction. The roll diameter controls the loads transmitted to the steel. The strength of the material will control at what stress the material will plastically deform and is influenced by temperature. Tensioning of the strip can reduce the load needed to be transmitted by the rolls, and can improve the flatness of the strip. Friction is a more complex variable as it varies throughout the rolling process.

When the material enters the roll it is moving slower than the roll. As the material is reduced the velocity increases. At one point in the process the velocity of the steel is equal to the roll velocity. When the material leaves the rolls it is moving faster than the roll. Friction acts to draw the metal into the rolls at the entrance and is reversed at the exit. Friction is assumed to be constant along the roll in most theories of rolling. This assumption does not reflect reality, but is necessary as it is difficult to measure the coefficient of friction along all points of contact. Several studies have been made with sensors imbedded in the roll to measure the friction during the rolling process. Dieter reports that the coefficient of friction for hot rolling varies from 0.2 to 1 (where sticking occurs) and for cold rolling with lubricant the
coefficient of friction varies from 0.05 to 0.1. The surface of the steel sheet is influenced by friction when small parts of the steel welds itself to the roll.

Tabor studied the interaction that occurs when two surfaces come into contact. The welded area is pulled from the steel and the resultant material can be flattened during a subsequent pass. This process is schematically illustrated in Figure 2.1. This feature will be referred to as a flap, but can have other names. Flaps are generally microscopic (1-10 μm) and cover a significant portion of the steel surface. Flaps are generally thought to be a negligible feature although some defects on coated products can be traced to the flaps.

The friction can be controlled to some extent by the use of lubricants. These lubricants can lead to chemical contamination of the sheet which will be covered in the next section.

2.1.2 Chemical Contaminants

The steel is subject to many different sources for contamination during strip processing. Rolling oils, greases from machinery, and alloying elements can contribute to contamination of the steel strip. Shaw reviewed and studied carbonaceous and non carbonaceous contaminants on steel surfaces.
Non-carbonaceous contaminants result from surface segregation of trace alloying elements during the annealing process. Elements such as aluminum, vanadium, titanium, and chromium exhibit surface segregation. This contamination was removed during the electrocleaning and electropolishing processes.

Carbonaceous contaminants can be a result of alloying elements (surface carbides) or external sources. Shaw\(^3\) reviewed the sources of various carbon contaminants. Amorphous carbon contaminants typically result from residual oils on the steel surface during the anneal process. This carbon can diffuse into the steel and subsequently exit forming crystalline graphite deposits\(^7\). The formation of graphite can be controlled by controlling the annealing atmosphere.

2.2 Electrogalvanization Process

The electrogalvanization process involves several steps.\(^8\) The process is schematically illustrated in Figure 2.2. The preplating processes include mechanical brushing, alkaline electrocleaning, and acidic electropolishing. During the electroprocesses conditions are favorable for hydrogen absorption.
2.2.1 Hydrogen Reactions

In an aqueous environment hydrogen is present as an ion $H^+$. The amount of hydrogen ions in solution is defined as the pH

$$pH = -\log(H^+)$$ \hfill (2.1)

A neutral solution will have a pH of 7 with an equal number of $H^+$ and $OH^-$ ions. Acidic solutions have lower pH's less than 7 and basic solutions have pH's greater than 7.

When a metal is placed in solution the hydrogen ions can interact with the metal surface. The extent of the interaction will depend on the pH of the solution and the metal. There are three common hydrogen reactions which can occur on the metal surface. The hydrogen discharge (HDR), hydrogen evolution (HER) and hydrogen absorption (HAR) reactions are illustrated in Figure 2.3.

For HDR to occur the $H^+$ ion would need to be reduced on the metal surface. In an acid solution the $H^+$ or a pronated water ($H_2O^+$) are reduced (Equation 2.2). In neutral and basic solutions water is reduced (Equation 2.3).
\[ H_3O^+ + e^- = H_{ads} + H_2O \]  
acid (2.2)

\[ H_2O + e^- = H_{ads} + OH^- \]  
neutral/basic (2.3)

Each of these reactions require that the metal surface donate an electron to the hydrogen ion. The ease of this donation is measured by the work function of the metal. After the HDR has occurred the adsorbed hydrogen on the surface can either combine to form hydrogen gas or be absorbed into the metal.

The formation of hydrogen gas or HER can occur via several different reactions depending on the solution environment. Two adsorbed hydrogen can combine in a catalytic manner

\[ H_{ads} + H_{ads} = H_2 \]  
(2.4)

For this reaction to occur two adsorbed hydrogen atoms must interact on the metal surface. Often these interactions are slow to occur and the product from a second discharge reaction reacts with the adsorbed hydrogen. The reaction that occurs is dependant on the pH of the solution
\[ H_{\text{ads}} + H_{\text{2O}} + e^- = H_{\text{2}} + H_{\text{2O}} \]  \hspace{1cm} \text{acid (2.5)}

\[ H_{\text{ads}} + H_{\text{2O}} + e^- = H_{\text{2}} + OH^- \]  \hspace{1cm} \text{neutral/basic (2.6)}

A measure of the hydrogen discharge process is the exchange current density. The exchange current density is the amount of current passed when the metal is polarized to an overpotential where hydrogen will evolve. The exchange current density will vary for different metals and similar metals in different conditions giving an indication of the number adsorption sites on the metal surface.

Alternately, the adsorbed hydrogen can be absorbed into the bulk material by the HAR as shown

\[ H_{\text{ads}} = H_{\text{abs}} \]  \hspace{1cm} (2.7)

The reaction is effected by several factors. The amount of adsorbed hydrogen influences the HAR process as is seen in equation 2.7. The HER process also competes with the HAR process for adsorbed hydrogen atoms. Therefore, the rate of the HER influences the HAR process. Finally, the bonding in the metal influences the amount of hydrogen absorbed. Hydrogen distorts the lattice of the metal and the activation energy \( (E_a) \) describes the resistance to hydrogen entry.
In a body centered cubic (BCC) lattice such as α iron, hydrogen will tend enter the interstitial sites as illustrated in Figure 2.4. There are octahedral and tetrahedral interstitial sites in the BCC lattice. For iron, the octahedral site can accommodate a 0.19 Å sphere while the tetrahedral site can accommodate a 0.36 Å sphere. The radius of a hydrogen atom is approximately 0.46 Å. It is apparent that some sort of lattice accommodation must be made for hydrogen to enter the iron lattice.

Iron has been shown to have a 9% increase in lattice spacing with hydrogen absorption.9 Oriani10,11 documented change in lattice parameter of Ti-30Mo, and films of iron, titanium, and tantalum on Ti-30Mo substrates12,13. Increases in lattice parameters were seen on thicker films while thinner films showed a decrease in lattice parameter due to internal stresses at the film surfaces. The hydrogen can also become "trapped" at internal sites, this phenomena will be discussed in a later section.

Hydrogen will be absorbed by the metal until equilibrium is reached. This equilibrium value is commonly called the hydrogen solubility. Iron has a fairly low hydrogen solubility compared to materials such as palladium and titanium. The low hydrogen solubility is related to the distortion of the iron lattice. The solubility of hydrogen in iron has been studied by many
researchers. Sievert$^{14}$ related the partial pressure of hydrogen, $p$, and temperature in kelvin, $T$, to the hydrogen solubility, $C$

$$C = A p^{1/2} \exp \left( - \frac{B}{T} \right)$$  \hspace{1cm} (2.8)

Where $A$ and $B$ are constants. Several studies$^{15,16}$ have determined $A$ and $B$ for conditions of elevated temperature and extrapolated to room temperature. Predictions for hydrogen solubility for iron at 1 atm and 25° C are one part in $10^9$ (10-7 mol/cm³), measured values reported are higher.

Some researchers report deviations from Sievert's law.$^{17,18,9,11}$ Explanations for this deviation include changes in the heat of solution and trapping of hydrogen in the iron.

### 2.2.2 Hydrogen Diffusion

Once inside a metal hydrogen can move about to some extent. This internal movement or diffusion is driven by concentration gradients or stress gradients within the material. The ease of movement is characterized by the diffusion coefficient. The diffusion coefficient, $D$, is exponentially related to temperature by the following equation

$$D = D_0 \exp \left( - \frac{Q}{RT} \right).$$  \hspace{1cm} (2.9)
Where $T$ is the temperature in Kelvin, $R$ is the gas constant, $Q$ is the activation energy, and $D_o$ is the intrinsic diffusion coefficient. Reported values for $D_o$ and $Q$ over various temperature ranges vary as reported by Amey. Values for $D$ at 25 degrees C ranged between $4.6 \times 10^9$ to $6.3 \times 10^5$ cm$^2$s$^{-1}$.

The diffusion of hydrogen can be described using Fick's laws of diffusion. With known boundary conditions these laws can establish concentration gradients over time and distance, $C(x,t)$. The first law relates the flux, $J$, of the diffusing species to the concentration gradient in the following equation

$$J = -D \frac{\partial C(x,t)}{\partial x} \quad (2.10)$$

Where $C(x,t)$ is the concentration of the diffusing species at a distance, $x$, from the surface at a time, $t$, and $D$ is the diffusivity. Fick's second law relates the time aspect of the concentration gradient to the distance term in the following manner:

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad (2.11)$$

The boundary conditions for these equations are important as they describe the system as a whole. In the case of hydrogen diffusion, boundary conditions include surface reactions and bulk reactions (e.g. trapping). The applicability
of different boundary conditions will not be covered here, but is treated by
Amey\textsuperscript{1}.

2.2.3 Trapping of Hydrogen

Trapping of hydrogen has been used to explain anomalies exhibited in
hydrogen diffusion studies. The large variation in reported values for $D$ give
an indication that there is more than simple diffusion occurring in some
systems. McNabb and Foster\textsuperscript{20} first explained the anomalies in hydrogen
diffusion by employing "traps" which interacted with the diffusing hydrogen.
Three type of traps were classified as to the ease of hydrogen removal: weak
traps, hydrogen easily removed; strong traps, traps which permanently hold
hydrogen; and active traps, in between permanent and weak traps in strength.

Oriani\textsuperscript{21} described a trap in a similar manner. A useful description of
trap strength is illustrated in Figure 2.5. Diffusion of hydrogen through the
lattice is described by a series of energy wells with a barrier of $E_a$ and spacing
of $\lambda$. A hydrogen trap will have a higher energy barrier $E_a + E'$ and a deeper
energy well $\Delta E_x$. The depth of the well and the energy barrier in addition to
the normal activation energy ($\Delta E_x + E_a + E'$) will describe the strength of the
trap. Interpreting the work of other researchers Oriani pointed out that
dislocations in cold worked material and interfaces (voids, cracks, grain boundaries) in non cold worked materials act as trapping sites.

Pressouyre\textsuperscript{22} attempted to describe cracking of steel by hydrogen by the presence of hydrogen traps. Traps were treated as both sinks and sources for hydrogen depending on the strength of the trap. Grain boundaries, dislocations, and titanium atoms were considered reversible traps (act both ways). High angle grain boundaries and titanium carbonitride particles were examples of irreversible traps.

Lee\textsuperscript{23,24,25} used a similar description as Oriani as to energy of a trap. A variation Lee employed was that $E'$ would be negative, that is, it would take less energy for hydrogen to enter a trap. The strength of various traps were measured by use of thermal analysis. The hydrogen evolution rate measured by thermal conductivity was related to the depth of the energy well, $E_{tr}$, by the following equation:

$$\frac{dx}{dt} = A(1-x)\exp\left(-\frac{E_{tr}}{RT}\right) \tag{2.12}$$

where $x = (N_0 - N)/N_0$, $N_0$ is the initial amount of trapped H at $t=0$, and $N$ is the amount of H at $t>0$, $A$ is a reaction constant, $R$ is the gas constant, and $T$
is the temperature in Kelvin. Hydrogen trapping TiC particles, dislocations, and sulphur inclusions were typical traps examined.

Once inside a trap, atomic hydrogen can recombine to form $\text{H}_2$ in voids or microcracks within the material. In the gaseous state the hydrogen is effectively immobile as it is too large to diffuse through the material. Podgurski\textsuperscript{26} examined the form of hydrogen in cold worked low carbon steel. It was found that the hydrogen combined with carbon in cementite to form methane by the reaction

$$2\text{H}_2 + \text{Fe}_3\text{C} \rightarrow \text{CH}_4 + 3\text{Fe}$$

(2.13)

Shewmon\textsuperscript{27} described a mechanism of methane bubble formation at grain boundaries in the intergranular cracking of Inconel alloys. These two researchers demonstrate that hydrogen can react with elements within a material in either atomic or gaseous states.

2.2.3 Hydrogen Adsorption During Plating Process

Amey\textsuperscript{1} studied the absorption of hydrogen during the plating process using the electrochemical permeation technique and developed a model to quantify the hydrogen absorbed. In electrochemical permeation a steel membrane was sandwiched between two electrochemical cells. One cell is
polarized so that the steel is a cathode. The other cell polarizes the steel to an anodic state. The cathodic side was used to simulate processes of electrocleaning, electopickling, and plating (with and without zinc). The anodic side measured the hydrogen passing through the sheet. The current in the anodic cell was a direct measure of hydrogen diffusion. The movement of hydrogen was described using an analytic model to be described in the next section.

Of the three processing steps, electopickling was shown to inject the most hydrogen. Simulated plating (no zinc in solution) was second followed by electrocleaning in terms of hydrogen charging. Zinc acted as a complete barrier to hydrogen when a 3 μm coating was present. Thinner coatings of zinc reduced the amount of hydrogen absorbed. Lead which can be a contaminant in the solutions was found to be an adsorption promoter when small amounts were present and a barrier when larger amounts were plated onto the steel surface.

2.2.4 Modeling Hydrogen Entry

Amey developed a phenomenological model to describe the entry and diffusion of hydrogen into a material. Figure 2.6 illustrates several parameters utilized in the model. The model is applied to the geometry of a permeation
experiment. The parameters $C_1$ and $C_2$ are the hydrogen concentrations predicted by the Nernst equation and Hirth's equation for the solubility of hydrogen in iron. The actual concentrations of hydrogen beneath the metal surfaces at $x=0$ and $x=L$ are $C(0,t)$ and $C(L,t)$ respectively. $J$ is the hydrogen flux through the sheet. The motion of the hydrogen through the sheet is controlled by Fick's second law with $D$ as an effective diffusivity as described by McNabb. The parameters $\kappa_1$ and $\kappa_2$ are constants termed mass transfer coefficients. These terms define the deviation from Sievert/Nernstian behavior.

