THE DISSOLUTION OF IRON FROM AUTOMOTIVE STEEL SHEETS
IN A MOLTEN ZINC BATH AND THE KINETICS OF THE
NUCLEATION AND GROWTH OF DROSS PARTICLES

By

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*We also certify that written approval has been obtained for any proprietary material contained therein.
Dedicated to my beloved parents
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The Dissolution of Iron from Automotive Steel Sheets in a Molten Zinc Bath and the Kinetics of the Nucleation and Growth of Dross Particles

Abstract

By

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Hot-dip galvanizing (HDG) is a well-known process that increases the resistance of a steel strip to corrosion. Immersion of an automotive steel sheet in a galvanizing bath initiates a dissolution reaction. The flux of iron from the steel surface into the liquid zinc bath provides a driving force for the formation of an inhibition layer and the precipitation of dross particles. Such reactions involve the kinetics of nucleation and growth of intermetallic phases. This study addresses two main issues. First, the iron dissolution rate constant is governed by the solubility of iron in the liquid zinc under a metastable state between the pure bcc iron and the liquid phases. Secondly, a model for the nucleation and growth of precipitates can reveal the dynamics associated with intermetallic compound formation. The nucleation and growth model developed predicts that the inhibition layer covers 99.9% of the steel surface in 0.0011 second with the iron supersaturation of 0.56wt.% and the aluminum concentration of 0.20wt.% in a molten zinc bath at 460°C.
1. Introduction

Steel is the most widely used material in the automotive industry because of its excellent strength and the economics of its use in the high volume production of components. However, steel is susceptible to a high rate of oxidation in the presence of water or moist air containing salt. Zinc coatings can effectively prevent the aqueous corrosion of steel by providing anodic protection. Common methods used to produce zinc coatings are hot-dip galvanizing, thermal-spray and electro-deposition. This study will focus on the continuous hot-dip galvanizing (HDG) process, i.e., the immersion of steel sheet in a molten zinc bath.

Traditional HDG processing uses a molten zinc bath that enables the formation of an inhibition layer and a final coating that a essentially pure zinc. Modern HDG processing adds a small amount of aluminum in the galvanizing pot to enhance the quality of the final product. The addition of aluminum in the galvanizing melts is not made to enhance the corrosion performance. Its use improves the formability of a galvanized sheet and maintains the adhesion of the coating during a forming operation. Practical HDG process manages the effective of aluminum content, indicated as the amount of aluminum dissolved in liquid zinc, between 0.13 and 0.25 wt.% which can effectively limit iron
dissolution and precipitate a thin layer of $\eta$-Fe$_2$Al$_5$Zn$_x$ phase as an inhibition layer on the product sheets. When the effective aluminum content is lower than 0.13 wt.%, the system will have a tendency to form $\delta$-phase (FeZn$_{10}$). The density of $\delta$-phase is 7.1 Mg·m$^{-3}$ which is greater than the density of liquid zinc, about 6.8 Mg·m$^{-3}$. The $\delta$-phase can sink to the bottom of a zinc bath forming bottom dross. When the effective aluminum content is greater than 0.13wt.%, the system will prefer to form the $\eta$-Fe$_2$Al$_5$Zn$_x$ phase. The density of $\eta$-Fe$_2$Al$_5$Zn$_x$ phase is 4.1 Mg·m$^{-3}$ which is lower than that of the galvanizing bath. The $\eta$-Fe$_2$Al$_5$Zn$_x$ phase forms top dross particles.

The formation of bottom dross particle which are often on the order of 200µm in size on a zinc coating that is normally 10µm thick degrades the surface appearance of the final galvanized product. Understanding the relationship between the rate and the extent of iron dissolution from the steel surface into the molten zinc and the kinetics of nucleation and growth of the inhibition layer and dross particles is a key issue in the control of the surface quality of automotive galvannealed steel sheet. The aluminum content and temperature of the molten zinc bath in addition to the concentration of dissolved iron determine the kinetics of nucleation and growth of the inhibition layer and dross particles. This study will establish a model for the dissolution of iron in molten zinc.
The model will be used to estimate the amount of iron dissolution that will occur under various galvanizing conditions including the effective aluminum content in the liquid zinc between 0 and 0.25 wt.%. Additional work will build models for the kinetics of nucleation and growth of dross particles that demonstrate how the kinetics are affected by the extent of iron and aluminum supersaturation in the molten zinc.

Recently several studies have investigated the initial phases of the galvanizing process [1-8]. Tang has proposed a model to estimate the thickness of the inhibition layer associated with a heterogeneous nucleation and growth rate controlled by the diffusivity of aluminum in liquid zinc [1]. Toussaint et al. used a stimulator to observe the short-time galvanizing treatment and found out that a 100nm of an inhibition layer can precipitate within 4 seconds in a galvanizing bath contained 0.16wt.% of aluminum at 460°C [2-3]. However, those studies only focused on the kinetics of nucleation and growth of an inhibition layer without the appropriate thermodynamic formalism [1-8]. The motivation of this work was to apply CALPHAD-based solution for thermodynamics analysis of the mass transport of iron in the molten zinc. The most recent thermodynamic parameters in the Fe-Al-Zn system were to be used understand the kinetics of formation of the
inhibition layer and dross particles, such as Fe$_2$Al$_5$Zn$_x$ and δ-phase, in order to improve the surface quality of the steel sheets by the reduction of dross particles.

1.1 Continuous Hot-Dip Galvanizing Process

In commercial continuous hip-dip galvanizing processing lines, a steel sheet is running at speeds of up to 200 m/min. Initially, the sheet enters the cleaning section, as shown in Figure 1, where its temperature increases from 500 to 750°C under a N$_2$/H$_2$ reducing atmosphere. After cleaning, the sheet enters the heating and holding zones of a radiant tube furnace where the sheet is annealed above its recrystallization temperature.

![Figure 1: A schematic diagram of the continuous hot-dip galvanizing process [1].](image)
On exiting the cooling section, the steel sheet is immersed in a liquid zinc bath, as shown in detail in Figure 2. The zinc bath has an aluminum content of 0.1 to 0.3 wt. pct. and is held at a temperature between 450 and 480°C. The purpose of adding aluminum to molten zinc is to suppress the formation of a multi-layered coating comprised of intermetallic phases. The commercial galvanizing plant usually manages the aluminum concentration in molten zinc pot by using the ingot basket which contained raw aluminum materials. During the dipping process, the steel sheet rapidly dissolves iron from its surface, raising the iron concentration in the molten zinc bath at the steel-liquid zinc interface. The increased iron content provides a huge driving force to form stable
aluminum-iron and aluminum-iron-zinc intermetallic compounds on the surface of the steel sheet. After immersion of the steel sheet in the molten zinc, the thickness of the liquid zinc film that adheres to the surface of steel sheet after it exits the molten zinc bath is controlled by air knives that literally blow away excess liquid. After the strip exits the air knives, it may undergo additional annealing to form desired Fe-Zn intermetallic compounds. The final product is then called galvannealed steel. If the steel is not galvannealed, it is designated HDG and has an essentially pure zinc coating.

The aluminum content (<0.3 wt. pct.) and working temperature (450-480°C) are key parameters that determine the concentration of dissolved iron and the kinetics of nucleation and growth of an inhibition layer that can form on the steel sheet/liquid zinc interface. Typical dipping times range from 2 to 4 seconds for strip speeds in excess of 175m/min [8]. Dissolved iron not consumed by the reaction that forms an inhibition layer can promote the precipitation of dross phases in the liquid zinc.

Dross particles in the molten zinc bath can be classified as oxides of Zn and/or Al and intermetallic compounds of Fe-Al and/or Fe-Al-Zn. Intermetallic compounds cause the primary dross problems and form in the molten zinc bath when Al and Fe are present at concentrations high enough to provide a driving force for their nucleate and grow. The
primary intermetallic compounds have been identified as “Fe$_2$Al$_5$Zn$_x$” and aluminum saturated “FeZn$_{10}$” (commonly identified as $\delta$ phase). Dross phase formation is unavoidable if iron continuously dissolves into the molten zinc bath, and aluminum is continuously added to the bath to enable the formation of an inhibition layer.

The presence of excessive amounts of dross depends on the extent of iron dissolution and the kinetics of nucleation and growth of intermetallic phases. The kinetics of iron dissolution when a steel sheet is dipped into a molten zinc bath will determine the amount of iron that can participate in the formation of an inhibition layer of Fe$_2$Al$_5$Zn$_x$, and also how much iron can precipitate in other dross phases. The kinetics of the nucleation and growth of intermetallic phases are controlled by a driving force defined by the difference in Gibbs free energy between the dross phase on a molar basis and the sum of the chemical potentials of the elements that combine to form that dross phase.

1.2 The Fe-Zn Phase Diagram

When a steel sheet contacts a molten zinc bath, a number of reactions happen depending the bath composition as defined by its iron and aluminum concentrations.
Before focusing on the compositional effects, it will be helpful to understand possible reactions between iron and zinc.

Figure 3: Fe-Zn phase diagram [10].

Figure 3 shows the Fe-Zn phase diagram [10]. Figure 4 shows the zinc rich side of the Fe-Zn phase diagram. The primary phases formed during long-time immersion of a sheet steel at galvanizing temperatures of 450 to 480°C are zeta (ζ), delta (δ), gamma1 (Γ1) and gamma (Γ). The intermetallic compound Fe₂Al₅Znx appears in the phase diagram for the Fe-Al-Zn ternary system.
1.2.1 The Zeta (ζ) Phase

The zeta (ζ) phase, FeZn₁₃, has an iron content of 5 to 6 wt. pct and a monoclinic crystal structure. It can be formed by a peritectic reaction between the delta (δ) phase and liquid zinc at a temperature of 530°C. The basis for the monoclinic structure is an iron atom surrounded by 12 zinc atoms.

1.2.2 The Delta (δ) Phase

The delta (δ) phase, FeZn₁₀, has an iron content of 7 to 11.5 wt. pct. and a hexagonal crystal structure. It is formed by a peritectic reaction between the Γ phase and liquid zinc at a temperature of 665°C.

1.2.3 Gamma₁ (Γ₁) Phase

The gamma₁ (Γ₁) phase, Fe₅Zn₁₂, has an iron composition ranging from 17 to 19.5 wt. pct. and a fcc-centered-cubic crystal structure. It is formed by a peritectoid reaction between the gamma (Γ) phase and the δ phase at a temperature of 550°C. In commercial practice the Γ₁ phase can form a continuous film between gamma (Γ) and delta (δ) layers, when galvannealing is conducted at low temperature over long periods of time.
1.2.4 Gamma (Γ) Phase

The gamma (Γ) phase, Fe$_3$Zn$_{10}$, has an iron content ranging from 23.5 to 28 wt. pct. and a body centered cubic crystal structure. It is formed by a peritectic reaction between α-iron and liquid zinc at a temperature of 782°C.
2. Mathematical Modeling of HDG

2.1 Thermodynamic Model of the Fe-Zn System

During its initial immersion in liquid zinc, a steel surface can dissolve until locally the concentration of iron reaches a level where the chemical potential of iron in the liquid zinc equals that in the steel. That iron concentration is the maximum that can be generated. CALPHAD modeling has been used to establish the maximum iron concentration that can be achieved in liquid zinc as a function of temperature.

2.1.1 CALPHAD Modeling of Liquid Iron-Zinc

The Gibbs free energy of one mole of atoms in an Fe-Zn binary system can be expressed empirically by equation (1).

\[
G_m^{\text{liq}} = X_{Fe} \, aG_{Fe}^{\text{liq}} + X_{Zn} \, aG_{Zn}^{\text{liq}} + RT \left[ X_{Fe} \ln X_{Fe} + X_{Zn} \ln X_{Zn} \right] \\
+ X_{Fe} X_{Zn} \left[ aL_{Fe-Zn} + aL_{Fe-Zn} (X_{Fe} - X_{Zn}) + aL_{Fe-Zn} (X_{Fe} - X_{Zn})^2 \right]
\]

In equation (1) \( aG_{Fe}^{\text{liq}} \) and \( aG_{Zn}^{\text{liq}} \) are the Gibbs free energy of pure liquid iron and zinc, respectively. The \( X_{Fe} \) and \( X_{Zn} \) are the mole fraction of iron and zinc, respectively. The L’s are interaction parameters. Nakano et al. [11] published a thermodynamic optimization of the binary Fe-Zn system in 2005 and presented a thermodynamic assessment of the ternary Fe-Zn-Al system in 2007 [12]. Xiong et al. [13] published a
refinement of previously published thermodynamic optimizations of the Fe-Zn system.

The Appendix I lists the interaction parameters published by these two research group.

The chemical potential of iron in the liquid phase is defined by differentiating $G_{m}^{\text{liq}}$ as indicated in equation (2).

$$
\mu_{Fe}^{\text{liq}} = G_{m}^{\text{liq}} + \frac{\partial G_{m}^{\text{liq}}}{\partial X_{Fe}} - X_{Fe} \frac{\partial G_{m}^{\text{liq}}}{\partial X_{Fe}} - X_{Zn} \frac{\partial G_{m}^{\text{liq}}}{\partial X_{Zn}}
$$

(2)

Inserting equation (1) into equation (2) and carrying out the required differentiation yields equation (3).

$$
\mu_{Fe}^{\text{liq}} = oG_{Fe}^{\text{liq}} + RT \ln X_{Fe}
+ X_{Zn}^{2} \left[ oL_{Fe,Zn}^{\text{liq}} + L_{Fe,Zn}^{\text{liq}}(3X_{Fe} - X_{Zn}) + L_{Fe,Zn}^{\text{liq}}(X_{Fe} - X_{Zn})(5X_{Fe} - X_{Zn}) \right]
$$

(3)

Equation (3) can be transformed from using the liquid phase based to bcc based with the aid of equation (4).

$$
oG_{Fe}^{\text{liq}} = oG^{\text{bcc}} + \Delta G_{Fe}^{\text{bcc-liq}} = oG^{\text{bcc}} - G_{Fe}^{\text{mag}} + \Delta G_{Fe}^{\text{bcc-liq}}
$$

(4)

In equation (4) the term $oG_{Fe}^{\text{bcc}}$ describes the Gibbs free energy of pure bcc iron. The term $G_{Fe}^{\text{mag}}$ represents for the magnetic contribution to the Gibbs free energy of bcc iron. The term $\Delta G_{Fe}^{\text{bcc-liq}}$ is the Gibbs free energy change associated with the transformation of hypothetical non-magnetic bcc (hbcc) iron to liquid iron. The value of $G_{Fe}^{\text{mag}}$ is described by equation (5) and (6) [9].
\[
G_{Fe}^{mag} = RT \ln(\beta + 1) f(\tau), \quad \tau = \frac{T}{T_C}
\]

\[
f(\tau) = 1 - \frac{0.9053}{\tau} - 0.30602\left(\frac{\tau^3}{2} + \frac{\tau^9}{45} + \frac{\tau^{15}}{200}\right)
\]

In equation (5) $\beta$ is the Bohr magneton number for iron equal to 2.22 and $T_C$ is the Curie temperature for iron equal to 1043K. The term $\Delta G_{Fe}^{bhc-c} \text{liq}$ is defined by equation (7).

\[
\Delta G_{Fe}^{bhc-c} \text{liq} = 12040.17 - 6.55843T - 3.675155 \times 10^{-21}T^7
\]

With the aid of equation (4), equation (3) is transformed into equation (8). The chemical potential term $\mu_{Fe}^{liq}$ now is equal to $\mu_{Fe}^{bhc}$ plus several terms that only depend on the concentration of the liquid ($X_{Zn}$=1-$X_{Fe}$) and its temperature.

\[
\mu_{Fe}^{liq} = \mu_{Fe}^{bhc} - G_{Fe}^{mag} + \Delta G_{Fe}^{bhc-c} \text{liq} + RT \ln X_{Fe}
\]

\[
+ X_{Zn}^2 \left[ 0 \nu_{Fe,Zn}^{liq} + (3X_{Fe} - X_{Zn}) \nu_{Fe,Zn,Fe}^{liq} + 2 \nu_{Fe,Zn}^{liq}(X_{Fe} - X_{Zn})(5X_{Fe} - X_{Zn}) \right]
\]

The maximum concentration of the bcc-iron that can be dissolved into the liquid zinc is described by equation (9) which states this occurs when the chemical potential of liquid iron is equal to the free energy of bcc-iron.

\[
\mu_{Fe}^{liq} = \mu_{Fe}^{bhc}
\]

Equation (8) defined values for $X_{Fe}$ as a function of temperature under the constraint imposed by equation (9) using the interaction parameters from 1.) Nakano,
2.1.2 Phases Described with a CALPHAD Multiple Sublattice Model

The thermodynamic model needed to describe the intermetallic compounds found in the Fe-Al-Zn system is based upon multiple sublattices. For example, Nakano et al. published the sublattice model \( (Fe, Va)_{0.072} (Zn, Va)_{0.072} (Zn)_{0.856} \) for the \( \zeta \) phase, shown in equation (10) [11,12].

\[
G_m^\zeta = y_{Fe}^{1} y_{Zn}^{2} \alpha G_{Fe:Zn:Zn}^{\zeta} + y_{Fe}^{1} y_{Va}^{2} \alpha G_{Fe:Va:Zn}^{\zeta} + y_{Va}^{1} y_{Zn}^{2} \alpha G_{Va:Zn:Zn}^{\zeta} + y_{Va}^{1} y_{Va}^{2} \alpha G_{Va:Va:Zn}^{\zeta} + 0.072RT \left[ y_{Fe}^{1} \ln y_{Fe}^{1} + y_{Va}^{1} \ln y_{Va}^{1} + y_{Zn}^{2} \ln y_{Zn}^{2} + y_{Va}^{2} \ln y_{Va}^{2} \right] \tag{10}
\]

In equation (10) \( \alpha G_{Fe:Zn:Zn}^{\zeta} \), \( \alpha G_{Fe:Va:Zn}^{\zeta} \), \( \alpha G_{Va:Zn:Zn}^{\zeta} \) and \( \alpha G_{Va:Va:Zn}^{\zeta} \) are the Gibbs free energy of the \( \zeta \) phase comprised of Fe:Zn:Zn, Fe:Va:Zn, Va:Zn:Zn and Va:Va:Zn, respectively, on three sublattices. Nakano et al. [12] published thermodynamic assessments of the intermetallic compounds in the Fe-Zn system in 2007.

The site fraction of iron in the first sublattice is denoted as \( y_{Fe}^{1} \) which is defined by equation (11) where \( n_{Fe}^{1} \) and \( n_{Va}^{1} \) are the number of moles of iron and vacancies, respectively, on the first sublattice [14].
The relationship between the site fraction of iron in the first sublattice and the mole fraction of iron is given by equation (12).

\[
y_{Fe}^{1} = \frac{n_{Fe}^{1}}{n_{Fe}^{1} + n_{Va}^{1}}
\]

The mole fraction of iron in the first sublattice is given by equation (12).

\[
X_{Fe} = \frac{n_{Fe}}{n_{Fe} + n_{Zn}} = \frac{y_{Fe}^{1}(0.072)}{y_{Fe}^{1}(0.072) + 0.856 + y_{Zn}^{2}(0.072)}
\]

In equation (12), \( X_{Fe} \) is the mole fraction of iron; \( n_{Fe} \) and \( n_{Zn} \) are the number of moles of iron and zinc, respectively, and \( y_{Fe}^{1} \) and \( y_{Zn}^{2} \) are the site fractions of iron in the first sublattice and zinc in the second sublattice, respectively. When an intermetallic compound is treated with a sublattice model, the chemical potential has to be determined with consideration to the stoichiometric constraint. For example, the chemical potential of the \( \zeta \) phase with a Va:Va:Zn structure can be obtained using equation (13).

\[
\mu_{Va_{1}Va_{2}Zn}^{\zeta} = 0.072\mu_{Va}^{1} + 0.072\mu_{Va}^{2} + 0.856\mu_{Zn}^{3}
\]

\[
= G_{m}^{\zeta} + \frac{\partial G_{m}^{\zeta}}{\partial y_{Va}^{1}} + \frac{\partial G_{m}^{\zeta}}{\partial y_{Va}^{2}} - y_{Fe}^{1} \frac{\partial G_{m}^{\zeta}}{\partial y_{Fe}^{1}} - y_{Va}^{1} \frac{\partial G_{m}^{\zeta}}{\partial y_{Va}^{1}} - y_{Zn}^{2} \frac{\partial G_{m}^{\zeta}}{\partial y_{Zn}^{2}}
\]

\[
= 0.856^{0}G_{Zn}^{hp} + 14T + y_{Fe}^{1}y_{Zn}^{2}[5370.91 - 17.816T] + 0.072RT[ln y_{Va}^{1} + ln y_{Va}^{2}]
\]

In equation (13), \( \mu_{Va}^{1} \) is the chemical potential of a vacancy in the first sublattice, and \( \mu_{Va}^{2} \) is the chemical potential of a vacancy in the second sublattice. The chemical potential of vacancies in a solid in equilibrium are taken as equal to zero [14]. The chemical potential of zinc in the third sublattice is \( \mu_{Zn}^{3} \) which equals \( \mu_{Zn}^{2} \) when the solid is in equilibrium.
A method to evaluate the chemical potential of an element in a sublattice is by substituting an element for another one in a certain sublattice, if there are vacancies in one of the sublattices [14]. For example, the second sublattice of the $\zeta$ phase has two components, zinc and vacancies. Equation (14) provides a method to obtain the chemical potential of zinc in the second sublattice because the chemical potential of a vacancy in the second sublattice is equal to zero at equilibrium.

$$\mu_{Zn}^\zeta = \frac{1}{0.072} (\mu_{Va:Zn:Zn}^\zeta - \mu_{Va:Va:Zn}^\zeta) = \mu_{Zn}^2 - \mu_{Va}^2 = \frac{1}{0.072} \left( \frac{\partial G_m}{\partial y_{Zn}^2} - \left( \frac{\partial G_m}{\partial y_{Va}^2} \right) \right)$$  \hspace{1cm} (14)

The chemical potential of zinc in the third sublattice is obtained by evaluating $\mu_{Va:Va:Zn}$.

$$\mu_{Zn}^3 = \frac{1}{0.856} \mu_{Va:Va:Zn}^\zeta = \frac{1}{0.856} \left[ 0.856 \sigma G_{Zn}^{lep} + 14T + y_{Va}^{1/2} y_{Zn}^{2/2} [5370.91 - 17.816T] \right]$$  \hspace{1cm} (15)

Appendix II will use equation (14) and (15) to show when the chemical potential of zinc in the second and third sublattices are the same, i.e., when the solid is in its lowest energy state.