The deviation from Sievert/Nernstian behavior is described in the following manner. When $\kappa$ is large (e.g., approaching $\infty$) the deviation from Sievert/Nernstian behavior is small. Conversely, when $\kappa$ is small (e.g., approaching 0) deviations from Sievert/Nernstian behavior are significant. The steady state permeation current is given by the following expression:

$$J^* = \frac{C_1 - C_2}{L + \frac{1}{D} \left( \frac{1}{\kappa_1} + \frac{1}{\kappa_2} \right)}$$  \hspace{1cm} (2.14)

where $J^*$ is the steady state permeation current and the other parameters are as previously defined. The effect of varying the diffusivity and the two $\kappa$ values was demonstrated under constant charging conditions on low carbon
steel used for electrogalvanizing \((L = 1 \text{ mm}, D = 10^{-5}-10^{-6} \text{ cm}^2/\text{s})\). It was shown that \(\kappa_i\) had the greatest impact on hydrogen permeation as is shown in Figure 3. As such, the decrease in permeation current seen in nonsteady state behavior can be described by a situation in which \(\kappa_i\) decreases as a function of time.

### 2.3 Zinc-Steel Interface

To understand how an interface behaves it is useful to review the thermodynamics of interfaces. When two materials are joined at an interface, the interface will have an energy \(\gamma_{12}\). The work required to separate the two halves of the interface \(W_A\) is given by

\[
W_A = \gamma_1 + \gamma_2 - \gamma_{12}
\]

where \(\gamma_1\) and \(\gamma_2\) are the surface free energies of the two materials.

The value of \(\gamma_{12}\) can be estimated from the geometric mean of the two surface free energies:\(^{28}\)

\[
\gamma_{12} = 2(\gamma_1^{1/2} \gamma_2^{1/2})
\]

(2.16)

So the work of adhesion can then be estimated from the surface free energies of the two constituents by substituting.
\[ W_A = \gamma_1 + \gamma_2 - 2(\gamma_1^{1/2} \gamma_2^{1/2}) \]  

(2.17)

The values of the surface free energies of iron and zinc are 2.55 and 1.02 J/m² respectively. These values give a theoretical work of adhesion for a iron-zinc bond of 0.344 J/m². This estimate is questionable as it treats the zinc and steel as brittle glass like materials. Both zinc and steel will exhibit some plastic deformation at a crack tip. A good example is the value measured for the adhesion of adhesive tape to steel\textsuperscript{29} which give a considerably higher adhesion energy. It is well known that the zinc layer adheres well to the steel during severe forming operations.

The adhesion energy \((W_A)\) between zinc and steel is a difficult quantity to measure. It is assumed that the zinc layer will be the weak link in the system. Therefore the fracture toughness for zinc will be used as an upper bound for the adhesion energy of the zinc steel interface.

The fracture toughness for polycrystalline zinc sheet was determined by Lemant and Pineau.\textsuperscript{30} They reported values ranging from 10-300 J/m². The values for polycrystalline materials are about an order of magnitude higher than values calculated from single crystal experiments.\textsuperscript{31,32} A value
of 150 J/m² will be assumed as the upper bound for the adhesion strength of the zinc-steel interface.

2.4 Zinc Coating

Since the blister defect is a deformation of the zinc layer, properties of the layer are an important factor in determining how blisters form. Properties of interest include: electrodeposit structure, mechanical behavior of zinc, and the deformation of the coating. These aspects of the zinc layer will be reviewed.

2.4.1 Electrodeposit Structure

The structure of the electrodeposit is an important factor in the behavior of the coating. The thickness of the coating can vary between 3 to 10 μm depending on end user specifications. The thickness can have important implications in the deformation of the layer as will be discussed later.

The electrodeposition of the zinc layer occurs in a hetero-epitaxial manner as described by Kamei. Substrate condition was important and zinc was shown to grow in different manners with substrate condition. Substrate grain orientation was also shown to influence deposit orientation. It was
demonstrated that the zinc crystals initially formed with \((0001)_{\text{Zn}}||(110)_{\text{Fe}}\) and \([\overline{2}110]_{\text{Zn}}\|[\overline{1}11]_{\text{Fe}}\) on the \(\alpha\) iron grains.

Marder\textsuperscript{34} reported similar growth of zinc on steel substrates. The effect of plating conditions was also mentioned as important in terms of the final morphology of the coating.

The orientation of the zinc layer can be altered with the addition of various chemicals or brighteners to the electroplating bath.\textsuperscript{35} It was also demonstrated that the orientation of the coating could change as the material was formed due to grain rotation.

2.4.2 Mechanical Properties of Zinc

The mechanical properties of zinc play an important role in the formation of blisters as the zinc coating is deformed. Zinc is a unique material as it can exhibit many different properties high plasticity with grain boundary sliding or brittle fracture. General properties of zinc include a modulus of 43-96 GPa, a flow stress between 160 and 420 MPa.\textsuperscript{36}
The flow of zinc sheets of different textures was examined by Sztwiertnia. The flow stresses varied between 225 MPa to 275 MPa depending on orientation. The changes in flow stress were attributed to changes between basal and pyramidal slip.

The pyramidal flow of zinc was investigated by Margolin. Single crystal specimens were shown to have a flow stress of approximately 3 MPa at room temperature. The flow stress increased sharply with lower temperatures to about 12 MPa at 50K. An increase in flow stress was also seen at temperatures of 300K. This temperature behavior was attributed to thermal activation at low temperatures and athermal at higher temperatures.

Grain boundary sliding of zinc bicrystals was studied by Beevers and coworkers. The sliding of the two crystals against each other was measured with different shear stresses and using the following sliding rate law an activation energy was determined.

\[
\dot{\varepsilon} = A\sigma^n t^{(n-1)} \exp\left(-\frac{Q_a}{RT}\right)
\]  

(2.18)

Where \(\dot{\varepsilon}\) is the strain rate, \(n\) is the strain sensitivity parameter, \(Q_a\) is the activation energy, \(\sigma\) is the shear stress, \(t\) is time, \(R\) is the gas constant, and \(T\)
is temperature in Kelvin. An activation energy of 31±5 kcal/mole was calculated with n=4.5±1.8 at a temperature of 320° C.

Using a constant strain rate deformation on bicrystals an a wider temperature range an activation energy between 175°-225° C of 4.2 kcal/mole and between 250-375° C 10.4 kcal/mole. The increase in activation energy at higher temperature was attributed to slide hardening. Figure 2.7 shows the amount of sliding expected against shear stress for various temperatures. The 200°C trace is of interest since this is near the paint bake temperatures. At a shear stress above 90 gm/mm² (0.88 MPa) sliding can occur.

The fracture of zinc has been studied at lower temperatures. Greenwood demonstrated that at -196° C the fracture stress of zinc increased with decreasing grain size. Gilman examined the fracture stress of mono and bicrystals of zinc and showed that symmetric and antisymmetric grain boundaries had no effect on fracture but asymmetric grains embrittled zinc. Impeded dislocation motion was thought to be the cause of these results. Kamdar calculated the surface energy (γ) of the (0001) planes of zinc from various reported results as 100 mJ/m². Similar energies for γ were reported by others.
Lemant and Pineau\textsuperscript{30} examined mixed mode fracture at -196° C of zinc sheets. The c axis of the zinc grains were normal to the rolling direction of the zinc sheet. Various orientations of the sheet were tested and the strain energy release rate ($G_c$) against angle to the cleavage plane is shown in Figure 2.8. The plot shows a variation between 300 to 50 J/m$^2$ in $G_c$. The $G_c$ term is similar to $\gamma$ but is applicable to materials which can exhibit plastic deformation at the crack tip.

2.4.3 Modeling Zinc Deformation

The bowing or expansion of a layer has been modelled using continuum mechanics. Three basic models exist which describe the elastic deformation of a layer by a uniform pressure: crack, plate, and membrane. The crack model describes the circumstance when the area of deflection is much smaller than the layer. The plate model treats a plate with clamped edges and applies when the size of the plate is on the same order of magnitude as the thickness of the plate. The membrane model applies when the size of the deflected area is much larger than the thickness of the layer. The geometry of the system is based on a circular area of deflection and is illustrate in Figure 2.9.
For the crack model the expression for the displacement is given by the following expression derived by Sneddon\footnote{\cite{Sneddon}}

\[
 w(r) = \frac{4p(1-v^2)}{\pi E} \sqrt{a^2 - r^2} \quad (2.19)
\]

where \( w(r) \) is the deflection, \( r \) is the distance from the center, \( a \) is the radius of the circle, \( p \) is the pressure, \( E \) is the modulus, and \( v \) is Poisson's ratio.

The plate model was derived by Timoshenko\footnote{\cite{Timoshenko}}. The following equation describes the shear stress at a position \( r \) from the center of a circular plate or radius \( a \).

\[
 \tau = \frac{prt}{2} \quad (2.20)
\]

The deflection in this case is in the form

\[
 w(r) = \frac{p}{64D} \left[ (a^2 - r^2)^2 + \frac{4r^2}{1-v}(a^2 - r^2) \right] \quad (2.21)
\]

where \( D \) is the flexural rigidity of the plate

\[
 D = \frac{E t^3}{12(1-v^2)} \quad (2.22)
\]

The second term in brackets in Equation 2.21 can be dropped when the crack radius is much larger than the thickness of the delaminated layer.
The membrane model does not have an expression for the displacement, but expressions exist for the volume and pressure expressions. With the volume and pressure expressions one can model a system where the deforming layer is adhered to a base and determine what pressures are necessary for delamination to occur. This approach will be taken in Chapter 4.
Figure 2.1. Schematic of the flap formation process. A small portion of the steel is welded to the roll and is pulled up. During a subsequent pass this "flap" is flattened into the steel surface.
Figure 2.2. Schematic of the precleaning and plating sections of a electrogalvanizing line.
Entry Processes

\[ k_1 \quad H^+ + e^- + Fe \leftrightarrow FeH_{ads} \]  
Hydrogen Discharge Reaction

\[ k_2 \quad 2FeH_{ads} \leftrightarrow H_2 + 2Fe \]  
Hydrogen Recombination Reaction

\[ k_3 \quad FeH_{ads} \leftrightarrow FeH_{abs} \]  
Hydrogen Absorption Reaction

Transport

Hydrogen Diffusion
Hydrogen Trapping
Hydride Formation

Exit Processes

\[ k_3 \quad FeH_{abs} \leftrightarrow FeH_{ads} \]  
Hydrogen Desorption Reaction

\[ k_2 \quad 2FeH_{ads} \leftrightarrow H_2 + 2Fe \]  
Hydrogen Recombination Reaction

\[ k_1 \quad H^+ + e^- + Fe \leftrightarrow FeH_{ads} \]  
Hydrogen Discharge Reaction

Figure 2.3. Schematic of the hydrogen reactions which can occur when a metal is placed in a solution.
Figure 2.4. Schematic showing the tetrahedral and octahedral sites in a body centered cubic lattice such as α iron.
Figure 2.5. Illustration of the energy description of a hydrogen trap. (From Orian\textsuperscript{21}) $E_a$ is the normal energy barrier for H diffusion, $E'$ is the increased energy to enter a H trap, $\Delta E$ is the increased energy well depth.
### Parameter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>How Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>Measure pH, $E_c$: Nernst &amp; Sievert's Law</td>
</tr>
<tr>
<td>$J_\infty$</td>
<td>From permeation data</td>
</tr>
<tr>
<td>$\kappa_1$</td>
<td>From model and permeation data</td>
</tr>
<tr>
<td>$C(0,\infty)$</td>
<td>From model and permeation data</td>
</tr>
<tr>
<td>$D$</td>
<td>Curve fit permeation data with model</td>
</tr>
<tr>
<td>$C(L,\infty)$</td>
<td>From model and permeation data</td>
</tr>
<tr>
<td>$\kappa_2$</td>
<td>Assume large $\rightarrow E_a$ and Pd coating</td>
</tr>
<tr>
<td>$C_2$</td>
<td>Measure pH, $E_a$: Nernst &amp; Sievert's Law</td>
</tr>
</tbody>
</table>

**Figure 2.6.** Schematic of the hydrogen model developed by Amey. The model utilizes the geometry of a permeation test. $C_1$ and $C_2$ are the hydrogen concentrations are the Nernstian predicted concentrations. $\kappa_1$ and $\kappa_2$ are the mass transfer coefficients for the entrance and exit of hydrogen. $D$ is the diffusion coefficient controlling the transport of H through the membrane.
Figure 2.7. Plot of the displacement vs shear stress for various temperatures (From Beevers\(^4\)). A typical paint bake is about 200° C. (1 gm/mm\(^2\) = 9.8 \times 10^3 MPa).
Figure 2.8. Plot of strain energy release rate vs angle to cleavage plane ($\beta$).
(From Lemant and Pineau[20])
Figure 2.9. Schematic of the geometry involved in bending a circular plate.
This chapter reviews the materials and methods used in the investigation. A variety of methods will be referred to in this chapter and also in chapters 5-8 describing the results of the specific experiments. The techniques to be described are: blister gas analysis, blister growth monitoring, pulsed hydrogen permeation, and hydrogen gas determination.

3.1 Materials

The substrate material used in this study was a low carbon sheet steel with the composition in weight percent shown in Table 3.1. The surface finish of the substrate material varied with experiment and will be specified in the relevant section. The steel substrate either had a production zinc coating, or a laboratory produced zinc coating. Production zinc coatings were both single and double sided coatings. The laboratory produced coatings were plated at the LTV Technology center by George Eierman. Both production and laboratory produced coatings were plated in sulfate plating baths.

3.2 Blister Gas Analysis

A mass spectrometer was used to determine the composition of the gas within blisters. The mass spectrometer was used in a ultra high vacuum...
A mass spectrometer was used to determine the composition of the gas within blisters. The mass spectrometer was used in a ultra high vacuum (UHV) system to allow a signal from gas released from within a blister to be detected. The prechamber to a Perkin Elmer vacuum system was used with a Dycor mass spectrometer. To release the gas within the blisters under vacuum, a linear motion feed though was used. A design factor which also had to be considered was zinc contamination in the vacuum system. To minimize contamination to the main chamber of the vacuum system, the apparatus was mounted to the prechamber of the system.

A sample holder was designed to hold samples 20 X 25 mm. The sample holder was constructed out of 300 series stainless steel and mounted to a stainless steel rotatable flange. A blade to scratch the surface of the sample was constructed from stainless steel and mounted to the linear feed.

Table 3.1: Compositions for the low carbon steel used in this investigation in weight percent.