Based on CALPHAD thermodynamic models for the liquid and intermetallic compounds with multiple sublattices, the Gibbs free energy diagram containing liquid, bcc, $\zeta$, $\delta$, $\Gamma$ and $\Gamma'$ phases in a binary Fe-Zn system can be defined at specific
temperatures. The driving force of precipitation of intermetallic phases and the solubility of iron in the molten zinc under a metastable or equilibrium state also can be determined.

2.2 A Thermodynamic Model of the Fe-Zn-Al System

2.2.1 CALPHAD Modeling of Liquid Iron-Zinc-Aluminum

The Gibbs free energy of one mole of atoms in a ternary Fe-Zn-Al liquid phase is defined in a CALPHAD based model by equation (16).

\[
G_m^{\text{liq}} = X_{Fe} \alpha G_{Fe}^{\text{liq}} + X_{Al} \alpha G_{Al}^{\text{liq}} + X_{Zn} \alpha G_{Zn}^{\text{liq}} \\
+ RT(X_{Fe} \ln X_{Fe} + X_{Al} \ln X_{Al} + X_{Zn} \ln X_{Zn}) \\
+ X_{Fe} X_{Zn} [\nu L_{Fe,Zn} + \frac{1}{2} L_{Fe,Zn} (X_{Fe} - X_{Zn}) + \frac{3}{2} L_{Fe,Zn} (X_{Fe} - X_{Zn})^2] \\
+ X_{Al} X_{Zn} [\nu L_{Al,Zn}] \\
+ X_{Fe} X_{Al} [\nu L_{Al,Fe} + \frac{1}{2} L_{Al,Fe} (X_{Al} - X_{Fe}) + \frac{3}{2} L_{Al,Fe} (X_{Al} - X_{Fe})^2]
\]

The values for the interactions parameters in equation (16) are cited in the recent work of Nakano et al. [12] and the paper by Mey and Seiersten [14] and are listed Appendix I.

The chemical potential of iron in the liquid phase is defined by differentiating \( G_m^{\text{liq}} \) as indicated in equation (17).

\[
\mu_{Fe}^{\text{liq}} = G_m^{\text{liq}} + \frac{\partial G_m^{\text{liq}}}{\partial X_{Fe}} X_{Fe} + \frac{\partial G_m^{\text{liq}}}{\partial X_{Zn}} X_{Zn} + \frac{\partial G_m^{\text{liq}}}{\partial X_{Al}} X_{Al}
\]

Inserting equation (16) into equation (17) and performing the required differentiation yields equation (18).
The chemical potential of aluminum in the liquid phase is defined by differentiating $G_m^{\text{liq}}$ as indicated in equation (19).

$$
\mu_{Al}^{\text{liq}} = G_m + \frac{\partial G_m}{\partial X_{Fe}} - X_{Fe} \frac{\partial G_m}{\partial X_{Fe}} - X_{Al} \frac{\partial G_m}{\partial X_{Al}} - X_{Zn} \frac{\partial G_m}{\partial X_{Zn}}
$$

(19)

Inserting equation (16) into equation (19) and carrying out the required differentiation yields equation (20).

$$
\mu_{Al} = ^{a}G_{Al}^{\text{liq}} + RT \ln X_{Al} + X_{Fe} \left( X_{Fe} + X_{Zn} \right)^{0} L_{Al,Fe}^{\text{liq}} + \left[ 2X_{Al} X_{Fe} \left( 2X_{Fe} + X_{Zn} \right) - X_{Fe}^{2} \right] L_{Al,Fe}^{\text{liq}} + \left[ X_{Fe} X_{Fe} \left( 3X_{Fe} - 3X_{Fe}^{2} + 6X_{Fe} X_{Fe} - 4X_{Fe} - 3X_{Fe}^{2} \right) + X_{Fe}^{3} \right] L_{Al,Fe}^{\text{liq}}
$$

(20)

The chemical potential of zinc in the liquid phase is defined by differentiating $G_m^{\text{liq}}$ as indicated in equation (21).

$$
\mu_{Zn} = G_m + \frac{\partial G_m}{\partial X_{Fe}} - X_{Fe} \frac{\partial G_m}{\partial X_{Fe}} - X_{Al} \frac{\partial G_m}{\partial X_{Al}} - X_{Zn} \frac{\partial G_m}{\partial X_{Zn}}
$$

(21)

Carrying out the required differentiation yields equation (22).
\[ \mu_{\text{Fe}} = \alpha G^{liq}_{\text{Fe}} + RT \ln X_{\text{Zn}} + X_{\text{Fe}} (X_{\text{Al}} + X_{\text{Zn}})^0 L^{liq}_{Fe,\text{Zn}} \]
\[ + \left[ 2X_{\text{Fe}} X_{\text{Zn}} (X_{\text{Al}} + X_{\text{Zn}}) - X_{\text{Zn}}^2 \right] L^{liq}_{Fe,\text{Zn}} \]
\[ + \left[ X_{\text{Fe}} X_{\text{Zn}} (3X_{\text{Fe}} - 3X_{\text{Fe}}^2 + 6X_{\text{Fe}}X_{\text{Zn}} - 4X_{\text{Zn}} - 3X_{\text{Zn}}^2) + X_{\text{Zn}}^3 \right] L^{liq}_{Fe,\text{Zn}} \]
\[ + X_{\text{Al}} (X_{\text{Fe}} + X_{\text{Al}})^0 L^{liq}_{Al,\text{Zn}} \]
\[ - X_{\text{Al}} X_{\text{Zn}}^0 L^{liq}_{Fe,\text{Zn}} + 2X_{\text{Al}} X_{\text{Fe}} (X_{\text{Fe}} - X_{\text{Al}})^1 L^{liq}_{Al,\text{Fe}} \]
\[ + X_{\text{Al}} X_{\text{Fe}} (-3X_{\text{Al}}^2 + 6X_{\text{Al}}X_{\text{Fe}} - 3X_{\text{Fe}}^2)^2 L^{liq}_{Al,\text{Fe}} \]  \hspace{1cm} (22)

The chemical potential of iron defined by Equation (18) can be transformed from liquid-based to bcc-based with the aid of equations (4) to (7). After transformation to a bcc-iron base, equation (18) was used to determine the maximum concentration of bcc-iron that can be dissolved into a liquid zinc-aluminum solution.

To convert the CALPHAD-based expression for the chemical potential of iron to activity requires rearranging equation (18) as indicated in equation (23) with a hypothetical non-magnetic bcc iron reference state.

\[ \mu^{liq}_{\text{Fe}} - \alpha G^{hbcc}_{\text{Fe}} = \Delta G^{hbcc\rightarrow liq}_{\text{Fe}} + RT \ln X_{\text{Fe}} + \left[ \text{Excess Terms} \right] = RT \ln a_{\text{Fe}} \]  \hspace{1cm} (23)

Substituting the excess terms results in equation (24).

\[ RT \ln a_{\text{Fe}} = \]
\[ \left\{ \begin{align*}
\Delta G^{hbcc\rightarrow liq}_{\text{Fe}} + RT \ln X_{\text{Fe}} + X_{\text{Zn}} (X_{\text{Zn}} + X_{\text{Al}})^0 L^{liq}_{Fe,\text{Zn}} \\
+ \left[ 2X_{\text{Zn}} X_{\text{Fe}} (2X_{\text{Zn}} + X_{\text{Al}}) - X_{\text{Zn}}^2 \right] L^{liq}_{Fe,\text{Zn}} \\
+ \left[ X_{\text{Zn}} X_{\text{Fe}} (3X_{\text{Fe}} - 3X_{\text{Fe}}^2 + 6X_{\text{Fe}}X_{\text{Zn}} - 4X_{\text{Zn}} - 3X_{\text{Zn}}^2) + X_{\text{Zn}}^3 \right] L^{liq}_{Fe,\text{Zn}} \\
+ X_{\text{Al}} (X_{\text{Fe}} + X_{\text{Al}})^0 L^{liq}_{Al,\text{Fe}} + \left[ X_{\text{Al}}^2 - 2X_{\text{Al}} X_{\text{Fe}} (2X_{\text{Al}} + X_{\text{Zn}}) \right] L^{liq}_{Al,\text{Fe}} \\
+ \left[ X_{\text{Al}} X_{\text{Fe}} (3X_{\text{Fe}} - 3X_{\text{Fe}}^2 + 6X_{\text{Fe}}X_{\text{Al}} - 4X_{\text{Al}} - 3X_{\text{Al}}^2) + X_{\text{Al}}^3 \right] L^{liq}_{Al,\text{Fe}} \\
- X_{\text{Al}} X_{\text{Zn}}^0 L^{liq}_{Fe,\text{Zn}} \end{align*} \right\} \]  \hspace{1cm} (24)
The same procedure can be applied to aluminum and zinc to estimate the activities of these components based on their reference states, fcc and hcp, respectively.

### 2.2.2 Modeling an Fe-Zn-Al Intermetallic Compounds

The same formalism contained in equation (10) is applied to the ternary Fe-Zn-Al system with additional terms used to describe the aluminum component. For example, with a sublattice model, the $Fe_2Al_5(Zn,Va)_3$ phase is described by equation (25) [12].

$$
G_m = y_{Zn}^3 \alpha G_{Fe;Al;Zn}^{Fe_2Al_5} + y_{Va}^3 \alpha G_{Fe;Al;Va}^{Fe_2Al_5} + 3RT \left[ y_{Zn}^3 \ln y_{Zn}^3 + y_{Va}^3 \ln y_{Va}^3 \right]
$$

In equation (25) $\alpha G_{Fe;Al;Zn}^{Fe_2Al_5}$ and $\alpha G_{Fe;Al;Va}^{Fe_2Al_5}$ are the Gibbs free energy of the hypothetical phases $Fe_2Al_5Zn_3$ and $Fe_2Al_5Va_3$, respectively.

The chemical potential of a compound, i.e. $\mu_{Fe;Al;Zn}$, is defined by equation (26).

$$
\mu_{Fe;Al;Zn} = G_m^0 + \frac{\partial G_m}{\partial y_{Zn}^3} y_{Zn}^3 + \frac{\partial G_m}{\partial y_{Va}^3} y_{Va}^3
$$

Carrying out the differentiation yields equation (27).

$$
\mu_{Fe;Al;Zn}^{Fe_2Al_5} = \alpha G_{Fe;Al;Zn}^{Fe_2Al_5} + 3RT \left[ \ln y_{Zn}^3 \right]
$$

Equation (28) defines the chemical potential of zinc in the third sublattice.

$$
\mu_{Zn}^3 = \mu_{Fe;Al;Zn} - \mu_{Fe;Al;Va} = \left( \frac{\partial G_m}{\partial y_{Zn}^3} - \frac{\partial G_m}{\partial y_{Va}^3} \right)
$$

$$
= \alpha G_{Fe;Al;Zn}^{Fe_2Al_5} - \alpha G_{Fe;Al;Va}^{Fe_2Al_5} + 3RT \left[ \ln y_{Zn}^3 - \ln y_{Va}^3 \right]
$$
After inserting interaction parameters of Nakano et al. [12] into equation (25), the intermetallic compound \( \text{Fe}_2\text{Al}_5 : \text{Fe}_2\text{Al}_5 (\text{Va}, \text{Zn})_3 \) with the stoichiometric composition \( \text{Fe}_2\text{Al}_5\text{Zn}_{1.32} \) was found to possess the minimum free energy at 465°C. The stoichiometric ratio is required to estimate the driving force for the nucleation and growth of this \( \text{Fe}_2\text{Al}_5\text{Zn}_x \) phase.

### 2.3 Dissolution Kinetic Model

The transport of iron from a steel sheet into a liquid zinc bath involves a two-step process. First, iron must leave its bcc matrix phase and then dissolve into the boundary layer of the liquid zinc. That process is indicated as dissolution in Figure 5. Secondly, iron after dissolving into liquid zinc has to diffuse across the boundary layer as also shown in Figure 5.

Equation (29) is widely used to investigate the dissolution of iron in liquid zinc and the diffusion of iron across its boundary layer [19][20].

\[
\frac{d w_{Fe}^w}{dt} = k_{dif} \frac{S}{V} \left( w_{MAX}^{Fe} - w_{Fe}^w \right) \tag{29}
\]

In equation (29) \( w_{Fe}^w \) is the concentration of iron (wt.%) in liquid zinc bath outside of the boundary layer. \( k_{dif} \) is the dissolution rate constant. The term \( S \) is the total
contact area \( (m^2) \) between the solid iron and the liquid bath. The term \( V \) is the volume of the liquid bath \( (m^3) \), and \( W_{Fe}^{MAX} \) (wt.\%) is the maximum solubility of iron in the molten zinc bath.

Figure 5: A schematic diagram showing iron dissolution to be a two-step process: 1.) transfer of iron from a steel sheet into a liquid zinc bath and 2.) diffusion of iron across a liquid zinc boundary layer.

The dissolution model can be represented in different forms. For example, when a dissolution experiment involves iron in a molten zinc bath, it is often convenient to measure the iron concentration as a weight fraction. Taking into account the density of the molten zinc bath, equation (29) can be adapted to evaluate the overall dissolution constant \( k_{dif} \) yielding equation (30).
In equation (30) the term $M_{\infty}^F$ is the mass of dissolved iron (kg), $\rho$ is the density of the molten zinc bath; $w_{Fe}^{MAX}$ is the maximum solubility (wt.%) of iron in liquid zinc and $w_{Fe}^\infty$ is the iron concentration (wt.%) in the liquid zinc just outside the boundary layer adjacent to a steel sheet surface. Equation (30) clearly indicates that the values for $w_{Fe}^{MAX}$ and $k_M$ will dictate the rate of iron dissolution predicted by a model based upon convective mass transport. If a dissolution experiment uses molar concentration, the mass transport is defined by equation (31).

$$\frac{dM_{Fe}^\infty}{dt} = k_{mol} S \left( \frac{\rho}{100} \right) (w_{Fe}^{MAX} - w_{Fe}^\infty)$$ \hspace{1cm} (30)$$

Multiplying equation (31) by $M_{Fe} + M_{Zn}$ and dividing by the atomic weight of iron yields the equation (32).

$$\frac{d}{dt} \frac{100M_{Fe}^\infty}{M_{Fe} + M_{Zn}} = k_{dif} \frac{S}{V} \left( \frac{100M_{Fe}^{MAX}}{M_{Fe} + M_{Zn}} - \frac{100M_{Fe}^\infty}{M_{Fe} + M_{Zn}} \right)$$ \hspace{1cm} (31)$$

Simplifying equation (32) results in equation (33).

$$\frac{dM_{Fe}^\infty}{dt} = k_{dif} \frac{S}{V} \left( \frac{M_{Fe}^{MAX}}{MW_{Fe}} - \frac{M_{Fe}^\infty}{MW_{Fe}} \right)$$ \hspace{1cm} (32)$$

$$\frac{dC_{Fe}^\infty}{dt} = k_{dif} \frac{S}{V} (C_{Fe}^{MAX} - C_{Fe}^\infty)$$ \hspace{1cm} (33)$$
In equation (33) \( C_{Fe}^{\infty} \) is the mole fraction of iron in the molten zinc and \( C_{Fe}^{MAX} \) is the maximum mole fraction of iron in the molten zinc. The units for dissolution rate constant (m/s) are the same as those in equation (29).

Equation (29) was integrated from the initial condition of \( w_{Fe}^{(i)} \) at \( t=0 \) to the final condition of \( w_{Fe}^{(f)} \) at \( t=t_f \) which produced equation (34).

\[
\ln \frac{w_{Fe}^{MAX} - w_{Fe}^{(i)}}{w_{Fe}^{MAX} - w_{Fe}^{(f)}} = \ln K_w = k_{dif} \frac{S}{V} t_f
\]  

(34)

To estimate the dissolution rate constant \( k_{dif} \), it is essential to measure \( w_{Fe}^{(f)} \) as a function of time, \( t_f \). If a linear dependence is observed, when the left side of equation (34), design at \( \ln K_w \), is plotted as a function of \( \frac{S}{V} t_f \), regression can determine its slope which defines the dissolution rate constant.

### 2.4 Dissolution Rate Associated with Diffusion Across a Boundary Layer

When dissolution is controlled by diffusion of a metal across a boundary layer in a liquid, it can be shown that the dissolution rate constant is defined by a relationship that depends on the Schmidt number, \( Sc = \frac{V}{D} = \frac{\mu}{\rho D} \), as indicated in equations (35) and (36) [19][22].

\[
k_{dif} = 0.62 D_{L}^{2/3} \nu^{-1/6} \omega^{1/2} \text{ for } Sc > 1000
\]  

(35)
In equations (35) and (36) \( f_{Sc} \) is a constant whose value depends upon \( Sc \) \[22\]; \( D_L \) is the diffusion coefficient of iron in a liquid zinc bath; \( \nu \) is the kinematic viscosity of the liquid zinc bath \( (5 \times 10^{-7} \text{ m}^2 \cdot \text{s}^{-1} \text{ for zine at } 465^\circ \text{C} \text{[19]} \) and \( \omega \) is the angular velocity of a rotating disc specimen. Equations (35) and (36) predict that \( k_{dif} \) should be a linear function of the square root of the angular velocity of the disc specimen.

The tangential (linear) velocity \( V \) of each point located \( r \) from the center of a disc specimen is given by equation (37).

\[
V = r \cdot \omega
\]

\[\text{(37)}\]

The mean (average) linear velocity for a disc with radius \( r_0 \) is given by equation (38).

\[
\bar{V} = \frac{2}{3} r_0 \cdot \omega
\]

\[\text{(38)}\]

Combining equations (36) and (38) reveals that the dissolution rate constant \( k_{dif} \) is a function of the square root of the mean linear velocity of a disc.

2.5 A Heat-Transfer Model

As a steel sheet exits the cooling section of a continuous annealing furnace and enters the molten zinc bath in commercial HDG processing, the strip entry temperature is
always higher than the zinc bath temperature. How the temperature of the strip changes after it contacts the liquid bath can be predicted. The duration of this transition state has a marked effect on the formation of dross phases. The change of temperature of the immersed strip after it enters a zinc bath is described by equation (39) which is based upon convective heat-transfer [23].

\[
T_S = (T_{set} - T_b) \times \exp\left[\frac{-h_S \times t}{(\rho_S \times 2a \times C_P^S)}\right] + T_b
\]  

In equation (39) \(T_{set}\), \(T_b\) and \(T_S\) are the strip-entry temperature, molten zinc bath temperature and steel strip temperature, respectively, at immersion time \(t\). The term \(h_S\) is the convective heat-transfer coefficient at the strip-bath interface. \(\rho_S\) is the density of the steel strip; 2a is the strip thickness and \(C_P^S\) is the heat capacity of the steel strip.

In this mathematical model, the important variables which affect the time dependence of the strip temperature are its velocity, dimensions and temperature when it first enters the liquid bath temperature. The value for \(h_S\) is estimated by using the local Nusselt number for a flat plate traveling through liquid metal at a constant temperature over its entire length [23].

\[
Nu = \frac{\sqrt{RePr}}{1.547Pr + 1.885 \sqrt{1 - 0.404}Pr} = \frac{hL}{K_{zn}}
\]  

In equation (40) Pr is the Prandtl number and Re is the Reynolds number.
\[
\text{Pr} = \frac{\mu_{\text{Zn}} C_{p}^{\text{Zn}}}{K_{\text{Zn}}} \tag{41}
\]
\[
\text{Re} = \frac{\rho_{\text{Zn}} v L}{\mu_{\text{Zn}}} \tag{42}
\]

In equations (41) and (42) \(C_{p}^{\text{Zn}}\) is the heat capacity of zinc; \(K_{\text{Zn}}\) is the thermal conductivity of molten zinc; \(v\) is the strip velocity; \(L\) is the characteristic length of the strip, and \(\mu_{\text{Zn}}\) is the viscosity of liquid zinc, an exponential function of the bath temperature as given by equation (43).

\[
\mu_{\text{Zn}} = \mu_{0} \exp\left(\frac{E}{RT_{b}}\right) \tag{43}
\]

In equation (43) \(\mu_{0}\) is equal to \(0.3699 \text{mNs/m}^2\), and \(E\) is equal to \(12.7 \text{kJ/mol}\).