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Al</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.040</td>
<td>0.22</td>
<td>0.012</td>
<td>0.012</td>
<td>0.012</td>
<td>0.057</td>
<td>0.18</td>
</tr>
<tr>
<td>Ti</td>
<td>Mo</td>
<td>Ni</td>
<td>Cu</td>
<td>N₂</td>
<td>O₂</td>
<td>Pb</td>
</tr>
<tr>
<td>0.003</td>
<td>0.003</td>
<td>0.024</td>
<td>0.026</td>
<td>0.003</td>
<td>0.005</td>
<td>0.0005</td>
</tr>
<tr>
<td>Sn</td>
<td>Nb</td>
<td>V</td>
<td>Sb</td>
<td>Ca</td>
<td>B</td>
<td>Fe</td>
</tr>
<tr>
<td>0.003</td>
<td>0.002</td>
<td>0.002</td>
<td>0.002</td>
<td>0.0005</td>
<td>0.0005</td>
<td>Bal</td>
</tr>
</tbody>
</table>
of the vacuum system and the mass spectrometer in the main chamber was used. In subsequent studies a mass spectrometer was mounted closer to the scratching apparatus as is shown in Figure 3.1.

For the exploratory experiment a heavily blistered production double sided zinc sample was evaluated. In subsequent studies, gas from a double sided production sample, and a back charged single sided sample were analyzed. An unblistered sample was used as a control.

All samples and fixtures were degreased in a four step process. Washing in acetone, methanol, isopropanol and an isopropanol vapor degrease. During degreasing, and subsequent handling of the samples and fixtures gloves and clean tools were used.

The scratching mechanism was mounted to a flange on the prechamber. A new copper gasket was used and the bolts were cross tightened. The torque of all bolts loosened on the prechamber and on the scratching mechanism was verified prior to pumping the prechamber down. The prechamber was pumped down by first turning on the secondary vacuum pump, then activating the turbo pump. The prechamber was pumped down
overnight. The pressure in the prechamber was in the range of $10^7$ to $10^8$ torr when the gate valve to the main chamber was opened.

The base line composition of the vacuum chamber was measured using the mass spectrometer. The mass spectrometer was set to read from 1 to 50 amu, using a 4 decade log scale for the pressure scale. The spectrometer was set so that scans were continuously made. The base line reading was stored in the mass spectrometer controller as channel A. The controller was then set so to channel B was scanned. The display was set so that the spectrum recorded had a baseline subtraction performed during the display.

With the spectrometer recording, the sample was scratched by pushing and pulling on the linear feed through. When a signal was seen, the spectrum was printed out on a dot matrix printer. The baseline spectrum from channel A, and the spectrum from channel B were also printed.

Subsequent studies were performed in a similar manner with production double sided blisters, back charged single sided, and uncharged (no blisters) single sided specimens. The mass spectrometer was set to record the partial pressures of five specific atomic masses over time while the sample was scratched.
3.3 Blister Growth Monitoring

Blister growth was monitored in both *ex-situ* and *in-situ* manners. The *ex-situ* monitoring was performed on laboratory produced coatings without any specific blister initiation sites. The effect of substrate surface finish on blister growth was also examined. *In-situ* monitoring was performed with intentionally contaminated substrates.

3.3.1 *Ex-situ* Growth Monitoring

For the blister growth characterization experiments, laboratory produced double sided coatings were provide by George Eierman at LTV Steel. The steel substrate was from coil 1363702 60 G 60. Different pickling conditions were performed on 4 x 10 inch panels prior to plating. Four sets of panels were provided with the following pretreatments.

- 10 seconds cathodic and 10 seconds anodic
- 30 seconds cathodic and 30 seconds anodic

After plating the panels were cut in two along the long axis. After labeling, one half of the panel was baked at 200°C for 1 hour. The two halves were then provided.
From the unbaked portion of the panels samples approximately 3/4 x 3/4 inches were cut. A grid of lines spaced 0.005 inches was scratched into the sample using a height gauge on a flat surface. The samples were labeled using a carbide tip pencil with the charging time.

An aluminum sample holder for a SEM was modified so that the sample could be removed easily without the use of double sided tape. Two holes were drilled and tapped for 6-32 screws. Two aluminum screws were used to secure the sample to the holder. Although the samples were conductive, the presence of iron and zinc in different areas caused charging problems in the SEM. A palladium coating was vapor deposited on the sample to alleviate this problem.

Scanning electron microscopy was done on a JOEL 35 CF microscope. Samples were examined prior to baking. The surface morphology at each grid was noted and recorded by hand. Features of interest were photographed. The samples were baked after removing them from the SEM mount. The 10 second sample was examined after baking for a total periods of 5, 15, 30, and 60 min. The 30 second sample was examined after periods of 5 and 15 minutes.
Blisters produced by baking were compared to blisters produced by backcharging by examining a back charged sample in the SEM. A single sided laboratory produced sample was used. A #7 O-ring joint was used as the charging cell (Figure 3.2). A solution of 5 wt% Na₂SO₄ with 5 ppm of lead acetate was used. A lead anode was used. A current density of 25 mA/cm² was applied using a Kepco JQE power supply. The sample was charged for 2 hours to produce blisters. The sample was mounted to a aluminum sample holder using double sided tape, and electrical contact was made using copper tape.

3.3.2 Effect of Surface Finish

Steel sheet from coil 1037519 was cut into approximately 2 x 2.5 cm rectangles. Specimens were ground using SiC paper to 500 grit (30 μm), 800 grit (22 μm), 1200 grit (15 μm), and 2400 grit (8 μm) finishes. Three specimens of each finish were made and coated with a storage oil. The specimens were given to George Eierman at LTV for plating. The specimens were spot welded to a larger steel sheet which was then electrocleaned, electropolished, and plated with a 60 g/m² zinc coating in sulfate bath.

After plating the specimens were stored at room temperature for a two month period. The specimens were examined using a stereoscope. The
samples were illuminated using a fiber optic light source with glancing light to highlight blistered areas. Optical micrographs of the specimens were taken to document the extent of blistering.

Profilometry was performed at the LTV Steel laboratories with the assistance of George Themolis. A Kosaka SE30AK profilometer was used to produce surface profile maps. A region of interest approximately 2 x 4 mm was marked on the zinc surface. A 1 x 3 mm map was made inside this region. The number and size of the blisters was determined.

After profilometry was performed the mapped specimens were mounted to aluminum SEM sample mounts using doubles sided tape. Electrical contact was made to the specimen using copper tape. A JOEL 35CF microscope was used with a 25 KV accelerating voltage. Because the zinc surface was uncoated, the condenser lens was set at the largest possible area (small setting). The areas that was mapped with the profilometer on the surface finish specimens were located and the images were recorded on film. Montages of the area were then assembled from the photographs.

An Olympus UH3 scanning acoustic microscope (SAM) was used to image the 500 grit specimen. A 600 MHz lens with a 120° angle was used to
image the specimen. The area of mapping was located using the attached optical microscope. A drop of water was placed on the area of interest and the acoustic lens. The lens was moved into position, and focused so that the maximum signal was achieved. This focusing point was assumed to be the surface of the zinc layer, and the z axis of the microscope was zeroed at this level. The focus level was then raised so that plane of focus was 5 μm above the surface. A scan was made and recorded as channel 1. The z axis was then adjusted back to zero and a scan was made and recorded as channel 2. Channel 3 was a scan made focusing the acoustic beam 7 μm below the surface. The secondary screen of the microscope was set to color so channels 1, 2, and 3 were red, green, and blue respectively. This image was stored in the video recorder and imaged. This process was repeated at different magnifications.

3.3.3 In-situ Growth Monitoring

Blister growth monitoring was conducted in an in-situ manner using SAM. Blisters were forced to grow using the backcharging method, in which hydrogen is driven through the steel and recombines at the steel-zinc interface to form blisters.
To provide initiation sites for blister growth, steel 10.2 cm x 30.5 cm substrates from coil 1037519 were contaminated with 6-9 µm iron powder to simulate iron fines. The contamination was done at LTV laboratories with the assistance of Gene Staib. A template of small holes was made with a 1 cm grid pattern. The template was placed over the steel substrate and iron powder was brushed over the template with a flux brush. The powder was seated into the steel with a 5% reduction by cold rolling. The substrate was given to George Eierman who then electrocleaned, electropickled, and plated on both sides with 60 gm/m² of zinc.

Samples 4.4 cm x 5 cm were cut from the contaminated area of the panel. The zinc coating from the contaminated side of the sample was coated with Micropeel stopoff. The non contaminated side was removed in a 50% HCl solution with Harry Miller Activol 1803 inhibitor. The stopoff was removed and the coated side was polished using 6 and 1 µm diamond paste.

To allow backcharging with the sample in a horizontal position a flowing backcharging cell was constructed (Figure 3.3). The electrolyte was a 5% sodium sulfate solution with 5 ppm lead acetate. A lead anode was used with a current density of 100 mA/cm². The electrolyte was heated to 60° C to optimize the acoustic microscopy.
An Olympus UH3 SAM was used with a 600 MHz burst lens. The coupling fluid was distilled water which was subsequently boiled to remove oxygen. A drop of a commercial ethylene glycol antifreeze (Prestone®) was added to every 5 ml of the coupling fluid. The antifreeze reduced the amount of evaporation and prevented film formation on the zinc surface. Images of the surface and the interface were recorded prior the start of charging. Charging was initiated and images of the surface and interface were recorded. After charging the zinc surface was examined in a JOEL 35CF SEM. The zinc coating was removed in inhibited 50% HCl, and the steel substrate was examined in the SEM.

3.4 Pulsed Hydrogen Permeation

Hydrogen permeation experiments were performed on steel membranes with a 1 μm surface finish on both sides. The 150 ml permeation cells were used with silicone rubber gaskets. A platinum counter electrode was used in the anodic "exit" cell and a dimensionally stable anode was used in the "entrance" cell. Saturated calomel reference electrodes were used in both cells. A schematic of the cell is illustrated in Figure 3.4.

The potentiostat use for the "exit" cell was an Aardvark V-2LR set at +0.450 V-SCE. For the "entrance" cell a Stonehart BC1200 potentiostat was
used in the galvanostat mode. The current was controlled using a Princeton Applied Research (PAR) 175 Universal Programmer. The current in the "entrance" cell was measured using a Keithley 195A multimeter. The voltage in the "entrance" cell was measured using the current interrupt technique. To allow current interrupt to be used during the pulse test a PAR 175 was modified by installing a double pull double throw relay in place of a polarity switch. This relay was then driven with a second PAR 175. The data was collected using a PC based data acquisition system.

The solutions for the tests were made with reagent grade chemicals. The solution for the anodic cell was 0.1 M NaOH. The cathodic or "entrance" cell used 0.1 M H₂SO₄. The acid solution was pre-electrolyzed to remove impurities in the electrolyte. This process utilized a steel cathode and a DSA anode charge at 4 mA/cm² for 24 hours.

The "exit" surface of the steel membrane was plated with palladium to promote hydrogen oxidation in the anodic cell. The palladium plating procedure is described by Amey. A modification of the procedure was to extend the plating time to 40 minutes instead of 30 minutes because of the different surface finish on the steel membranes.
The current in the "entrance" cell was set to 100 mA/cm². The current was first set to the lowest current possible. When the cathodic current was started the current was slowly ramped up to the 100 mA/cm². Initial test kept the current in the cathodic state. Subsequent tests pulsed the current between cathodic and anodic currents after the 100 mA/cm² level had been reached. Current pulses varied from 1 to 2 to 5 seconds in duration. Test duration was generally on the order of 2-3 hours after which the current to the "entrance" cell was turned off. The cell was subsequently drained and rinsed with distilled water, and acetone. The anodic current in the "exit" cell was monitored for a additional hour after rinsing of the "entrance" cell.

After the permeation test one "entrance" surface was examined using x-ray photoelectron spectroscopy (XPS). Survey scans were taken on the initial surface and after 30 seconds of sputtering. Atomic concentrations from theses scans were calculated. Multiplexes on the sputtered surface were taken to determine the chemical state of the elements on the surface.

3.5 Hydrogen Determination

Hydrogen determination is a technique where the hydrogen content of a material can be measured. The measurement involves measuring the thermal conductivity of a ultra high purity nitrogen carrier gas. As the gas is
passed over a heated sample the hydrogen diffuses out of the sample and is carried by the gas stream. The change in thermal conductivity of the gas is related to the hydrogen content of the material.

The hydrogen content of steel coupons was measured after simulated electroprocesses. The processes of electrocleaning and electropickling were simulated in the laboratory. The hydrogen content in the coupon was evaluated as to the current pulsing sequence at 150 mA/cm². The sequences compared cathodic-anodic and anodic-cathodic as is described in Table 3.2. There were at least four coupons run for each condition. A set of coupons which had no simulated processes was also run as a control.

Table 3.2. Experimental matrix for the hydrogen gas analysis using the LECO hydrogen determinator.

<table>
<thead>
<tr>
<th>EC AC</th>
<th>EC CA</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP AC</td>
<td>EP CA</td>
</tr>
</tbody>
</table>

EC = electrocleaning, EP = electropickling, AC = anodic cycle first, CA = cathodic cycle first.

The each coupon (8 mm x 38 mm) was polished to a 1 µm finish on one side. A sheet metal lead was spot welded to each coupon and a identifying mark was scribed onto the unpolished surface. The coupons were wiped with
a Kimwipe soaked in acetone and ultrasonically cleaned in acetone for at least 5 minutes.

Two lead electrodes separated by 2-2.5 cm were used at a current density of 150 mA/cm². A PAR 173 potentiostat/galvanostat was used in the galvanostatic mode. A PAR 175 Programmer was used to control the current to produce 2 second pulses. The programmer was set so that the end of cycle switch was at D. The A setting was at zero and B and C were set to produce a current which would produce a 150 mA/cm² current of the desired polarity. The potential of switch D was also set at zero. Using the one cycle feature and pressing activate the galvanostat would cycle through the pulse sequence once.

Electrocleaning was performed in 15 gram/liter of Parker Amchem EC76 solution. EC76 is an alkaline cleaner with a mixture of sodium, calcium, and potassium hydroxide. A 0.1M H₂SO₄ solution was used for the simulated electropickling. Both of the simulations were run at a temperature of 61±3º C.

After the simulated process was completed the coupon was dipped in distilled water and acetone. The lead was broken off and the coupon stored
in liquid nitrogen. When a set of coupons was complete they were transported to LTV Steel for hydrogen determination.

A LECO RH-402 and HF-402 hydrogen determinator was used for the analysis. A coupon was extracted from the liquid nitrogen dewar with a magnetic teflon stir bar remover. The sample ID was entered into the unit. After the coupon had reached room temperature to prevent condensation, it was rinsed and wiped with petroleum ether.