The density of liquid zinc \(\rho_{\text{Zn}}\) as a function of temperature is given as follows:

\[
\rho_{\text{Zn}} = \rho_{0} + (T_{b} - T_{0}) \frac{d\rho_{\text{Zn}}}{dT} \tag{44}
\]

In equation (44) \(\rho_{0} = 6.575 \times 10^3 \text{kg/m}^3\); \(T_{0}\) is the melting temperature of zinc, 692.5K and \(\frac{d\rho_{\text{Zn}}}{dT}\) is equal to \(-1.1 \text{kg/m}^3 \cdot \text{K}\).

Based on equations (40) to (44), the heat-transfer coefficient at the strip-bath interface is a function of the strip velocity. The average heat-transfer coefficient was found to fall in the range of 5000 to \(15000 \text{W/m}^2\cdot\text{K}\) for strip velocities of 1 to 4m/s [1].
2.6 Nucleation Rates

This section will construct a model to estimate the heterogeneous nucleation rate of the $\text{Fe}_2\text{Al}_5\text{Zn}_x$ intermetallic compound and the homogeneous nucleation rate of the delta phase.

2.6.1 The Heterogeneous Nucleation of $\text{Fe}_2\text{Al}_5\text{Zn}_x$

The nucleation rate of $\text{Fe}_2\text{Al}_5\text{Zn}_x$ embryos on the surface of a steel strip can be predicted based upon heterogeneous nucleation theory. A schematic diagram for heterogeneous nucleation of a particle on a steel strip is shown in Figure 6.

![Figure 6: A schematic diagram illustrating the interfacial energies associated with heterogeneous nucleation of a particle on a steel strip.](image)

The analysis of interfacial tensions $\gamma_{s/l}$, $\gamma_{p/s}$ and $\gamma_{p/l}$ leads to an equilibrium defined in equation (45).

\[
\gamma_{s/l} = \gamma_{p/s} + \gamma_{p/l}\cos\theta \quad \text{or} \quad \cos\theta = \left(\frac{\gamma_{s/l} - \gamma_{p/s}}{\gamma_{p/l}}\right)
\]  

(45)
To simplify the problem, it is assumed that the wetting angle of the particles is 90°, i.e., \( \gamma_{s/l} = \gamma_{p/s} \), which results in the nucleation of a hemisphere. The same assumption is found in the published studies by Tang et al. [1] and Giorgi et al. [7]. The free energy change per volume of the intermetallic compound formed is determined by using a CALPHAD analysis. For the Fe\(_2\)Al\(_5\)Zn\(_x\) phase, the arrangement associated with the minimum free energy is that \( x \) equals 1.32 based upon the thermodynamic assessments published by Nakano et al. [11][12]. A factor of 8.32 must be used when converting from a formula unit to a gram-atom, i.e., mole of formula units to mole of atoms, basis for \( \Delta G \).

The precipitation of a particle is driven by the supersaturation of the elements of Fe, Al and Zn in the bath. These components combine to form a particle with a lower energy state. The driving force for the precipitation of a particle is given by the energy difference of each component between being in the liquid phase to being in the intermetallic compound, e.g., Fe\(_2\)Al\(_5\)Zn\(_x\). The reaction needed to form Fe\(_2\)Al\(_5\)Zn\(_{1.32}\) is shown in equation (46) and the \( \Delta G \) for that reaction is defined in equation (47).

\[
\begin{align*}
\left\{ \frac{2}{8.32} Fe_{(liq, \text{in molten zinc})} + \frac{5}{8.32} Al_{(liq, \text{in molten zinc})} + \frac{1.32}{8.32} Zn_{(liq, \text{in molten zinc})} \right\} & \rightarrow \frac{1}{8.32} Fe_2Al_5Zn_{1.32} \\
\end{align*}
\]
\[
\Delta G = \Delta G_{ref} + RT \ln \frac{a_{Fe_{2}Al_{5}Zn_{1.32}}^{\frac{1}{2}}}{a_{Fe}^{\frac{2}{5}} a_{Al}^{\frac{5}{5}} a_{Zn}^{1.32}}
\]  \hspace{2cm} (47)

In equation (47) the term \( \Delta G \) is the driving force of formation \( Fe_{2}Al_{5}Zn_{1.32} \) and the term \( \Delta G_{ref} \) is the formation energy of one mole of atoms of \( Fe_{2}Al_{5}Zn_{1.32} \) from hbcc-Fe, fcc-Al and hcp-Zn in the reference states. The terms \( a_{Fe_{2}Al_{5}Zn_{1.32}}, a_{Fe}, a_{Al}, \) and \( a_{Zn} \) are the activities of \( Fe_{2}Al_{5}Zn_{1.32} \) on the steel strip, and iron, aluminum and zinc in the molten zinc, respectively. The relationship between the driving force corresponding to one mole of atoms and the driving force per unit volume of the \( Fe_{2}Al_{5}Zn_{1.32} \) is given by equation (48).

\[
\Delta G_v = \frac{\rho_{Fe_{2}Al_{5}Zn_{1.32}}}{MW_{Fe_{2}Al_{5}Zn_{1.32}}} \Delta G = \Delta G \times 117952.85 \left[ J / m^3 \right]
\]  \hspace{2cm} (48)

In equation (48), \( \rho_{Fe_{2}Al_{5}Zn_{1.32}} \) is the density of \( Fe_{2}Al_{5}Zn_{1.32} \), given as \( 4720,000 g/m^3 \), and \( MW_{Fe_{2}Al_{5}Zn_{1.32}} \) is the atomic weight of one mole of atoms of \( Fe_{2}Al_{5}Zn_{1.32} \), given as 39.95. The free energy change associated with heterogeneous nucleation of a particle on a liquid/solid interface is described by equation (49).

\[
\Delta G_{het} = \left\{ -\frac{1}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \gamma_v \right\} S(\theta), S(\theta) = (2 + \cos\theta)(1 - \cos\theta)^2 / 4
\]  \hspace{2cm} (49)

In equation (49) \( \Delta G_v \) is the free energy associated with the formation of unit volume of \( Fe_{2}Al_{5}Zn_{1.32} \) and \( r \) is the radius of the nucleus. \( S(\theta) \) is the structure factor.
equal to 0.5 for nucleation of a hemisphere. The term $\gamma_{p/l}$ is the interfacial energy between the particle and the liquid (taken to be 0.245 J/m$^2$ [7]).

The activation energy barrier of heterogeneous nucleation $\Delta G^*$ at the critical radius $r^*$ is given as follows:

$$
\Delta G^* = \frac{16\pi \gamma_{p/l}^3}{3\Delta G^*_f} S(\theta)
$$

(50)

$$
r^* = \frac{2\gamma_{p/l}}{\Delta G^*_f}
$$

(51)

The number of embryos that reached the critical size is given by equation (52) if every aluminum atom that impinges on the steel surface is captured and forms a cluster.

$$
N = \Omega f C_{Al} \exp\left(-\frac{\Delta G^*}{kT}\right)
$$

(52)

In equation (52) the term $N$ is the heterogeneous nucleation rate per unit area per second. The term $\Omega$ is the concentration of heterogeneous nucleation sites per unit area, given as $\sim 10^{19}$ m$^{-2}$, and the term $C_{Al}$ is the mole fraction of aluminum at the steel/liquid interface. The term $f$ is a complex function that depends on the vibration frequency of the atoms, the activation energy of Al diffusion in the molten zinc, and the surface of the nucleus, and it is usually taken to be equal to $10^{11}$ s$^{-1}$ [27].
2.6.2 The Homogeneous Nucleation of the δ-Phase

The delta phase also can nucleate when the Fe content is in a molten zinc bath is in a supersaturated state. Different from Fe$_2$Al$_5$Znx, the bottom dross, delta phase, forms by a homogeneous nucleation mechanism. The homogeneous nucleation rate is defined by equation (53).

\[
N = fC \exp \left( \frac{-\Delta G_{\text{hom}}^*}{kT} \right)
\]  
(53)

In equation (53) the term \( N \) is the nucleation rate, \( f \) is the thermal vibration constant, given as $10^{11} \text{s}^{-1}$, and \( C \) is the number of atoms per unit volume in a liquid zinc bath, estimated as $\sim 10^{29} \text{atom/m}^3$ [27]. The term \( \Delta G_{\text{hom}}^* \) is the activation energy barrier for the formation of a nucleus, defined by equation (54).

\[
\Delta G_{\text{hom}}^* = \left( \frac{16 \pi \gamma_{p/l}^3}{3 \Delta G_{\text{p}}^2} \right)
\]  
(54)

In equation (54) \( \gamma_{p/l} \) is the interfacial tension between a delta phase particle and the liquid zinc, and \( \Delta G_{\text{p}}^2 \) is the driving force per unit volume for the formation the delta phase. The reaction to form delta phase is shown in equation (55) and the \( \Delta G \) for that reaction is defined in equation (56).

\[
\begin{align*}
0.1288 & Fe_{\text{(lq, in molten zinc)}} \\
+0.0667 & Al_{\text{(lq, in molten zinc)}} \\
+0.8045 & Zn_{\text{(lq, in molten zinc)}} \\
\implies & Fe_{0.058} \left( Fe_{0.39} , Al_{0.375} , Zn_{0.235} \right)_{0.180} Zn_{0.525} Zn_{0.237},
\end{align*}
\]  
(55)
\[ \Delta G = G_{ref} + RT \ln \frac{a_g}{a_{Fe}^{0.1288} a_{Al}^{0.0667} a_{Zn}^{0.8045}} \]  

Equation (56) describes the free energy change associated with precipitation of the delta phase at a given temperature. Equation (57) is used to convert \( \Delta G \) based upon one mole of atoms to \( \Delta G_v \), the free energy associated with the formation of a unit volume of the delta phase.

\[ \Delta G_v = \frac{\Delta G}{V_M^{\delta}} = \Delta G \times 119927.4 \left[ \frac{J}{m^3} \right] \]  

With the aid of equations (53) to (57), the nucleation rate of a delta phase can be calculated as a function of the iron concentration, the aluminum concentration and the bath temperature.

2.7 Precipitate Growth Rate

During the nucleation process, the inhibition layer on a steel surface forms a continuous array of hemispherical precipitates until they fully cover the steel surface [7]. Then, the inhibition layer grows in a planar like mode into the liquid bath, and the growth rate is controlled by the diffusivity of iron in the liquid zinc. The precipitation of the \( \delta \)-phase occurs in the form of spherical particles. To analyze both situations, two kinds of
growth models are required: 1.) the growth of a spherical precipitate and 2.) the growth of a planar precipitate.

### 2.7.1 Growth of a Spherical Precipitate

For a galvanizing process, where the Al content in the molten zinc bath is between 0.1-0.3 wt. pct., the rate-controlling step for the growth of the inhibition layer was found to be the diffusion of Al in the molten zinc bath [1,7,29]. Zener [26] published “Theory of Growth of Spherical Precipitates from Solid Solution,” which provides a solid fundamental model that describes the growth of precipitates. To derive an equation for the growth of a spherical particle, it is essential to use Fick’s second law applied to a spherically symmetric system.

\[
\frac{\partial C}{\partial t} = D \frac{\partial}{\partial r} \left( r^2 \frac{\partial C}{\partial r} \right) \quad (58)
\]

Assuming the operator in a steady-state regime and integrating twice yields:

\[
C(x) = A + B / r \quad (59)
\]

The concentration profile across the precipitate and into the liquid bath is shown in Figure 7.
In Figure 7, if the radius of the precipitate is large enough, the Gibbs-Thomson effect at the interface is insignificant. The concentration of a solute in the intermetallic compound is given by $C_\beta$, and the concentration of a solute in the liquid bath is given by $C_0$. The term $C_e$ is the concentration of the solute in a liquid bath in equilibrium with the intermetallic compound.

\[
\frac{\partial C}{\partial r} = D \frac{\partial^2 C}{\partial r^2} = -D \frac{B}{r^2}
\]

Figure 7: The concentration profile for a growing precipitate.

The growth of the intermetallic compound involves a moving boundary and spherical coordination. The mass balance is defined by the following equation [26]:

\[
\frac{d(C_\beta - C_e)}{dt} = D \frac{\partial C}{\partial r} = D \frac{\partial(A + B/r)}{\partial r} = -D \frac{B}{r^2}
\]  

(60)

In equation (60) the term $D$ is the diffusivity of the diffusion-controlling component. For example, the growth rate of the Fe$_2$Al$_5$Zn$_x$ is controlled by the diffusivity

35
of Al in the molten zinc bath. Tang et al. [6] published the Al diffusivity in molten zinc in the temperature range pertinent to the galvanizing process is shown in equation (61).

\[ D_{Al}^{Zn(L)} = 2 \times 1.12 \times 10^{-7} \exp \left( \frac{-2809}{T_b} \right) \left[ \frac{m^2}{s} \right] \]  

(61)

The terms A and B are established by two positions in the concentration profile. The conditions determined by these two cases are given in equation (62).

\[ C_e = A + \frac{B}{r} \]  
\[ C_o = A + \frac{B}{\infty} \]  

(62)

Inserting equation (62) into equation (60) yields equation (63).

\[ \left( C_\beta - C_c \right) \frac{dr}{dt} = D \frac{\left( C_o - C_e \right)}{r} \]  

(63)

Equation (63) can be simplified by multiplied both sides by \( r \) and integrating to produce equation (64).

\[ r = \sqrt{\frac{2 \left( C_o - C_e \right)}{C_\beta - C_c}Dt} \]  

(64)

Equation (64) shows that the precipitates grow as a function of the square root of time. However, as the precipitates start to have overlapping diffusion fields, the growth rate slows and equation (64) no longer applies.
2.7.2 Growth of a Plate Precipitate

The derivative of the growth of a planar precipitate controlled by the diffusivity of solute in the matrix is given as equation (65). This growth velocity, \( v \), is controlled by the diffusivity of solute in the matrix and the concentration difference between the solute in the matrix and that at the interface [26].

\[
v = \frac{dx}{dt} = \frac{D}{C_\beta - C_e} \frac{dC}{dx}
\]  

(65)

In equation (65) the term \( D \) is the diffusivity of solute in the matrix. The terms \( C_\beta \) and \( C_e \) are the concentration of solute in the intermetallic compound and in the liquid zinc bath, respectively. Figure 8 contains a schematic diagram describing the concentration profile associated with a growing precipitate.

![Figure 8: The concentration profile of a growing planar interface.](image)

Figure 8: The concentration profile of a growing planar interface.
The model associated with planar growth plays an important role in the study of the rate of formation of the inhibition layer. The Johnson-Mehl-Avrami equation is used to predict the overall phase transformation rate by combining the kinetics of nucleation and growth.

2.8 Johnson-Mehl-Avrami Equation

The Johnson-Mehl-Avrami equation usually is used to describe the rate of a phase transformation at a constant temperature. The amount of new phase will depend on the kinetics of nucleation and growth. In a continuous hot-dip galvanizing process, as the steel strip enters the molten zinc bath, the Al atoms begins to diffuse to the surface of the strip and form an intermetallic compound, i.e. Fe$_2$Al$_5$Zn$_x$. The immersion time of a strip usually is between 2 and 4 second [1], which means the inhibition layer has to cover the whole steel strip in much less than that period of time.

2.8.1 Phase Transformation on a Plane

When a Fe$_2$Al$_5$Zn$_x$ embryo forms on the surface of a steel sheet, it will continue to grow out until it impinges upon another growing particle. If the cells grow as spheres
with a radius, \( r \), as given in equation (64), the area on the surface of the steel sheet covered by the particle is given as a function of time by equation (66).

\[
A = \pi r^2 = \pi 2 \frac{C_o - C_i}{C_i - C_i} D_{liq}^{zn} t = kt, \quad k = \pi 2 \frac{C_o - C_i}{C_i - C_i} D_{liq}^{zn}
\]

(66)

A particle does not reach the critical radius \( r^* \) until time \( \tau \). Also, the number of nuclei that formed will be \( N dt \) per unit area of untransformed phase. Thus, if the particles do not impinge on one another, the total area they would cover is given by equation (67).

\[
A_i = \sum A' = kN \int_0^\tau (t - \tau) d\tau = \frac{1}{2} Nkt^2
\]

(67)

Equation (67) is only valid for the fraction of the surface covered \( f << 1 \). As time passes, the particles of the transforming phase will eventually impinge on one another and the transformation rate will decrease. In that case, the equation valid for randomly distributed nuclei for both long and short times is:

\[
f = 1 - \exp\left(-\frac{1}{2} Nkt^2\right)
\]

(68)

Equation (68) is known as a Johnson-Mehl-Avrami equation for a phase transformation occurring on a surface. In equation (68) the term \( f \) is the fraction of the surface covered by the transforming phase, \( D \) is the diffusivity of the rate determining
component in the molten zinc; \( N \) is the nucleation rate per unit area (\#·m\(^{-2}\)·s\(^{-1}\)) and \( t \) is the reaction time. With the aid of the John-Mehl-Avrami equation, the total number of nuclei formed, \( N_T \), in time, \( t \), is given as:

\[
N_T = \int_0^t N(1 - f) \, dt = N \frac{1}{2} \sqrt{\pi} \text{erf}\sqrt{at}, \quad a = \pi N \frac{C_{Al}^0 - C_{Al}^e}{C_{Al}^0 - C_{Al}^e} D_{Al}^{\text{eq}} Zn
\]

(69)

The average area, \( \bar{A} \), occupied by the nuclei that have formed in time, \( t \), is given as:

\[
\bar{A} = \frac{A_T}{N_T} = \frac{A_0 \left(1 - \exp\left(-\frac{1}{2} Nkt^2\right)\right)}{N_T}
\]

(70)

The area of each hemispheric particle, \( A \), can be converted to its volume, \( V \), with the aid of equation (71).

\[
V = \frac{2}{3} \pi \left(\frac{A}{\pi}\right)^{3/2} = 0.376 A^{3/2}
\]

(71)

The total volume, \( V_T \), of all of the Fe\(_2\)Al\(_5\)Zn\(_x\) phase formed in time, \( t \), is given by:

\[
V_T = 0.376 \left(\bar{A}\right)^{3/2} N_T
\]

(72)

Dividing \( V_T \) by unit area, \( A_0 \), yields the average thickness of the Fe\(_2\)Al\(_5\)Zn\(_x\) inhibition layer as a function of time, \( t \). The relationship between the average layer thickness and the size of individual particles of Fe\(_2\)Al\(_5\)Zn\(_x\) that have nucleated on the steel sheet surface is schematically illustrated in Figure 9.
Figure 9: A schematic diagram of the relationship between the average layer thickness and the size of individual particles of $\eta$-phase on the steel sheet surface.

After the $\text{Fe}_2\text{Al}_5\text{Zn}_x$ completely covers the surface of the sheet, the growth of the inhibition layer is controlled by the diffusivity of iron in the liquid zinc. The flux of iron to surface of the $\eta$-phase is less than that of aluminum during its planar growth stage for two reasons. First the large supersaturation of iron that caused rapid nucleation and surface coverage is dissipated by the formation of the $\eta$-phase and a much smaller iron supersaturation remains to drive the planar growth. Secondly, the diffusivity of aluminum in molten zinc is four times greater than that for iron [6].

The total thickness of the inhibition layer accounting for its initial kinetics of formation and then planar growth is given in equation (73).

$$X_T = \frac{0.376}{A_o} A^{3/2} N_T + \frac{2}{\sqrt{\pi}} \frac{C_{Fe}^\infty - C_{Fe}^c}{C_{Fe}^\infty - C_{Fe}^c} \sqrt{D_{\text{Zn}}^{\text{liq}} t}$$  \hspace{1cm} (73)
The thickness of the inhibition layer can be converted to the mass of aluminum per unit area it contains by using the relationship $0.444\text{nm}$ of the $\eta$-phase inhibition layer requires $0.001\text{g/m}^2$ of aluminum.

### 2.8.2 Phase Transformation in a Volume

The nucleation and growth of $\delta$-phase particles appears to occur in the interior of a zinc bath where it causes the formation of bottom dross. The $\delta$-phase contains twice as much iron as aluminum. The rate of diffusion of iron in liquid zinc is one fourth that of aluminum. As such, the flux of iron should control the nucleation and growth of $\delta$-phase particles. If the $\delta$-phase particles precipitate in the interior of a zinc bath, it is reasonable to treat their formation as due to homogeneous nucleation. A method is presented to estimate the size and number of $\delta$-phase particles formed by homogeneous nucleation and diffusion controlled growth by introducing a depletion volume. A region depleted of iron expands around each growing $\delta$-phase particle. When the depletion volumes enlarge to the point where they occupy all of the available volume, growth of the $\delta$-phase particles ceases. The size of $\delta$-phase particles can be estimated through a mass balance between
the amount of iron lost in the depletion region and the amount of iron absorbed into the δ-phase. The mass balance is defined through equation (74).

$$\left( C_{Fe}^{e} - C_{Fe}^{o} \right) \frac{4}{3} \pi r_d^3 = \left( C_{Fe}^{\delta} - C_{Fe}^{e} \right) \frac{4}{3} \pi r_p^3$$  \hspace{1cm} (74)$$

In equation (74) \( r_d \) and \( r_p \) are the radii of the depleted region and the δ-phase particle, respectively. The concentration parameters in equation (74) are defined in Figure 8. The factor of 0.5 associated with the iron content extracted from the depleted region follows the simplified linear approach originally due to Zener [26].