The coupon was weighed on the built in balance and the value was entered into the analyzer. The loader control was pressed and the coupon inserted into the drop chamber of the analyzer. The loader control was activated and the analysis was begun.

The analysis cycle consisted of two steps: a 20 second step at full power to clear out the quartz crucible and a ramp up to 40% of full power for 250 seconds, or until a preset hydrogen evolution rate was reached. The unit automatically stopped when either the time was up or the value was reached. The data was then analyzed by selecting specific areas of the plot for area analysis. The areas were computed and an output of the hydrogen concentration was printed.
Figure 3.1. Schematic of the scratching mechanism and mass spectrometer location for the identification of blister gases.
Figure 3.2. Schematic of the O-ring joint cell used in backcharging samples for ex-situ blister growth studies. A current density of 100 mA/cm² was used to charge hydrogen into the steel.
Figure 3.3. Schematic of the flowing backcharging cell used in the \textit{in-situ} blister growth studies.
Figure 3.4. Schematic of the experimental apparatus for the pulse permeation studies.
4.1 Introduction

Electrogalvanized sheet steels are used in the automotive and appliance industries for a more corrosion resistant end product. For electrogalvanized steels the overall surface appearance of the final painted surface can be affected by microscopic defects on the zinc surface. These defects are caused by localized adhesion losses and are commonly known as blisters. Because of the size and nature of the blisters, they are often only detectable after the final paint bake. Therefore, it is desirable to minimize the occurrence of blisters.

It has been determined that blister formation is influenced by the cleanliness of the steel substrate and the amount of hydrogen injected into the steel during the electrogalvanizing process\textsuperscript{1,2}. In order to prevent the occurrence of blisters it is necessary to understand how their growth occurs. The approach of this study was to characterize the blister growth process and apply models to the growth process to identify parameters which would affect blister growth. This chapter applies and compares three continuum models to the process of blister growth.
An internally pressurized delamination at an interface is a defect that has been modeled in the fracture mechanics literature. Several different models exist that predict the behavior of the weaker half of the interface depending on the size of the delamination and the thickness of the layer. When the thickness of the layer is large compared to the diameter of the delamination, the defect is modeled as a crack. When the delamination is comparable in size to the thickness of the layer, plate theory can be used to describe the system. Membrane theory can be used to describe the behavior of the deformed layer when the delamination is much larger than the thickness of the coating. Finite element modeling has also been used to describe the growth of internally pressurized delaminations.

These continuum models treat the zinc layer elastically. Due to the low flow stress of zinc plastic behavior may be observed. Nevertheless, these models can identify the parameters which will affect the growth of blisters. Once the factors that control blistering are identified, steps can be taken to minimize blistering.

4.1.1 Adhesion Energy

The adhesion energy \( (W_a) \) between zinc and steel is a difficult quantity to measure. Several theoretical values of the zinc-steel bond strength can be


calculated, but their values can be questioned. For this analysis it is assumed that the zinc layer will be the weak link in the system. Therefore the fracture toughness for zinc will be used as an upper bound for the adhesion energy of the zinc steel interface.

The fracture toughness for polycrystalline zinc sheet was determined by Lemant and Pineau.\textsuperscript{29} They reported values ranging from 10-300 J/m\textsuperscript{2}. The values for polycrystalline materials are about an order of magnitude higher than values measured from single crystal experiments.\textsuperscript{30,31} For this paper a value of 150 J/m\textsuperscript{2} will be assumed as the upper bound for the adhesion strength of the zinc-steel interface.

4.1.2 Energy Balance

The incremental amount of work, dW, to separate an interface is then given by

\[
dW = d\varepsilon + d\Gamma
\]  \hspace{1cm} (4.1)

where d\varepsilon is the incremental strain energy, and d\Gamma is the incremental surface energy. Assuming that the delamination is circular with a radius a, for an incremental growth da the surface energy term is given by
\[ d\Gamma = 2\pi ad\sigma W_a \] (4.2)

The incremental strain energy term can be determined for the blister geometry is illustrated in Figure 4.1 if the pressure \((p)\) and volume \((V)\) of the blister are known. Both these terms can be determined if a function for the deflection \((w(r))\) exists. The function \(w(r)\) varies depending on the model used to describe the disbonded layer. The pressure in the blister will be a function of the size of the disbonded region, \(a\), and the deflection \(w(r=0)\)

\[ p = f(a, w(r=0)) \] (4.3)

The volume of the delaminated region is determined from integrating the deflection around a surface of revolution
The internal strain energy of the disbonded layer, which is the work done by pressure is

\[ \mathcal{G} = \int p \, dV \]  \hspace{1cm} (4.5)

where

\[ dV = \frac{\partial V}{\partial p} \]  \hspace{1cm} (4.6)

When the derivative of the volume with respect to pressure is taken for the various models and is substituted in equation 5 the final form of \( \mathcal{G} \) is typically in the form of

\[ \mathcal{G} = kpV \]  \hspace{1cm} (4.7)

where \( 0 < k < 1 \). If \( k = 1 \) then all the energy involved is used to deflect the coating elastically. Similarly, if \( k = 0 \) all the energy is used in separating the two surfaces.

The expressions for the incremental strain and surface energies can be substituted into the energy balance to yield
\[ pdV = kpdV - 2\pi W_A da \quad (4.8) \]

substituting,

\[ dV = \frac{\partial V}{\partial a} da \quad (4.9) \]

and solving to find \( p \)

\[ p = \frac{2\pi a W_A \frac{\partial a}{\partial V}}{(1-k) \frac{\partial V}{\partial a}} \quad (4.10) \]

Similarly, the expression can be rearranged to find \( W_A \).

\[ W_A = \frac{(1-k)p \frac{\partial V}{\partial a}}{2\pi a \frac{\partial a}{\partial V}} \quad (4.11) \]

The function for the displacement (\( w(r) \)) will depend on how the system is modeled. Y.L. Lee reviewed the treatment of \( w(r) \) for the cases of crack, plate, and membrane models. The conditions under which each model is satisfied in the electrogalvanized steel system will be reviewed.

4.1.3 Crack Model

The crack model treats the delaminated layer as a semi-infinite medium. For this treatment to be accurate the crack radius has to be much smaller than
In electrogalvanized steel systems the zinc layer is not usually thicker than 10 μm, therefore, the crack model is only applicable for blister initiations (a < 1 μm).

The expression for the displacement $w(r)$ was derived by Sneddon\(^3\)

\[
w(r) = \frac{4p(1-v^2)}{\pi E} \sqrt{a^2 - r^2}
\]

where $E$ is the modulus for the zinc coating. The expression for the pressure with $y = w(r=0)$ is

\[
p(y) = \frac{\pi Ey}{4(1-v^2)a}
\]

The volume is given by

\[
V = \frac{8p(1-v^2)a^3}{3E}
\]

The critical pressure for growth of the delamination is

\[
p_{crw} = \left( \frac{\pi EW_a}{2a(1-v^2)} \right)^{\frac{1}{2}}
\]

It is useful to separate the terms in the equation in the following manner to emphasize the factors which influence the critical pressure for growth.
\[ p_{\text{cri}} = \left( \frac{\pi E}{2(1-v^2)} \right)^{\frac{1}{2}} \left( \frac{W_A}{a} \right)^{\frac{1}{2}} \] (4.16)

The first term contains constants, while the second term has the crack size dependance and the work of adhesion terms. As the crack size increases the critical pressure for further growth is reduced in an asymptotic manner. The term \( W_A \) would have a square root dependence if changed, but this term could not be varied to a large extent.

4.1.4 Plate Model

The plate model applies when the radius of the crack is comparable to the thickness of the delaminated layer. The disbonded material is treated as a plate subject to bending. It is assumed that only elastic deformation occurs. The displacement of a clamped circular plate under uniform pressure is given by Timoshenko\(^4^4\) as

\[ w(r) = -\frac{P}{64D} \left[ (a^2 - r^2)^2 + \frac{8r^2(a^2 - r^2)}{1-v} \right] \] (4.17)

where \( D \) is the flexural rigidity of the zinc layer
\[ D = \frac{Et^3}{12(1-v^2)} \]  

(4.18)

The second term in brackets in Equation 4.17 can be dropped when the crack radius is much larger than the thickness of the delaminated layer.

The pressure in the blister is dependant on the displacement at the origin, \( y \), and is given by 4.19

\[ p = \frac{64Dy}{a^2 \left( a^2 + \frac{4s^2}{1-v} \right)} \]  

(4.19)

The volume is given by the expression

\[ V = \frac{\pi p}{192D} \left( a^4 + \frac{6a^2s^2}{1-v} \right) \]  

(4.20)

The critical pressure for growth of the disbonded region is

\[ P_c = \left( \frac{32E W_A}{3(1-v^2)} \right)^{\frac{1}{2}} a \left( \left( \frac{a}{t} \right)^3 + \frac{4}{1-v} \left( \frac{a}{t} \right) \right)^{-\frac{1}{2}} \]  

(4.21)

As with the crack model the properties which can be modified is \( W_A \). Both of these parameters will have a square root dependence on the critical pressure.
4.1.5 Membrane Model

The membrane model applies when $a >> t$. No expression for the displacement $w(r)$ exists, but estimates of the volume and maximum deflection have been developed by Henky. Using series expansions, the expressions for $V$ and $p$ for materials with $\nu = 0.3$ are

$$V = 0.52 \pi a^2 y$$  \hspace{1cm} (4.22)

$$p = 3.8 \frac{y^3 E_t}{a^4}$$  \hspace{1cm} (4.23)

The critical pressure for growth is

$$p_{\text{crit}} = 4.8 \left( \frac{W_2 E_t}{a^4} \right)^{\frac{1}{4}}$$  \hspace{1cm} (4.24)

This relation differs from the previous two models in that $p_{\text{crit}}$ is dependant on $1/a$ and not $(1/a)^{1/2}$. The work of adhesion also plays a greater role as it is raised to the $3/4$ power instead of the $1/2$ power.

4.2 Application and Comparison of Models

The values of critical pressure and volume of blisters in the size range of 1-150µm are of interest. From $p_{\text{crit}}$ and $V$ the number of moles of gas can be calculated. The properties of the zinc layer portion of the electrogalvanized steel system will determine the values of $E$ and $\nu$. The elastic modulus was
estimated to be on the order of 50 GPa. This estimate was based on data for rolled material\(^9\). The tensile strength of these rolled materials was between 120-150 MPa. Coating thickness in production product is in the range of 3-10 \(\mu\text{m}\). The work of adhesion was estimated to be 150 J/m\(^2\).

Applying these values to the crack model simplifies Equation 4.20 to

\[
p_{\text{crit}} = 3.6 \left( \frac{1}{a} \right)^{\frac{1}{2}}
\]

(4.25)

where \(p_{\text{crit}}\) is in MPa, and \(a\) is in meters. The equation for \(V\) in cubic meters becomes

\[
V = 4.9 \times 10^{-11} p a^3
\]

(4.26)

Similarly, \(p_{\text{crit}}\) and \(V\) for the plate model are

\[
p_{\text{crit}} = 9.4 \left( \frac{a}{t} \right)^3 \left\{ 5.71 \left( \frac{a}{t} \right) \right\}^{-\frac{1}{2}}
\]

(4.27)

\[
V = 3.5 \times 10^{-11} \frac{P}{t^3} [a^6 + 8.6t^2a^4]
\]

(4.28)

For membrane theory the two equations of interest reduce to
\[
\rho_{cr} = 0.097 \left( \frac{t}{a^4} \right)^{\frac{1}{4}}
\]  \hspace{1cm} (4.29)

\[
V = 2.8 \times 10^{-4} \left[ \frac{pa_{10}^{10}}{t} \right]^{\frac{1}{3}}
\]  \hspace{1cm} (4.30)

Most production blisters fall into the 5-150 \( \mu \)m radius range. Over this range the assumptions of the plate model are satisfied. The assumptions of the crack model are satisfied only at delaminations smaller than the thickness of the coating. The assumptions used in the membrane model are satisfied only when the delamination is much larger than the thickness of the coating. As the plate model is applicable over the range of production blisters, analysis of factors in the system which change the system will be examined. The crack and membrane models will also be applied for lower and upper limits.

The critical pressures for the three models are compared in Figure 4.2. Coating thicknesses of 3, 5, and 10 \( \mu \)m were applied to the plate model. The thickness for the membrane model was 3 \( \mu \)m. At small blister radii the pressure asymptotically increases for all models. As the tensile strength of zinc is in the 120-150 MPa range, pressures greater than the tensile strength will cause the zinc to fail. The crack model has a lower critical pressure than the plate model at small delamination sizes. At values near the thickness of
the coating the plate model has a lower critical pressure. Because of the assumption that the delaminating layer is semi-infinite, crack theory is not valid for blister radii greater than the thickness of the coating. As the blister radius approaches a value near 20 times the coating thickness, the pressures for the plate and membrane models cross. At these radii, the assumptions of the membrane model begin to be satisfied.

At a constant blister radius, $p_{\text{crit}}$ for the plate and membrane models decreases with decreasing coating thickness. The critical pressure for the crack model is not a function of thickness since it treats the delaminating layer as a semi-infinite body.

The volumes of blisters at $p_{\text{crit}}$ are compared in Figure 4.3. For blisters less than 5 μm in size, all three models have similar volumes at $p_{\text{crit}}$. For blister radii from 10 to 20 μm the plate and crack models behave similarly. With blister radii above 20 μm, the volume for the plate model is greater than volumes predicted by crack theory. Membrane theory predicts a volume that is about two orders of magnitude greater than volumes predicted by crack theory. The volumes of membrane and plate theory are equal at radii about 50 times greater than the thickness of the coating.
Figure 4.2. Plot of Critical pressure for growth of blisters from crack, plate, and membrane models. Coating thicknesses of 3, 5, and 10 μm were used for the plate model. A 3 μm thickness was utilized for the membrane calculations.

Figure 4.3. Volumes of blisters at critical pressure using crack, plate, and membrane models. Coating thicknesses of 3, 5, and 10 μm were used for the plate model. A 3 μm thickness was utilized for the membrane calculations.
Using the plate model, decreases in the coating thickness cause an increase in the volume of the blister. Thinner coatings can deform to a greater extent, and hence generate greater volumes. Decreasing the thickness in membrane theory also creates a greater volume, but the effect is not as large. If there was a transition between plate and membrane behavior, it would most likely occur when the volumes became equivalent. This cross over occurs in a size range of blisters that are not normally seen in production blisters. Therefore, it is thought that membrane like-behavior is not reached.

When the pressure and volume are used to find the number of moles of gas that are in a blister at critical pressure, plate theory requires the least amount of gas (Figure 4.4). For all models the number of moles of gas varies between $10^{14}$ to $10^9$ depending on blister radius.