The combined process of homogeneous nucleation and growth of δ-phase particles and their corresponding sphere of depletion of iron can be treated by the Johnson-Mehl-Avrami equation based upon the rate of nucleation and growth of the depletion regions. The volume occupied by a depletion region around a δ-phase particle in given by equation (75).

$$V = \frac{4}{3} \pi r_d^3 = \left( \frac{4}{3} \right) \left( \frac{1}{2} \right) \pi \left( \frac{C_{Fe}^{e} - C_{Fe}^{o}}{C_{Fe}^{\delta} - C_{Fe}^{e}} \right) \left( 2 \frac{C_{Fe}^{e} - C_{Fe}^{o}}{C_{Fe}^{\delta} - C_{Fe}^{e}} D_{Fe}^{eq \tau} \right)^{3/2} t^{3/2} = mt^{3/2}$$  \hspace{1cm} (75)$$

The total volume occupied by all of the depleted regions independently of impingement is given as follows:

$$\sum V = mN \int_{0}^{t} (t - \tau)^{3/2} d\tau = \frac{2}{5} mN t^{5/2}$$  \hspace{1cm} (76)$$
Inserting of equation (76) into the Johnson-Mehl-Avrami equation applied to homogeneous nucleation and growth yields equation (77).

\[ f = 1 - \exp \left( -\frac{2}{5} Nt \delta^2 \right) \]  

(77)

In equation (77) \( f \) is the fraction of the total volume consumed by the depletion regions surrounding the \( \delta \)-phase particles at time, \( t \). Equation (77) was used to determine the length of time required for the depletion region around each \( \delta \) phase particle to occupy a certain fraction of the total volume.
3. Results and Discussion

3.1 Solubility of Iron in Liquid Zinc

The solubility lines for bcc-iron in liquid zinc are plotted in Figure 10 where $X_{Fe}$ has been converted into Fe wt. pct. and the working temperature is in Celsius. Figure 10 shows that the maximum local concentration of bcc-iron in the liquid zinc can be quite high. When a steel strip contacts the molten zinc pot, Giorgi et al. [5] and Liu and Tang [6] agree that the driving force is huge for bcc-iron to dissolve into the liquid zinc. The solubility of iron does not reach 4 wt.% in practice because an inhibition layer $Fe_2Al_2Znx$ forms on the steel that effectively suppresses further dissolution of bcc-iron.

Figure 10: The solubility of bcc iron in liquid zinc according to two CALPHAD-based assessments of the Zn-Fe binary system.
3.2 Solubility of Iron in Liquid Zinc Solutions as a Function of Aluminum Content

The solubility of bcc-iron over the temperature range 400-500°C and effective aluminum contents of 0, 0.125 and 0.25 wt. pct. in a galvanizing pot is displayed in Figure 11. Figure 11 shows that the aluminum content in a liquid zinc solution reduces the maximum solubility of bcc-iron. The largest effect occurs at 500°C where the presence of 0.25 wt pct. aluminum in solution is predicted to reduce the solubility of bcc-iron in the liquid phase from 5.2 to 4.8 wt. pct according to the data of Nakano et al.[12].

Figure 11: The solubility of bcc iron in liquid zinc containing 0, 0.125 or 0.25 wt. pct. aluminum according to two CALPHAD-based assessments of the Zn-Fe-Al ternary system.
Figure 11 clearly shows that the maximum solubility of bcc-iron in molten aluminum-zinc solutions is not significantly reduced by an aluminum concentration that would be found during commercial galvanizing. Increasing the effective aluminum content in a zinc bath slightly decreases the thermodynamic driving force for the dissolution of iron from an immersed steel strip. The dominant influence of effective aluminum content on iron dissolution is kinetic in nature. Higher effective aluminum contents greatly increase the rate of nucleation and growth of a Fe$_2$Al$_5$Zn$_x$ inhibition layer which then suppresses iron dissolution. As such, the effective aluminum content does have a strong influence upon the amount of iron that dissolves during galvanizing due to its kinetic effect on the formation of Fe$_2$Al$_5$Zn, not because of its small effect of reducing the thermodynamic driving force for the dissolution of iron from a steel strip immersed in the bath.

3.3 The Dissolution Rate Constant Associated with Diffusion Across a Boundary Layer

The work by Giorgi et al. [5] determined the dissolution rate constant of iron in molten zinc based on measurements of the concentration of iron in the molten zinc as a
function of immersion time from a disc of commercial interstitial-free (IF) steel. Giorgi et al. used a molten zinc bath with initially \( w_{Fe}^{x(i)} = 0.003 \) wt. pct. and measured \( w_{Fe}^{x(f)} \) as a function of time, \( t_f \). They then used equation (34) to evaluate their data as a function of rotational velocity. They found that when the left side of equation (34) designate \( \ln K_w \) was plotted as a function of \( \frac{S}{V} t_f \), straight lines were generated with a slop that depended on the rotational velocity of the disc specimen. Plots of their data obtained for immersion times of 30, 60, 120, 180, 240 and 300 seconds for rotational velocities of 100 and 500 rpm and a value of 3.94 wt. pct. for \( w_{Fe}^{MAX} \) are displayed in Figure 12.

![Graph showing lnKw as a function of S/Vt f for 100 and 500 rpm.](image)

**Figure 12:** The values for \( \ln K_w \) as defined by equation (34) as a function of immersion time modified by \( S/V \) for a disc specimen rotating at speeds of 100 and 500 rpm.
When the dissolution rate is controlled by diffusion of a metal across a boundary layer in a molten zinc bath, equations (35) and (36) apply. Equations (35) and (36) predict a linear relationship between $k_{\text{dif}}$ and $\omega^{1/2}$. The value of $k_{\text{dif}}$ should be a linear function of the square root of galvanizing line speed, $\sqrt{V^{0.5}}$, according to equations (36) and (38) as shown in Figure 13. For commercial galvanizing, speeds of 60 to 150 m/min [$\sqrt{V^{0.5}}$ of 1 to 1.58 (m/s)$^{0.5}$] predicted values for $k_{\text{dif}}$ range from $6 \times 10^{-7}$ to $9.5 \times 10^{-7}$ $m \cdot s^{-1}$ based upon the data generated by Giorgi et al. [5].

![Figure 13: Values of $k_{\text{dif}}$ as a function of the square root of the mean linear velocity of a steel strip.](image-url)
3.4 The Dissolution Rate Constant for the Total Amount of Iron Transferred from a Steel Strip into Liquid Zinc

A wide range of values for the dissolution rate constant, $k_M$, are found in the galvanizing literature. Experimental measurements of $k_M$ that apply to the initial dissolution of iron prior to the formation of a reaction layer are difficult to perform. A $\zeta$ or $\delta$ phase interfacial layer in low aluminum concentration zinc baths ($\text{Al} < 0.13$ wt. pct.) or a $\eta$ phase inhibition layer in higher aluminum concentration ($\text{Al} > 0.13$ wt. pct.) zinc baths can form in the vicinity of 0.1 second at galvanizing temperatures. The measurements of $k_M$ for immersion times greater than 5 seconds by Yamauchi and Hisamatsu [30] and greater than 30 seconds by Giorgi et al. [5] must have evaluated iron transport across an interfacial phase.

Liu and Tang developed a computer model called MAP (Modeling Aluminum Pick-up) to predict the formation of intermetallic compounds for the range of aluminum contents found in a commercial liquid zinc bath [6]. They investigated the short time reaction of a steel strip in a galvanizing bath. They found that the concentration of iron could increase from 0.03 wt. pct. to 3.0 wt. pct. after an immersion time of 0.04 second at a temperature of 450°C.
Iron dissolution produces an iron concentration depth profile across the boundary layer in a liquid zinc that is a function of time and $k_M$. Another form of the solution to Fick’s second law subject to a convective mass transport boundary condition is given by equation (78) that defines the relationship among the concentration of iron as a function of distance normal to the steel sheet/liquid zinc interface, $x$, the time, $t$, and $k_M$ [31].

$$w_{Fe}^r = w_{Fe}^{MAX} + \left(w_{Fe}^{MAX} - w_{Fe}^r\right) \left[ \text{erfc} \left( \frac{x}{2\sqrt{D}t} \right) - \exp \left( \frac{k_M}{D} x + \frac{k_M^2 t}{D} \right) \text{erfc} \left( \frac{x}{2\sqrt{D}t} + k_M \sqrt{\frac{t}{D}} \right) \right]$$ \hspace{1cm} (78)

The flux of iron as a function of the immersion time of a steel sheet in a bath is defined by equation (79) [31].

$$M_{Fe}^\infty = \left( \frac{\rho}{100} \right) \left( \frac{D}{k_M} \right) \left( w_{Fe}^{MAX} - w_{Fe}^r \right) \left[ \exp \left( h^2 Dt \right) \text{erfc} \left( \frac{t}{D} \sqrt{\frac{t}{D}} \right) - 1 - \frac{2}{\pi^{0.5}} k_M \sqrt{\frac{t}{D}} \right]$$ \hspace{1cm} (79)

Taking values for the concentration of iron at the surface ($w_{Fe}=3.0$ wt.%) at an immersion time of 0.4 second, combined with $w_{Fe}^{MAX} : w_{Fe}^r$ equal to 4.5 : 0.03 wt. pct. and using the diffusivity of iron through a molten zinc for 450°C, the dissolution rate constant, $k_M$, is estimated by solving equation (78) to be $2.4 \times 10^{-4} m \cdot s^{-1}$.

Giorgi et al. [5] measured the total amount of iron that dissolved from a disc specimen immersed in a molten zinc bath as a function of time. The total amount of iron dissolution was determined by weighing each steel disc after its removal from the liquid.
zinc and dissolving away the zinc coating that adhered to each disc specimen. The total mass of iron dissolution per unit area measured by Giorgi et al. [5] for immersion time from 30 to 300 seconds and specimen rotational velocities of 100 and 500 rpm is plotted in Figure 14.

![Figure 14](image)

**Figure 14:** The total amount of iron dissolution and the amount of iron that diffused across the boundary layer as a function of disc specimen immersion time for rotational speeds of 100 and 500 rpm.