In order to determine the amount of hydrogen necessary to produce blistering, the number of moles of gas was normalized with respect to the area of the blister base (Figure 4.5). The crack and membrane models require a constant number of moles/cm$^2$ ($5.1 \times 10^6$ and $1.0 \times 10^5$ respectively). The plate model requires less gas in the delamination with respect to the crack and membrane models, but is not a constant. Smaller delaminations require a greater amount of gas to pass through an area. As the radius increases the
Figure 4.4. Number of moles of gas required to reach critical pressure using crack, plate, and membrane models. Coating thicknesses of 3, 5, and 10 μm were used for the plate model. A thickness of 3 μm was utilized for the membrane calculations.

Figure 4.5. Amount of gas per unit area for blisters of different radii using crack, plate and membrane theory. Coating thicknesses of 3, 5, and 10 μm were used for the plate model. A thickness of 3 μm was utilized for the membrane calculations.
pressure levels off at a value near 10 times the thickness of the delaminating layer. The decrease in amount of gas/area for the plate model does not mean that once $p_{cm}$ is reached that the interface will completely delaminate. As the base size increases the amount of gas/area also decreases, so there is a reduction in pressure.

An aspect of blister formation is the density of blisters. This analysis has shown that blister can form with $3 \times 10^4$ moles of gas per cm$^2$. Avey$^1$ predicted that $4 \times 10^6$ moles/cm$^3$ of hydrogen are absorbed by the steel during the preplating and plating processes. The steel sheet is typically 0.8 mm thick, and if one assumes that hydrogen will diffuse from the center of the sheet towards the nearest surface (0.4 mm of steel) there will be $1.6 \times 10^7$ moles/cm$^3$ of hydrogen available for diffusion to blisters on each side of the steel sheet. With the amount of gas available to diffuse into blisters, the blister densities, $d$, that could be produced can be calculated from the following equation

$$d = \frac{h_s}{g_a A_b}$$  \hspace{1cm} (4.31)

Where $h_s$ is the available hydrogen (moles/cm$^2$), $g_a$ is the moles of gas required to pass through the blister base to reach the critical pressure (moles/cm$^3$), and $A_b$ is the area of the blister base (cm$^2$). For blisters with a 10 μm radius enough hydrogen is present to form $1.8 \times 10^4$ blisters/cm$^2$. 
Similarly for blisters with radii of 50 and 100 μm, densities of $6.7 \times 10^2$ and $1.8 \times 10^2$ blisters/cm$^2$, respectively, could be seen. These calculated densities are within the range of blister densities that are seen in heavily blistered areas on production coatings.

A feature of blister growth worth noting is the formation of methane from hydrogen and interfacial carbon as seen in equation 4.32:

$$2H_2 + C \rightarrow CH_4$$  \hspace{1cm} (4.32)

This process will reduce the internal pressure by a factor of two. In addition the carbon can act as a sink for hydrogen in the lattice. Since hydrogen can combine with carbon to form methane, the hydrogen activity near the carbon will be low, this in turn will set up a gradient for diffusion.

The size of the initially delaminated area is dependant on the size of flaws on the substrate surface. Flaws such as iron fines, carbides, flaps, and contamination from oils have been found inside blisters. These flaws can persist after the various cleaning stages prior to plating, and act as initiation sites for blister growth. As it is difficult to ensure that the substrate is defect free, it is useful to understand how the variables that can be controlled effect the plate model. These variables include modulus, adhesion energy and
coating thickness. The increasing the thickness of the coating was shown to increase the pressure needed to cause blistering.

The elastic modulus of the zinc layer, and the work of adhesion are two variables that could be controlled to some extent. The modulus of the zinc layer could be changed by orientation, alloying, or additions of ceramic particles. The work of adhesion can be modified with the use of flashes (thin electroplated layers of different metals). Contamination of the interface by an organic could also be considered as a modification of the work of adhesion.

![Graph showing the effect of coating thickness on blistering pressure](image)

**Figure 4.6.** Effect of changing the adhesion strength on the critical pressure for growth of a 10 μm thick zinc coating using plate theory.
in a negative sense. Although these parameters can be modified, the extent of change is limited. Figure 4.6 demonstrates the effect of decreasing $W_A$ by one and two orders of magnitude for a 10 $\mu$m zinc layer using plate theory. For every two orders of magnitude decrease in $W_A$, $P_{ctt}$ decreases by an order of magnitude. A similar effect would be seen for changes in the modulus. Although the modulus could not be changed to such a large extent.

4.3 Limits of Plate Model

Although all three models show similar behavior, based on the assumptions of the models, the plate model best describes blisters in the zinc-steel system. The low flow stress of zinc though is the limiting factor in the validity of the plate model as it treats the deformed layer elastically. The flow stress of zinc sheets has been reported by Sztwiertnia.\textsuperscript{36} The flow stresses varied between 225 MPa to 275 MPa depending on orientation. The changes in flow stress were attributed to changes between basal and pyramidal slip. Single crystal zinc has a lower flow stress\textsuperscript{37}, but the applicability to the zinc coating is limited.

Grain boundary sliding of zinc bicrystals was studied by Beevers and coworkers.\textsuperscript{38,39,40} The sliding of the two crystals against each other was measured with different shear stresses. At 200°C (paint bake temperatures) grain boundary sliding could occur at shear stresses above 90 gm/mm$^2$ (0.88
MPa). This stress is quite low, but is only applicable at relatively high
temperatures. A higher stress would be needed at lower temperatures.

The shear stress, $\tau$, in the coating for the plate model is given by the
following equation

$$\tau = \frac{pr}{2t} \quad (4.33)$$

As can be seen $\tau$ increases with the radius, $r$. Therefore the maximum shear
stress will occur at the edge of the delamination. Figure 4.7 shows the
maximum shear stress vs blister diameter along with the critical pressure for
blister growth. The maximum shear stress is above the flow stress of zinc for
blisters under about 60 microns in radius. Therefore, blisters with radii under
60 microns will be subject to plastic deformation and likely will not
delaminate the interface. Once plastic deformation occurs the volume of the
blister will increase. This increase in volume will decrease the pressure within
the blister causing deformation to cease until a higher pressure of gas is
achieved.

Figure 4.8 shows the maximum shear stress seen in a 10 $\mu$m coating at
various pressures for blister radii of 1, 5, 10, 20, and 40 micron blisters. The
micron trace ends at 2000 MPa which produces a shear stress near the critical
Figure 4.7. Plot of critical pressure and maximum shear stress vs blister radius.

Figure 4.8. Plot of maximum shear stress vs internal pressure for 1, 5, 10, 20, and 40 μm blisters.
stress for flow of zinc. The 5, 10, 20, and 40 micron traces end at the critical pressure for delamination. These traces also end above the critical shears stress for flow. The smaller blisters will not only reach the flow stress at higher internal pressures, but will remain far from the critical pressure for delamination.

The ability of zinc to creep via grain boundary sliding at low temperatures allows for a different mode of deformation rather than plastic flow. This can occur at higher temperatures at low shear stresses and using values from Figure 4.8 would occur if a small amount of gas entered the delaminated region.

4.4 Summary of Models

The blisters that form on electrogalvanized sheet steel can be modeled as internally pressurized delaminations. Models treating the delaminated layer elastically as a crack, plate, or membrane have been compared. The crack model applies when the initial delamination is much smaller than the thickness of the coating, and is only satisfied at small blister sizes. Plate theory applies when the delamination size is comparable to the thickness. Membrane theory applies when the delamination is much larger than the thickness. Plate theory is most applicable to the system as most production
blisters are larger than the thickness of the coating, but are still within an order of magnitude of the thickness. A limitation of the models is that they treat the zinc layer elastically. Zinc has a low flow stress and can creep at low temperatures. This analysis is useful in identifying the parameters that can effect blister growth.

Using plate theory, the pressure required to propagate a delamination is dependant on the size of the initial delamination, the adhesion of the two materials, thickness of the coating, and modulus of the coating. Larger delaminations require less pressure to induce further delamination. Thicker coatings require greater pressures to cause blisters to grow. The critical pressure for growth is dependant on the square root of the modulus of the material and the work of adhesion between the coating and substrate. A factor that must be considered is that as long as there are delaminations at the interface that hydrogen gas can recombine and cause deflections in the zinc layer without propagating the delamination.

Application of the models allows the determination of the volume of the blisters and amount of gas within blisters. For blisters to grow $10^4$ moles/cm$^2$ is required. There is enough hydrogen injected into the steel substrate during processing to cause blisters to form.
5.1 Introduction

A great deal of information on the process of blister formation can be gained from analysis of the gas within the blisters. Podgurski\textsuperscript{25} found that hydrogen can combine with carbon in iron to form methane after cold working and hydrogen charging. Shewmon\textsuperscript{26} has also proposed a mechanism for intergranular stress corrosion cracking of Inconel 600 in which hydrogen combines with carbon in solution to form methane bubbles. Methane forms in the voids as a reaction product of carbon in solution with hydrogen in the voids through the following reaction.

\[ C + 2H_2 \rightarrow CH_4 \]  

(5.1)

From this reaction, one can see that one methane molecule is produced for every two hydrogen molecules. At higher pressures the reaction to the right is favored according to Le Chatlier’s principle. Le Chatlier’s principal states that a system will react in such a way as to counter any departure from equilibrium.

Identifying the gas within a blister formed in a steel-zinc interface would identify the process that is involved during the formation of blisters.
If hydrogen from the plating process is responsible for the formation of blisters, hydrogen or methane should be found within the blister. If larger molecular weights are detected, another mechanism would be responsible for blistering. Comparison of the gas from production and laboratory produced blisters would also indicate whether simulated blister growth produces blisters similar to natural blisters.

5.2 Experimental

A mass spectrometer was used to determine the composition of the gas within blisters. Details of the procedure are described in Chapter 3. The mass spectrometer was mounted to the prechamber of a ultra high vacuum (UHV) system and the blisters were broken by scraping a sharp blade attached to a linear feedthrough over the coated steel surface. The experimental setup is schematically shown in Figure 5.1.

For the initial scouting experiment a production double sided zinc sample which was evaluated as having a high blister density was evaluated. In subsequent studies, gas from a double sided production sample, and a back charged single sided sample were analyzed. An unblistered single sided sample was used as a control.
The scouting experiment utilized baseline subtraction on a pressure vs mass trace. Subsequent tests utilized monitoring the pressure vs time traces of five selected gases (1, \( \text{H}_2 \); 2, \( \text{H}_2\text{O} \); 3, \( \text{CH}_3 \) (15 amu); 4, \( \text{CH}_4 \) (16 amu); 5, \( \text{N}_2 \)). The data was recorded on a dot matrix printer.

5.3 Results

The baseline subtracted spectrum from the initial gas analysis experiment is presented in Figure 5.2. The largest peaks are at 1 and 2 amu corresponding to atomic and diatomic hydrogen gases. Peaks at 16 and 15 amu correspond to \( \text{CH}_4 \) and \( \text{CH}_3 \) respectively. From the spectrum of the emitted gas, the masses of hydrogen gas (2 amu), methane (16 amu), and methane’s radical methyl (15 amu) were selected as masses to be traced in the subsequent studies. The masses of water (18 amu) and nitrogen gas (28 amu) were also monitored.

A pressure-time curve for a production double sided specimen is shown in Figure 5.3. It is evident that the nitrogen gas and water are the main components of the atmosphere in the chamber. The traces of the three blister gases show several peaks. The methyl trace (15 amu) has the largest peaks. The methane (16 amu) and hydrogen gas traces show only small increases at these times. The difference in the peak heights is due to the log scale used in
the trace. There is an order of magnitude less methyl than methane and hydrogen, and any change in pressure will be more obvious for the methyl trace.

The pressure time trace for a blister created by backcharging a single sided sample is seen in Figure 5.4. Again the main components of the system were water and nitrogen gas. A lower baseline pressure is a result of a longer pumpdown time. In the 50 second time period peaks are evident in the three blister gas traces.

For the unblistered control sample (Figure 5.5), a high base line pressure for water is seen. The traces for the three blister gases shown no large peaks. This result indicates that the peaks seen in the blistered samples could not have been caused from gas absorbed on the zinc surface.

5.4 Discussion

The results from the blister gas analysis indicate that hydrogen gas and methane and its radicals are present within the blisters. The presence of hydrogen supports the theory that the exit of hydrogen which is in the steel from processing is the cause of blisters in electrogalvanized steels. The
formation of methane would reduce the pressure within blisters compared to the pressure resulting from hydrogen gas alone.

In order for methane to be formed in a blister, carbon must be available. Carbon can come from different sources. Carbides on the surface of the steel can act as a source for carbon. Carbon contamination from the various oils and other surface species during processing can also be a source for carbon. Because of the low carbon content of the steel, it is unlikely that carbon in the steel could react with hydrogen to form methane as is the case in high carbon steels.

The thermodynamics of hydrogen gas formation and methane formation from both carbon and iron carbide were calculated using data from the JANAF tables. Two temperatures of interest were room temperature (298 K) and the paint bake temperature (about 500 K). The formation of hydrogen gas by the reaction

\[ H + H \rightarrow H_2 \]  \hspace{1cm} (5.2)

has a free energy of formation at 298 K is -49 kcal/mole and -46 kcal/mole at 500 K. For the formation of methane by the reaction in equation 5.1
the free energy of formation is -12 kcal/mole at 298 K and -7.8 kcal/mole at 500 K. The reaction of atomic hydrogen with carbon the reaction will be:

\[ \text{C} + 4\text{H} = \text{CH}_4 \]  \hspace{1cm} (5.3)

This reaction will have a free energy of formation of -110 kcal/mole at 298K and 99 kcal mole at 500K. The favorability of the reaction in equation 5.3 over the reaction in equation 5.1 is thermodynamically possible, but will be dependant on the kinetics of hydrogen gas formation.

The reaction of the carbon with atomic hydrogen has been examined by Shustorovich and Bell.\textsuperscript{52} They used the Morse potential approach to examine the reaction of H\textsubscript{2} and CO to form CH\textsubscript{4} and other organic molecules in the Fischer-Tropsch process. The Fischer-Tropsch process is run at temperatures of 200\textdegree C and above. In their analysis they assumed that the CO dissociated to deposit carbon on a surface. Metal surfaces of Cu, Pt, Ni, and Fe/W were treated. The Fe/W surface showed similar behavior as a Fe (110) surface. The following reaction steps for the interaction of surface carbon with atomic hydrogen were proposed:

\[ \text{C}_x + \text{H}_y = \text{CH}_z \]  \hspace{1cm} (5.4)

The activation barrier in the forward direction was 46 kcal/mol and 3 kcal/mol in the reverse direction for this reaction.
\[ \text{CH}_4 + \text{H}_2 \rightarrow \text{CH}_4 \]  \hspace{1cm} (5.5)

For the reaction of the second hydrogen as described in equation 5.5 an activation barrier of 24 kcal/mol in the forward direction was calculated and a barrier of 22 kcal/mol in the reverse direction.

\[ \text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 \]  \hspace{1cm} (5.6)

For the reaction in equation 5.6 the forward and reverse reactions was 19 and 21 kcal/mol, respectively.

\[ \text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 \]  \hspace{1cm} (5.7)

\[ \text{CH}_4 + \text{H}_2 \rightarrow \text{CH}_4 \]  \hspace{1cm} (5.8)

The two reactions to form CH4 (equations 5.7 and 5.8) had similar activation barriers in the forward direction of 24 kcal/mol. The reverse reaction for the absorbed methane had a higher activation barrier of 8 kcal/mol compared to the reaction of the gaseous molecule which had a barrier of 1 kcal/mol.

The rate of the production of methane will be dependant on the ratio of carbon to hydrogen. This was demonstrated by Krebs who again examined the Fischer-Tropsch reaction. The production of methane was examined between 460-750 K. It was found that the turnover number (measure of reaction rate) for the formation of methane showed Arrhehius
behavior over the lower temperatures studied. The activation energy was between 20 and 22 kcal/mol which agrees well with the value calculated by Shustorovich and Bell\textsuperscript{52}. The implications of these results to blister formation are that at higher temperatures the formation of methane will occur at a faster rate. Additionally the rate of this reaction will be dependant on the ratio of available hydrogen to carbon.

In addition to the reaction step, the source of carbon will have an effect on the free energy of formation. For the decomposition of iron carbide

\[ \text{Fe}_3\text{C} + 2\text{H}_2 \rightarrow \text{CH}_4 + 3\text{Fe} \] \hspace{1cm} (5.9)

has a free energy of formation of -17 kcal/mole at 298 K and -12 kcal/mole at 500 K. These reactions have a negative energy of formation at room and paint bake temperatures and are therefore thermodynamically possible.

The thermodynamic treatment above treats the system in standard state of 1 atmosphere of pressure. However, within the blister higher pressures exist. The change in the free energy of formation with pressure for equation 5.1 is given by:

\[ \Delta G = \Delta G^\circ + RT \ln \left( \frac{p_{\text{CH}_4}}{p_{\text{H}_2}^2 a_c} \right) \] \hspace{1cm} (5.10)
If one assumes the activity of carbon is 1, then as long as the partial pressure of hydrogen gas is greater than the square root of the partial pressure of methane the reaction will be driven to a more negative value. At lower hydrogen partial pressures the free energy of formation may still be negative. Similarly, the effect of pressure for the reaction in equation 5.3 will have a more negative value as long as $p_H > p_{CH4}^{1/4}$.

The backcharged sample showed the presence of hydrogen and methane within the blister. These results were similar to the production sample. This is an indication that the qualitative backcharging test produces blister gases that are similar to production blisters.

5.5 Conclusions

Analysis of the gas within blisters in electrogalvanized sheet steels showed that hydrogen, methane, and methane radicals were present. Hydrogen from the processing of the sheet steel exits the sheet steel and reacts with carbon at the interface to form methane. Carbon can be present as a contaminant or from decomposition of carbides at the interface. Blisters produced by the backcharging method showed similar gases to production blisters.
Figure 5.1. Schematic of the scratching mechanism and mass spectrometer location for the identification of blister gases.
Figure 5.2. Baseline subtracted spectrum from a production blisters on double sided electrogalvanized sheet.

Figure 5.3. Pressure vs time plot for a production double sided sample. 1, H₂; 2, H₂O; 3, CH₄ (15 amu); 4, CH₄ (16 amu); 5, N₂. Peaks near 15 and 25 seconds are from blisters.
Figure 5.4. Pressure vs time plot for a back charged single sided sample. 1, H₂; 2, H₂O; 3, CH₄ (15 amu); 4, CH₄ (16 amu); 5, N₂. Peaks near 50 seconds are caused by blisters.

Figure 5.5. Pressure vs time plot for an uncharged single sided sample. 1, H₂; 2, H₂O; 3, CH₄ (15 amu); 4, CH₄ (16 amu); 5, N₂.
6.1 Introduction

For electrogalvanized sheet steels, blisters form during paint bake cycles. To promote blister growth for in adhesion evaluations for quality control purposes and laboratory studies, a simulated paint bake at 200°C for 1 hour is used. The resulting amount of blistering is used to gauge the adhesion of the zinc to the steel.

During the qualitative rating of zinc coated steels, the process of blister growth is not monitored. The goal of this series of experiments was to characterize the blister growth process, by monitoring the growth of blisters over time.

6.2 Experimental

The growth process was characterized by monitoring changes in the surface topography. The topography of the surface was examined in both ex-situ and in-situ manners. Ex-situ studies examined the surface before and after short periods of simulated paint bake using scanning electron microscopy (SEM). The effect of substrate finish was also examined using surface profilometry, SEM and acoustic microscopy. Acoustic microscopy was also
used in an *in-situ* study of blister growth. The experimental procedures for blister growth monitoring will be reviewed here, detailed accounts of the experimental procedures are in Chapter 3.

6.2.1 *Ex-situ* Growth Monitoring

For the *ex-situ* blister growth characterization experiments, laboratory produced double sided coatings were studied with 10 second and 30 second charging cycles prior to plating. The zinc coating was characterized as having 60 gm Zn/m² which is equivalent to a 10 µm coating. A grid of lines spaced 0.13 mm was scribed into a 2 x 2 cm sample. The sample was mounted to a modified SEM mount (sample held with screws) and coated with palladium.

Scanning electron microscopy was performed on a JOEL 35 CF microscope. Samples were examined prior to baking and after baking. The surface morphology at each grid was noted and recorded by hand. Features of interest were photographed. The samples were baked after removing them from the SEM mount. The 10 second sample was examined after baking for a total periods of 5, 15, 30, and 60 min. The 30 second sample was examined after periods of 5 and 15 minutes.
Blisters produced by baking were compared to blisters produced by backcharging by examining a back charged sample in the SEM. A single sided laboratory produced sample was used. A #7 O-ring joint was used as the charging cell shown in Figure 6.1. A solution of 5 wt% Na₂SO₄ with 5 ppm of lead acetate was used. A lead anode was used. A current density of 25 mA/cm² was applied using a Kepco JQE power supply. The sample was charged for 2 hours to produce blisters. The sample was mounted to a aluminum sample holder using double sided tape, and electrical contact was made using copper tape.

6.2.2 Effect of Surface Finish

Steel sheet from a coil identified as 1037519 was cut into approximately 2 x 2.5 cm rectangles. Specimens were ground using SiC paper to 500 grit (30 µm), 800 grit (22 µm), 1200 grit (15 µm), and 2400 grit (8 µm) finishes. Three specimens of each finish were made. The specimens were taken to LTV laboratories for plating. The specimens were spot welded to a larger steel sheet which was then electrocleaned, electropickled, and plated with a 60 g/m² zinc coating. Plating was performed in a sulfate ion bath.
After plating, the specimens were examined using a stereoscope. The samples were illuminated with glancing light to highlight blistered areas. Optical micrographs of the specimens were made.

Profilometry was performed at the LTV Steel laboratories with the assistance of George Themolis. A Kosaka SE30AK profilometer was used to produce surface profile maps. A region of interest approximately 2 x 4 mm was marked on the zinc surface on each specimen. A 1 x 3 mm map was made inside these regions. The blisters density in each area was determined by counting the blisters.

After profilometry was performed, the mapped specimens were examined using SEM. A JOEL 35CF microscope was used with a 25 KV accelerating voltage. The areas that were mapped with the profilometer on the surface finish specimens were located and the images were recorded on film. Montages of the area were then assembled from the photomicrographs.

An Olympus UH3 SAM was used to image the 800 grit and 1200 grit specimens. A 600 MHz lens with a 120° angle was used to image the specimen. The area of mapping was located using the attached optical microscope. A drop of water was placed on the area of interest and on the
acoustic lens. The lens was moved into position, and focused so that the maximum signal was achieved. This focusing point was assumed to be the surface of the zinc layer, and the z axis of the microscope was set to zero at this level. The focus level was then raised so that plane of focus was 5 μm above the surface. A scan was made and recorded as channel 1. The z axis was then adjusted back to zero and a scan was made and recorded as channel 2. Channel 3 was a scan made focusing the acoustic beam 7 μm below the surface. The secondary screen of the microscope was set to color so channels 1, 2, and 3 were red, green, and blue, respectively. This image was stored in the video recorder and printed.

6.2.3 In-situ Growth Monitoring

Blister growth monitoring was conducted in-situ using scanning acoustic microscopy (SAM). To provide initiation sites for blister growth steel substrates 10.2 cm x 30.5 cm were contaminated with 6-9 μm iron powder in a 1 cm grid pattern. The powder was intended to simulate iron fines on the steel surface. The powder was seated into the steel with a 5% reduction by cold rolling. The substrate was then electrocleaned, electropolished, and plated on both sides with 60 gm/m² of zinc.
Samples 4.4 cm x 5 cm were cut from the contaminated area of the panel. The zinc coating from the contaminated side of the sample was coated with Micropeel stopoff. The non-contaminated side was removed in a 50% HCl solution with Harry Miller Activol 1803 inhibitor. The stopoff was removed and the contaminated side was polished to a 1 μm finish.

To allow backcharging with the sample in a horizontal position, a flowing backcharging cell was constructed (Figure 6.2). The electrolyte was a 5% sodium sulfate solution with 5 ppm lead acetate. A lead anode was used with a current density of 100 mA/cm². The electrolyte was heated to 60°C to optimize the acoustic microscopy.

An Olympus UH3 SAM was used with a 600 MHz burst lens. The coupling fluid was boiled distilled water with 1 drop of a commercial ethylene glycol antifreeze (Prestone®) per 5 ml of water. Images of the surface and the interface were recorded prior to the start of charging. Charging was initiated and images of the surface and interface were recorded. After charging the zinc surface was examined in a JOEL 35CF SEM. The zinc coating was removed in inhibited 50% HCl, and the steel substrate was examined in the SEM.
6.3 Results and Discussion

6.3.1 Ex-situ Growth Monitoring

A series of micrographs of the same area is shown in Figures 6.3 and 6.4 of the 10 second sample is shown at baking times of 0 and 30 minutes. A blister is visible in both pictures and no changes occurred after 30 minutes of total baking. Examination of the area after 60 total minutes of baking showed no change. Figures 6.5 an 6.6 show an area on the sample subject to 30 seconds of cathodic and anodic charging. A blister is visible prior to baking. After 15 minutes of baking, no visible change in the surface morphology occurred.

Figure 6.7 shows blisters from the back charged sample. The blisters from back charging are larger and more numerous than the two baked samples. The blisters are otherwise similar. A higher magnification image of blisters indicates that there may be breaks in the coating near the base of the blisters as shown in Figure 6.8.

Although no change was seen in the surface of the samples after baking, several points can be made. Blisters can form at room temperature, as blisters were seen prior to baking. Blisters appeared to have breaks in the coating near the base. These breaks would relieve the pressure within the
blister, and no further growth would occur. This pressure relief mechanism would explain why none of the blisters detected grew after baking. Blisters produced by back charging are similar to blisters produced by baking, although larger amounts of hydrogen were available to cause blister growth.

A factor that must be considered in future studies is the need to know where blisters are likely to grow. In this study the surface was not modified prior to plating to promote blistering. Because of this procedure blisters formed in random areas, making studies difficult in that large areas had to be examined in the SEM. Future studies should use flawed or contaminate surfaces which will form blisters in a known location.

6.3.2 Effect of Surface Finish

Optical micrographs using glancing light are shown in Figures 6.9 to 6.12. Stains on the zinc surface are from the plating solution. As the surface finish proceeds from 500 grit to 800 grit the blister density increases. The amount of blistering between the 800 and 1200 grit specimens are fairly equivalent. The 2400 grit specimen has smaller blisters than the rougher specimens. All four surface finishes exhibit poor adhesion of the zinc coating.
The profilometry maps for the four specimens are shown in Figures 6.13 to 6.16. The magnifications in the x, y, and z directions are not equivalent, which distorts the map of the surface. The y direction has twice as magnification as the x direction. The z axis has a 5 times the magnifications as the x directions. A similar trend is seen in the progression from rough to smooth surfaces. The 500 and 800 grit samples have similar blister densities of 54 and 52 blisters/mm², respectively. The blister density for the 1200 grit specimen was 75 blisters/mm². The 2400 grit specimen had a blister density of 140 blisters/mm².

The micrographs from SEM examination of the plated surfaces (Figures 6.17 to 6.20) confirm the results of profilometry. An advantage to the profilometer map is that the various stains on the zinc surface are not seen. The maps also allow for the measurement of heights of the blisters relative to the zinc surface.

Results of scanning acoustic microscopy on the 800 grit sample confirm that there are delaminations at the zinc-steel interface. Figure 6.21 shows a blister on the 800 grit specimen. The dark color is a characteristic of areas at a level above the surface of the specimen. Lighter shaded signals are from deeper in the coating. Figure 6.22 is a SEM image of this blister. The lines
that are evident on the SAM image are shown to be the crystalline structure of the coating. Figure 6.23 is the area viewed by profilometry on 1200 grit specimen. Blisters are evident as dark spots on the surface the scribe appears bright and the coating surface is green. Smaller blisters of less height appear lighter.

The results of the effect of surface finish are somewhat surprising in that blisters formed very easily. It was thought that polishing the steel surface would remove surface defects which are considered to be a prime site for blister initiation. The fact that blisters still formed emphasize the complex nature of blister formation. The presence of hydrogen from the electrocleaning, electropickling, and electroplating processes allowed blisters to form. The variation in blister density for the samples can be explained in terms of true surface area. A rougher surface will have more surface area allowing from more bonding across the interface.

6.3.3 In-situ Growth Monitoring

The initial uncharged surface is seen in a SAM image in Figure 6.24. Several pores are seen on the surface. Focusing the lens at the interface (Figure 6.25) reveals several interfacial features as bright spots. When backcharging was initiated blisters were first seen after 7 minutes. Figure 6.26
shows the SAM surface image after 15 minutes. The blisters seen are large >10 μm. Figure 6.27 is the interfacial image after 15 minutes of charging. It can be seen that blisters tended to form near interfacial features, but not all interfacial features were blister initiation sites. Similarly surface and interfacial images after 25 minutes are seen in Figures 6.28 and 6.29. Several smaller blisters can be seen in these images. The blisters that formed initially did not show any further growth.

SEM images of the zinc coating shows good correspondence with the SAM images (Figure 6.30). The steel surface is shown in Figure 6.31, again there is correlation seen between the SEM and SAM images. A larger magnification image of the zinc coating (Figure 6.32) shows a several step like ledges. These ledges are individual zinc grains which have been pushed out. The zinc grains tend to be 3 to 5 μm in size.

*In-situ* blister growth monitoring revealed several features of blister growth. It was shown that larger blisters formed first. This indicates that there are preferential initiation sites for blister growth. These preferential sites are likely to be the sites that blister in baking cycles. Preferential sites have a larger area of poor adhesion, allowing deflection of the coating at lower pressure as was described by blister modelling. Smaller blisters formed later
in the test, indicating that a higher pressure is required for smaller blisters to form.

The role interfacial features play was demonstrated using SAM. Interfacial images showed features acted as blister initiation sites, but not all features acted as a site for blister growth. A feature of blister growth also seen is that once blisters form they tend not to grow further. This indicates that there is a pressure relief mechanism. A means for gas escape from the blister must be forming (void or crack), to relieve the pressure inside the blister.

The mechanism by which the zinc layer deforms was also seen by examining the polished surface with SEM after backcharging. A ledge like structure was seen on large blisters, and small blisters consisted of several small ledges. These ledges are individual zinc grains indicating that a grain boundary sliding mechanism is responsible for the deformation of the zinc layer. This mechanism is consistent with the behavior of zinc which is known to exhibit grain boundary sliding at temperatures above 20° C\(^{38,39,40}\). A grain boundary sliding mechanism gives insight into why blisters tend to form at higher temperatures. Higher temperatures will lower the creep resistance of zinc, thereby allowing lower pressures of gas to cause deformation. The
backcharged specimen from the ex-situ examination (Figure 6.8) also showed indications of grain boundary sliding. Although there is ample evidence for grain boundary sliding in this work, the work of Zhou\textsuperscript{44} showed no obvious evidence of grain boundary sliding.

6.4 Conclusions

From examining the plated surface of electrogalvanized steel before and after baking, characteristics of blister growth were identified. The blisters formation process can occur at room temperature. Once a blister forms, growth will occur as long as the coating does not break, relieving the pressure within the blister. Blisters that form during the backcharging process are similar to blisters that form naturally.

Qualifying the adhesion of electroplated zinc to steel substrates with different surface finishes provided a basis for comparison of techniques to examine the electroplated surface. As the surface became smoother the blister density increased. Optical microscopy is the most commonly used way to rate the degree of blistering on a specimen. Although this technique provides a quick quality check over a larger area, staining of the zinc can make blister identification difficult. SEM images can identify blisters, but similar limitations as optical microscopy exist. Surface profilometry maps provide
additional information on heights of blisters, but a rough production surface makes blister identification difficult. SAM is a useful way to identify delaminations at the interface, but to fully utilize the subsurface imaging capabilities of SAM a polished surface must be used.

Monitoring the growth of blisters in-situ indicated that blisters form near interfacial features, but not all interfacial features act as initiation sites. Large blisters formed initially and smaller blisters formed on further charging. The initial formation of large blisters confirms predictions from blister modeling (Chapter 4) that lower pressures are needed to deflect coatings with a larger initiation site. The zinc layer deforms by a grain boundary sliding mechanism. The movement of grains leads to a void or gap in the coating by which the pressurized gas can escape.
Figure 6.1. Schematic of the O-ring joint cell used in the back charging of electrogalvanized steel sheet.
Figure 6.2. Schematic of the flowing backcharging cell used in the in-situ growth monitoring study.
Figure 6.3. SEM image of an area on the sample with 10 seconds of cathodic and anodic charging prior to baking. A group of blisters are visible near the center of the area.

Figure 6.4. SEM image of an area on the sample with 10 seconds of cathodic and anodic charging after 30 minutes of baking. No change occurred in comparison to the unbaked sample.
Figure 6.5. SEM image of an area on the sample with 30 seconds of cathodic and anodic charging prior to baking. Two blisters are visible near the center of the area.

Figure 6.6. SEM image of an area on the sample with 30 seconds of cathodic and anodic charging after 15 minutes of baking. The two blisters near the center have not changed.
Figure 6.7. SEM image of an area of the single sided specimen after 2 hrs of backcharging. Numerous blisters are visible on the surface.

Figure 6.8. SEM image of two blisters from the above area. Gaps or cracks are visible near the bases of both blisters.
Figure 6.9. Optical micrograph of the 500 grit sample at 5X. Blisters are visible over most of the surface. The stains on the surface are from electrolyte on the surface.

Figure 6.10. Optical micrograph of the 800 grit specimen at 5X. A greater degree of blistering compared to the 500 grit specimen is evident.
Figure 6.11. Optical micrograph of the 1200 grit specimen at 5X. The degree of blistering is fairly equivalent to the 800 grit specimen.

Figure 6.12. Optical micrograph of the 2400 grit specimen at 5x. Blistering is evident, but the blisters are smaller than the rougher specimens.
Figure 6.13. Profilometry map of a 1 x 3 mm area on the 500 grit specimen. Blisters are evident. The magnifications in the three directions are not equivalent. Blister density was determined to be 54 blisters/mm².
Figure 6.14. Profilometry map of a 1 x 3 mm area on the 800 grit specimen. Blisters are evident. The magnifications in the three directions are not equivalent. Blister density was determined to be 52 blisters/mm².
Figure 6.15. Profilometry map of a 1 x 3 mm area on the 1200 grit specimen. Blisters are evident. The magnifications in the three directions are not equivalent. Blister density was determined to be 75 blisters/mm².
Figure 6.16. Profilometry map of a 1 x 3 mm area on the 2400 grit specimen. Blisters are evident. The magnifications in the three directions are not equivalent. Blister density was determined to be 140 blisters/mm².
Figure 6.17. SEM montage of the area mapped by profilometry on the 500 grit specimen.
Figure 6.18. SEM montage of the area mapped by profilometry on the 800 grit specimen.
Figure 6.19. SEM montage of the area mapped by profilometry on the 1200 grit specimen.
Figure 6.20. SEM montage of the area mapped by profilometry on the 2400 grit specimen.
Figure 6.21. SAM image of a blister on the 800 grit specimen. The dark shade is from upper areas of the coating the lighter shades are from lower in the coating. The small lines are from the crystalline nature of the coating.

Figure 6.22. SEM image of a blister on the 800 grit specimen seen in Figure 6.21. The crystalline nature of the coating is evident.
Figure 6.23. SAM image of the area examine by profilometry on the 1200 grit specimen. The dark areas are from 5 μm above the surface. The lighter shades are from surface and subsurface signals.
Figure 6.24. SAM image of the zinc surface with no charging (t=0). Several pores are visible on the surface.

Figure 6.25. SAM image of the zinc-steel interface with no charging (t=0). Interfacial features appear as bright spots.
Figure 6.26. SAM image of the zinc surface after 15 minutes of backcharging at 100 mA/cm². Several large blisters are seen to have formed.

Figure 6.27. SAM image of the zinc-steel interface after 15 minutes of charging. Blisters are seen to have formed near interfacial features.
Figure 6.28. SAM image of the zinc surface after 25 minutes of charging. Several smaller blisters are seen to have formed at longer charging times.

Figure 6.29. SAM image of the zinc-steel interface after 25 minutes of charging.
Figure 6.30. SEM image of the zinc surface after backcharging at 100 mA/cm². Image confirms presence of blisters seen using SAM.

Figure 6.31. SEM image of the steel surface after removal of the zinc coating. Good correspondence with SAM image is seen.
Figure 6.32. SEM image of blisters on the zinc coating. Step like ledges are visible. These ledges correspond to zinc grains.
7 Effect of Cathodic and Anodic

Current Pulses on Hydrogen Permeation

7.1 Introduction

The effect of various simulated electroleaching and electropickling processes on hydrogen permeation was studied by Amey\(^1\). These processes were simulated by cathodic charging in a permeation cell. However, the commercial zinc plating lines utilize a bimodal current which pulses between anodic and cathodic currents. The effect of these pulses on hydrogen permeation was examined in this section.

Amey\(^1\) demonstrated that the electropickling process was the most detrimental preplating process in terms of amount of hydrogen adsorbed. It was found that the electropickling process produced a permeation current of 13 \(\mu\)A/cm\(^2\) at room temperature compared to 4 \(\mu\)A/cm\(^2\) for electroleaching. The plating solution (without zinc) generated a higher permeation current, but the simulation was not comparable to line conditions. The presence of zinc in solution would limit the amount of hydrogen absorbed because of the blocking effect of the zinc coating.
The switching of the current on the electrogalvanizing line is time based. Every 2 seconds the polarity of the electrodes is switched. This results in sections of sheet entering in an anodic state and exiting in a cathodic state or vice versa. To examine the effect of the current pulses on hydrogen uptake the current on the "entrance" side of a permeation cell was pulsed in a simulated electropickling solution.

7.2 Experimental

Details of the experimental technique are described in chapter 3. The test utilized the permeation cell test geometry with an "entrance" and "exit" sides. The "entrance" surface normally is tested with a cathodic current. In this series of tests the current was pulsed between cathodic and anodic states for periods of 1, 2, and 5 seconds at a current density of 100 mA/cm². The solution was 0.1 M H₂SO₄ to simulate the electropickling environment. A comparison was made to a test run with only cathodic current at similar current densities.

The "entrance" surface was examined after a permeation test using x-ray photoelectron spectroscopy (XPS). Survey spectra were taken on unsputtered surfaces and surfaces subjected to 30 Å of sputtering. Multiplexes, high
resolution scans over energy ranges of interest, were taken after sputtering for
the elements of Fe and O.

7.3 Results

The results for the cathodic current test are shown in Figure 7.1. The
initial plateau at 20 μA is due to the current ramping process as described in
Chapter 3. The large plateau at 160 μA is the resulting current from 100
mA/cm² on the "entrance" surface. The permeation current reaches a
maximum near 160 μA and decreases to about 130 μA.

Figure 7.2 illustrates the results for the permeation test with 1 sec
pulses. A large initial spike is present in the permeation current which is
thought to be from the initial cathodic charging. The subsequent current
consists of several small spikes in the negative direction with the a current
plateau at about 15 μA. When the "entrance" current was turned off a large
spike in the anodic current was seen which then decayed. When the
apparatus was disassembled the "entrance" surface had developed a dark
blackish grey film.
The results for the permeation test with 2 second pulses on the "entrance" surface exhibit similar behavior (Figure 7.3). There was no initial large spike, but there were several small negative spikes. The base permeation current reached a maximum of 15 μA at about 5000 seconds into the test. There was a positive spike in the permeation followed by a decay when the "entrance" current was turned off. The dark film was also present on the "entrance" surface after the test.

Figure 7.4 shows the results for the 5 second pulse test. The anodic trace shows similar behavior to the other two tests. The curve consists of several large negative spikes with the base permeation current of 18 μA. The permeation current decreased to about 15 μA where the "entrance" current was turned off. There was a large spike followed by a decay. The dark film was present on the "entrance" surface.

The film that was formed on the "entrance" surface is the probable cause of the maxima seen in the permeation current. The applied current was monitored for all tests and is shown for the 5 second pulse test in Figure 7.5. The current was fairly constant for the first 1000 seconds then decreased. This decrease was due to the compliance voltage of the galvanostat being reached.
The inability of the galvanostat to drive the system is due to the increase in resistance from the film that was formed.

The results of the XPS survey of the unsputtered surface are illustrated in Figure 7.6. The survey spectrum after 30 Å of sputtering is shown in Figure 7.7. The atomic composition as computed from the survey data is shown in Table 7.1. Atomic composition of the film formed during the pulse permeation experiment.

<table>
<thead>
<tr>
<th></th>
<th>C 1s</th>
<th>N 1s</th>
<th>O 1s</th>
<th>Fe 2p3</th>
<th>Cu 2p3</th>
</tr>
</thead>
<tbody>
<tr>
<td>unsputtered</td>
<td>21%</td>
<td>4%</td>
<td>63%</td>
<td>6%</td>
<td>5%</td>
</tr>
<tr>
<td>30 Å sputter</td>
<td>12%</td>
<td>7%</td>
<td>56%</td>
<td>16%</td>
<td>9%</td>
</tr>
</tbody>
</table>

Table 7.1. The main components of the film are oxygen, carbon, iron, copper, and nitrogen. After sputtering the carbon and oxygen content of the film decreased while the copper, iron, and nitrogen contents increased. The iron multiplex displayed both iron in the metallic and oxide states as is shown in Figure 7.8. The presence of copper in the film is surprising as there is less than 0.026 wt% Cu in the bulk material. The most probable source of the copper on the surface is plating of copper from solution.
7.4 Discussion

From the results of the pulse permeation tests it can be seen that the permeation current is reduced by about 90% compared to a straight cathodic permeation test. The cause of this reduction is two fold. Hydrogen can be drawn out of the steel during the anodic cycle and anodic film formation on the entrance surface may prevent hydrogen adsorption during the cathodic cycle.

A schematic of a hydrogen profile after an anodic current is shown in Figure 7.9a. The maximum hydrogen concentration is at the surface. The effect of a subsequent anodic current would be to draw the hydrogen out of the steel as is illustrated in Figure 7.9b. The amount of hydrogen that would be available to permeate through the membrane would be significantly reduced.

Anodic film formation on the electrode surface could lead to a significant reduction in the amount of hydrogen adsorbed. The hydrogen would be absorbed onto an oxide surface and would have to diffuse through the oxide prior to adsorption into the steel membrane. In addition a portion of the cathodic current would be needed to reduce the oxide that is formed.
during the anodic cycle. This current would lower the amount of hydrogen that is reduced on the membrane surface.

The copper that was seen in the film could also lead to a decrease in hydrogen adsorption. Amey reviewed several studies on the effect of Cu on H adsorption and found reports of both decreased and increased hydrogen adsorption. The effect of Cu on hydrogen adsorption is not clear but it is probably minor compared to the effect of the anodic film.

7.5 Conclusions

Pulsing the current between cathodic and anodic states causes a 90% reduction in the permeation current compared to constant cathodic charging. The reduction in the amount of hydrogen permeated is an effect of the anodic current extracting hydrogen from the steel surface and the formation of an anodic film. The anodic film was a mix of carbon, oxygen, nitrogen, iron and copper.
Figure 7.1. Permeation curve for a low C steel membrane with a cathodic current of 100 mA/cm².
Figure 7.2. Permeation curve for a low C steel membrane with current pulses of 1 second at a current of 100 mA/cm².
Figure 7.3. Permeation curve for a low C steel membrane with current pulses of 2 seconds at a current of 100 mA/cm².
Figure 7.4. Permeation curve for a low C steel membrane with current pulses of 5 seconds at a current of 100 mA/cm².
Figure 7.5. Plot of the applied current for the 5 second pulse permeation test. The decrease in current is due to the compliance voltage of the galvanostat being reached.
Figure 7.6. XPS survey of the film formed on the "entrance" surface of a steel membrane during a pulse permeation test.
Figure 7.7. XPS survey of the film formed on the "entrance" surface of a steel membrane during a pulse permeation test after 30 Å of sputtering.
Figure 7.8. XPS multiplex of the iron region on a film formed during pulse permeation after 30 Å of sputtering.
Figure 7.9. Schematic of the hydrogen profile after cathodic charging (a) and a subsequent anodic charging (b).
8.1 Introduction

During the electrogalvanizing process the steel sheet is subjected to several cleaning steps. The sheet is alkaline cleaned, electrocleaned in an alkaline solution, and electropickled in an acid solution. During these electroprocesses conditions are ripe for hydrogen absorption.

Armey\(^1\) investigated the effect of the electroprocesses on hydrogen absorption using the hydrogen permeation test. In the permeation test a metal membrane is sandwiched between a cathodic "entrance" cell and an anodic "exit" cell. Hydrogen is driven into the steel and as it exits, the anodic current is a measure of the hydrogen permeating through the steel. Although the permeation test is an effective test for the study of hydrogen it requires that the system reach steady state (about an hour). This time period is extensive compared to the seconds of time the sheet is in the preplating section on the plating line.

A technique which can analyze the amount of hydrogen in a metal measures the thermal conductivity of a carrier gas. When hydrogen is
introduced into the gas it raises the thermal conductivity. Thereby the thermal conductivity can be related to hydrogen content of a metal which is heated in the gas stream. The instrument which is dedicated to this analysis is termed a hydrogen determinator.

The amount of hydrogen absorbed during a preplating process is of interest. Another factor of interest is the effect of polarity cycle on absorption of hydrogen. To investigate these effects simulations of electroprocesses were made and the absorbed hydrogen measured using a hydrogen determinator.

8.2 Experimental

The process simulations were performed on eight coupons with the conditions listed in Table 8.1, in addition 6 unexposed coupons were also analyzed. An electrocleaning solution of 15 g/l of Parker Amchem EC76 was used. The electropolishing solution was 0.1M H₂SO₄. Both solutions were held

<table>
<thead>
<tr>
<th>EC AC</th>
<th>EC CA</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP AC</td>
<td>EP CA</td>
</tr>
</tbody>
</table>

Table 8.1. Experimental matrix for the hydrogen gas analysis using the LECO hydrogen determinator.

EC = electrocleaning, EP = electropolishing, AC = anodic cycle first, CA = cathodic cycle first.
at 60±2°C during the simulation. The current was galvanostatically controlled at 150 mA/cm² using a PAR 173 potentiostat/galvanostat. A lead electrode was spaced 2-2.5 cm away from each side of the coupon. After charging coupons were stored in liquid nitrogen after rinsing in distilled water and dipping in acetone. Samples were taken to LTV for hydrogen determination using a LECO 402 hydrogen determinator. The procedure is covered in greater detail in Chapter 3.

8.3 Results

A result from the hydrogen determinator analysis for a electropickled sample with an AC cycle is shown in Figure 8.1. As the sample was heated an initial spike was seen in the hydrogen. This initial spike is an anomaly from the initial air in the chamber. The second broader peak is the signal from the hydrogen in the coupon. Using software within the unit the area under the two peaks was calculated and related to hydrogen content in ppm. Table 8.2 shows the average hydrogen content in ppm and the standard deviation for the conditions of the test. The number of samples is listed because several coupons did not fall into the crucible during the test and therefore the results from the test had to be disregarded. The standard deviations are relatively high, which limits the confidence of the comparisons made since the numbers begin to overlap.
Table 8.2. Hydrogen contents in ppm the hydrogen gas analysis using the hydrogen determinator.

<table>
<thead>
<tr>
<th>Number of Samples</th>
<th>Average</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>4</td>
<td>0.265</td>
</tr>
<tr>
<td>EC CA</td>
<td>3</td>
<td>0.349</td>
</tr>
<tr>
<td>EC AC</td>
<td>6</td>
<td>0.480</td>
</tr>
<tr>
<td>EP CA</td>
<td>8</td>
<td>0.448</td>
</tr>
<tr>
<td>EP AC</td>
<td>4</td>
<td>0.548</td>
</tr>
</tbody>
</table>

EC = electrocleaning, EP = electropickling, AC = anodic cycle first, CA = cathodic cycle first.

8.4 Discussion

The results from the hydrogen determination analysis on simulated electrocleaning and electropickling processes show that about 0.1 ppm and 0.2 ppm, respectively, are absorbed during the simulated processes compared to control samples. These results confirm the work of Amey\textsuperscript{1} on the favorable environment for hydrogen absorption in the acid electropickle. Although, Amey\textsuperscript{1} showed a 3 fold increase in the permeation current under electropickling conditions. The acidic environment provides a higher hydrogen activity as compared to the alkaline electroclean.

The cathodic-anodic cycling sequence results in less absorbed hydrogen
than the anodic-cathodic sequence. This result is not surprising as the anodic cycle will draw hydrogen out of steel. When the anodic cycle is the last in the sequence the hydrogen that has been absorbed during the cathodic cycle will be drawn out of the steel. In the opposite sequence the hydrogen that is injected into the steel during the cathodic cycle will remain in the metal.

8.5 Conclusions

Analyzing hydrogen contents after simulated electroprocesses using thermal hydrogen analysis demonstrated that electropickling is a more severe environment for hydrogen absorption. The anodic charging cycle drew absorbed hydrogen out of the steel. Therefore when the anodic cycle was the last cycle in the charging sequence, lower hydrogen contents were observed.
Figure 8.1. Result from the hydrogen determinator for a simulated electropickled sample with an AC cycle. The linear trace is the power to the heater, the curves are the hydrogen peaks. The area under the peaks was determined and related to hydrogen content. The first peak is an anomaly from the initial air in the system.
9.1 Initiation Site

Several conclusions on the formation and growth of blisters can be drawn from the studies on blisters. From blister modelling and growth studies it was seen that an area of poor adhesion at the zinc-steel interface is required. *In-situ* growth studies clearly showed that blisters tended to form at interfacial features. The size of this initiation site will regulate the ease of blister growth as was demonstrated by the models. A small initiation site will require higher internal pressures to deform the coating compared to a larger initiation site.

The initiation site is typically caused by a mechanical defect coupled with carbon contamination. The presence of carbon is important as was demonstrated by the analysis of the gas within the blisters. The presence of methane in the blisters indicates that carbon is an integral part of the blister formation process. Carbon contamination at the zinc-steel interface can weaken the interfacial strength and act as a hydrogen sink. When carbon is present with hydrogen one methane molecule can be formed, as compared to two hydrogen gas molecules. This reaction will lower the internal pressure by a factor of two. This reaction will also lower the H activity as hydrogen
will be removed from the immediate vicinity. This lower H content near the initiation site will allow more H to diffuse to the area.

9.2 Hydrogen Egress

The second factor in blister formation is the transport of hydrogen to the initiation site. It was demonstrated in this investigation and by Amey\textsuperscript{1} that significant amounts of hydrogen are injected into the steel during processing. This injected hydrogen is trapped in the steel by the zinc coating. After plating the hydrogen can diffuse through the steel but not the zinc. The diffusion of hydrogen and blister formation can occur at room temperature. At elevated temperatures (paint bakes) the diffusion rate through the steel is increased and traps in the steel can release hydrogen. These two effects can lead to the hydrogen diffusing to the initiation sites. When adequate pressure is built up the zinc coating deforms to form a blister.

9.3 Coating Deformation

Once hydrogen begins to diffuse into the initiation site pressure begins to build up. The zinc coating can deform in two different manners elastically and plastically. Plastic deformation can occur via plastic flow or grain boundary sliding. Grain boundary sliding was seen in the in-situ blister growth studies. Deformation by plastic flow was documented by Zhou\textsuperscript{4}. 


Once plastic deformation begins the volume of the blister will increase tending to lower the pressure within the blister, causing deformation to stop unless there is a continuous supply of gas (CH₄ or H₂).

### 9.4 Pressure Release

Deformation will continue until the pressure in the blister is relieved or the supply of gas to the blister is exhausted. This relief mechanism is the development of a path for the internal gases to escape. In *in-situ* blister growth studies, it was seen that once blisters formed they did not increase in size. This indicated that the blister were no longer building up internal pressure, i.e. the gas was escaping. The grain boundary sliding which was seen in the coating during the study could provide many paths of escape. As grains slip past one another, voids between the grains could quite easily form. In some cases cracks trough the zinc coating over a blister were observed.

### 9.5 Effect of Temperature

Temperature will have many effects on the processes which effect blister growth. Increased temperature will increase the diffusion rate of hydrogen in the steel. The internal pressure of gas within the blister will increase with increasing temperature as is governed by the ideal gas equation. In addition the properties of the zinc coating will be effected by temperature.
The resistance to grain boundary sliding will be lowered with increasing temperature. Hydrogen traps can also release the trapped gas at higher temperatures. The recombination of hydrogen and the formation of methane will also occur at a faster rate at increased temperatures. The net result of these effects is that increased temperature provides favorable conditions for blister formation. This also indicates why blisters are seen to form during paint bake cycles.

9.6 Summary of Growth Mechanism

The formation of blisters can be summarized in the following manner and is illustrated in Figure 9.1. The presence of areas of poor adhesion at the zinc steel interface act as initiation sites for blister growth. Hydrogen which is injected into the steel during the plating process will diffuse into the initiation site. If carbon is present at the initiation site the formation of methane is favorable. When the internal gas pressure builds up the coating is deformed. Plastic deformation can occur by flow or grain boundary sliding. Deformation will continue until the pressure is relieved by a void or a crack in the coating or the supply of gas to the blister is depleted.
Areas of poor adhesion act as initiation sites

Hydrogen egress from steel to initiation sites
Forms H₂ or methane

Zinc layer deforms when sufficient pressure develops
Blisters form

Blisters stop growing when pressure is relieved

Figure 9.1. Schematic of the blister growth mechanisms. Blisters form at areas of poor adhesion when hydrogen diffuses into these areas. Growth will continue until the internal pressure is released.
9.7 Implications to Alleviate Blister Formation

This study of blister growth has identified several features of blister growth. An aspect of blister growth that must be realized is that it is not governed by one single effect, rather a combination of events must occur for blister to be formed. In this respect, to reduce blister formation the number and size of initiation sites should be minimized, the amount of hydrogen in the steel should also be decreased, and the carbon available at the zinc-steel interface should be reduced. The reduction in initiation sites and carbon available at the zinc-steel interface may be achieved by controlling the texture of the steel sheet and by better cleaning practices before the annealing of the steel. The reduction of hydrogen absorption could be attained by modifying the preplating processes of electrocleaning and electropickling. Modifications can include longer anodic cycles to extract hydrogen, lower current densities, and hydrogen absorption inhibitors. It is not known if inhibitors for hydrogen absorption would have an negative effect on the plating of the steel.
10 Directions for Future Work

10.1 Initiation Sites

Although attempts were made in this work to simulate initiation sites, the formation of initiation sites under production conditions is still somewhat of a mystery. The accumulation of iron fines on the steel surface is a process that is easy to picture. Questions still remain where the fines come from. In addition to this the question of flap formation is still unanswered. It is easy to imagine localized welding and subsequent deformation of the surface but little documentation of this process exists. The presence of carbon under these surface features has been found but is not publicly documented. The presence of carbon has been seen in the initiation sites of blisters. The effect of these features on the formation of blisters, or other defects is not clear and needs to be addressed.

10.2 Hydrogen Absorption

Although a great deal of work focused on the absorption of hydrogen during the electroprocesses in work by Amey and in this work some questions remain. Is hydrogen preferentially absorbed by local areas? If so, this would explain why blisters do not always form. If hydrogen is not preferentially absorbed, perhaps local hydrogen traps exist. Future work with
the hydrogen determinator may be useful (A programmable version of the instrument will allow for precise temperature profiles and subsequent determination of trap strength). Difficulties in identifying the localization of these traps will be difficult to overcome.

10.3 Methane Formation

The formation of methane was documented in analysis of blister gas. Several questions remain as to rate of formation and the ratio of hydrogen to methane. The formation of methane could be examined using mass spectrometry or gas chromatography. To simulate the environment of blisters carbon could be sputter deposited on a steel substrate. The steel substrate could then be backcharged and the subsequent formation of methane could be examined using the gas analysis technique chosen. Gas chromatography may be superior in this respect since it would give more quantifiable results.

10.4 Deformation of the Coating

Although grain boundary sliding was definitely seen in this study, typical production blisters do not readily demonstrate this deformation. The fact that the zinc surface was polished could have two effects namely thinning the coating or highlighting the grains. The thinner coating would have less material to resist deformation. Typical production coatings have rough
surfaces which makes singling out grain boundaries difficult. The fact that 
grain boundary sliding can occur at much lower stresses as compared to 
stresses necessary to cause plastic flow makes this question critical in defining 
the pressures necessary for blistering to occur.

Once the mode of plastic deformation is clearly defined the stresses 
necessary to activate that mode need to be independently measured. Thin 
films of zinc could be plated on carbon or aluminum substrates (both exhibit 
poor adhesion) and subsequently removed. Alternatively vapor deposited 
films could be produced. The mechanical behavior of these thin films could 
then be documented. Difficulties would exist in correlating the structure of 
the films to the structure of the production electrodeposits.

Another factor to be considered in the deformation of the zinc coating 
is the effect of various brighteners. The brighteners promote specific 
orientations of the zinc coating. Therefore changes in the mechanical 
properties of the coating could be expected.

10.5 Modeling Studies

The models which were used to describe the zinc-steel system in this 
study were somewhat simplistic in that they did not treat the plastic
deformation of the zinc layer. Although factors which lead to blister growth were determined by the elastic models, the plastic behavior of the coating was clearly demonstrated. Models which do take into account plastic deformation should be considered in the future to gain a better understanding of the amount of hydrogen which would be necessary to cause blisters to grow. Again the mode of plastic deformation that occurs on production samples would need to be determined since this will determine how the system would be modeled.
References