The mass of iron per unit area that diffused across the boundary layer and into the bulk of the liquid zinc bath is also shown in Figure 14. The rate of iron diffusion across the boundary layer increased by a factor of two as the rotational velocity increased from 100 to 500 rpm. The total amount of iron dissolution from each disc specimen is
essentially independently of the rotational velocity. The values estimated for $k_M$ for the 100 and 500 rpm data were $6.8 \times 10^{-7} \text{m} \cdot \text{s}^{-1}$ and $6.4 \times 10^{-7} \text{m} \cdot \text{s}^{-1}$, respectively.

Section 3.3 discussed the mass transfer coefficient associated with an iron atom crossing a boundary layer in a molten zinc bath, $k_{\text{diff}}$. $k_{\text{diff}}$ from Figure 13 showing data by Giorgi et al. [5] for 100 and 500 rpm rotational disc velocities yields values of $2.0 \times 10^{-7} \text{m} \cdot \text{s}^{-1}$ and $3.7 \times 10^{-7} \text{m} \cdot \text{s}^{-1}$, respectively. The trend in Figure 13 indicates that as the rotational velocity or the mean linear velocity increases, $k_{\text{diff}}$ approaches the value for $k_M$. Figure 13 predicts that at a mean linear velocity of $1.5 \text{m} \cdot \text{s}^{-1}$ corresponding to an angular velocity of 720 rpm, $k_{\text{diff}}$ would increase to $7 \times 10^{-7} \text{m} \cdot \text{s}^{-1}$ which is about equal to the value of the overall dissolution rate constant, $k_M$.

Figure 15: Iron dissolution as a function of immersion time in molten zinc with 0.2 wt. pct. Al under turbulent conditions.
Toussaint et al. simulated the short reaction associated with a commercial galvanizing treatment at temperatures of 480 and 460°C using an advanced stimulator apparatus [1][3]. The original work by Toussaint et al. [1][3] measured the mass of aluminum that accumulated at the steel/liquid interface. The relationship between the mass of iron in an inhibition layer and that of aluminum is based on the stoichiometric ratio of Fe$_2$Al$_5$Zn$_x$, two iron atoms corresponds to five aluminum atoms. Taking values for the mass of iron at the end of the initial linear portion of the curves in Figure 15 combined with $w_{Fe}^{MAX} : w_{Fe}^{w}$ values of 4.65:0.010 wt. pct. and 4.75:0.018 wt. pct. for 460 and 480°C, respectively, and using the diffusivity of iron, for time equal to 0.1 second, $k_M$ was calculated by using equation (79) to be $3.5 \times 10^{-6} m/s$ and $8.3 \times 10^{-6} m/s$ for 460 and 480°C, respectively.

### 3.5 Dissolution of Iron in a Commercial Galvanizing Bath

An extensive study conducted at the POSCO Gwangyang Works determined the amount of iron that dissolved per unit surface area from a variety of steels processed through their galvanizing lines. The total amount of iron that dissolved was defined by taking measurements of the amount of iron 1.) in dross particles skimmed from a
galvanizing bath, 2.) dissolved in the liquid zinc, 3.) contained in dross particles dispersed in the liquid zinc and 4.) contained in the coating remaining on the steel sheet after passing through the zinc bath. Data generated by POSCO of the total amount of iron dissolved per unit area of steel strip (mg·m⁻²) as a function of coil width (mm), line speed (m·min⁻¹), strip entry temperature (°C), zinc bath temperature (°C) and effective aluminum concentration in the liquid zinc (wt. pct.) are listed Appendix III. The data for the mass of iron dissolved are given in terms of unit area of steel strip. Iron dissolves from both the top and bottom surfaces of a steel strip. Therefore, the total dissolution of iron per unit surface area of a steel strip is one half of the value listed in Appendix III.

The values for $M_{Fe}$, the total dissolution of iron per unit surface area of a steel strip, listed in Table A1 were converted to $k_M$ using equation (30). The time during which iron dissolution occurred when a steel strip was immersed in the molten zinc was assumed to be 0.1 second based upon the study by Giorgi et al. [5]. The surface, $S$, was 1 m²; the density of molten zinc, $\rho_{Zn}$, was 6,575,000 g·m⁻³ and the values for $w_{Fe}^{\text{Fe}}$ and $w_{Fe}^{\infty}$ were taken to be 3.94 and 0.003 wt. pct., respectively. The calculated value for $k_M$ for each of the steel coils is listed in Table A1.
Values for $k_M$ plotted as a function of the square root of the steel strip line speed $(\text{m}$·$\text{s}^{-1})^{1/2}$ are displayed in Figure 16. The best fit line through the data shown in Figure 16 resulted in equation (80) where $V$ is in units of $\text{m}$·$\text{s}^{-1}$ and $k_M$ is in units of $\text{m}$·$\text{s}^{-1}$.

$$k_M \times 10^6 = 0.1045V^{0.5} + 5.1844$$ (80)

The models that predict that $k_M$ should increase with the square root of steel strip line speed cannot be valid for arbitrarily high values of line speed. At higher line speeds such as those encountered in commercial galvanizing the transfer of iron across the steel strip/liquid zinc interface in the controlling mechanism for iron dissolution. The kinetics of that interfacial dissolution mechanism are not a function of steel strip line speed.
Figure 17: The nature logarithm of \( k_M \) as a function of the reciprocal of the steel strip entry temperature given in degrees Kelvin.

The natural logarithms of the \( k_M \) values listed in Table A1 are plotted in Figure 17 as a function of the reciprocal of the strip entry temperature give in degrees Kelvin. An Arrhenius relationship is observed. For strip entry temperatures ranging from 473 to 500°C values for \( k_M \) varied from \( 5.6 \times 10^{-6} \) to \( 7.4 \times 10^{-6} \text{ m} \cdot \text{s}^{-1} \) corresponding to an activation energy of 39,600 J/mol. That value for the activation energy of iron atoms transferring from a steel sheet to molten zinc is comparable to the 33,600 J/mol activation energy for the diffusion of iron in liquid zinc published by Kato and Minoura [28] [29].
In Figure 18 values for $k_M$ from the POSCO-data-base are plotted as a function of the effective aluminum content in wt. pct. The values for $k_M$ decrease as the effective aluminum content increases. That response is as expected because an inhibition layer will form in less time if the concentration of aluminum in solution in the molten zinc bath is higher. If an inhibition layer forms in less time, then the total amount of iron that dissolves from a steel strip will be reduced. A lower amount of iron being dissolved will cause the value of $k_M$ to decline because values for $k_M$ are calculated based upon a constant dissolution time of 0.1 second. Changes in effective aluminum content will cause the iron dissolution time to vary.
3.6 Effect of $k_M$ on Predictions Associated with Iron Dissolution

A 100 nm thick layer of Fe$_2$Al$_5$Zn$_x$ requires a minimum of approximately 0.18 g·m$^{-2}$ of iron to dissolve into the liquid zinc. Applying the dissolution rate constants estimated at the previous section into equation (79), Figure 19 displays the amount of iron per unit area that would dissolve as a function of time at 460°C for a range of $k_M$ values. Figure 19 reveals that $k_M$ must be larger than $5.5 \times 10^{-6} \text{ m} \cdot \text{s}^{-1}$ in order to form an inhibition layer 100 nm thick in less than 0.1 second. Figure 19 illustrates that for a short period of time the dissolution rate of iron is not a function of time.

Figure 19: The amount of iron dissolution as function of immersion time in molten zinc at 460°C for four values of $k_M$. 
With \( w_{Fe}^{MAX} : w_{Fe}^{\infty} \) equal to 4.65 : 0.01 wt. pct. and the diffusion coefficient of iron in a liquid zinc (\( D_{Fe}=1.21 \times 10^{-9} \text{m}^2/\text{s} \)) for a temperature of 460°C, equation (78) was used to generate iron concentration profiles for times ranging from 0.01 to 1 second and \( k_M \) values of \( 6.5 \times 10^{-6} \), \( 1.7 \times 10^{-5} \) and \( 2.4 \times 10^{-4} \) m·s\(^{-1}\) as displayed in Figure 20. The \( k_M \) values were chosen based upon those found in the literature [6][7], or an average value of \( k_M \) derived from the data for iron dissolution obtained from commercial galvanizing practice.

Figure 20 illustrate how rapidly a supersaturation of iron can develop in the liquid zinc adjacent to the steel sheet surface. Even with \( k_M \) equal to \( 6.5 \times 10^{-6} \) m·s\(^{-1}\) the concentration of iron at the steel sheet/liquid zinc interface increases from 0.01 to 0.1 wt. % in 0.01 seconds. For \( k_M \) equal to \( 2.4 \times 10^4 \) m/s the concentration of iron at the steel sheet/liquid zinc interface increases from 0.01 to 2.2 wt.% in 0.01 seconds.
3.7 The Temperature Profile in a Steel Strip

The temperature of an immersed steel strip is always higher than that of the molten zinc bath in commercial practice. The heat-transfer coefficient between the strip and liquid zinc based upon equation (40) has been estimated as a function of strip speed. The
average heat-transfer coefficient was found to be approximately \((0.5 \sim 1.5) \times 10^4 \text{W/m}^2\cdot\text{°C}\) [1]. The temperature as a function of time for a steel strip surface for steels with thicknesses of 1.5/1.0/0.7mm is shown in Figure 21.

![Figure 21: Temperature change of immersed strips as a function of immersion time](image)

The calculations were carried out using a heat-transfer coefficient \(h = 12.5\text{kw/m}^2\cdot\text{K}\), a strip-entry temperature 480°C, molten zinc temperature 460°C, strip speed 2m/s and the heat capacity of the strip being 655 J/kg K. As expected, the thickest strip has the slowest cooling rate. All three strips cool by greater than 15°C in 1 second. However, during initial entry into the zinc when the immersion time is less than 0.1 second, the three strips
will have cooled less than 5°C. That indicates when a strip just enters the molten zinc bath, the driving force for the dissolution of a steel strip and the driving force for the formation of intermetallic compounds will be dependent upon the strip entry temperature and the zinc bath temperature.

Figure 22: Temperature change of immersed strips as a function of line speed.

The velocity of a HDG process can vary from 1 m/s to 3 m/s due to the requirements of the coating process. With the entry temperature of 480°C and the bath temperature of 480°C, Figure 22 displays the temperature profile of a strip 1mm thick as a function of the immersion time for three strip line speeds. Figure 22 indicates that the fastest line
speed generates the highest cooling rate. Based upon equation (40), the heat transfer coefficient between a steel strip and liquid zinc is proportional to the square root of the steel strip’s line speed.

### 3.8 Driving Force for the Formation of Dross Particles

Combining theories of nucleation and growth, thermodynamics provides a solid foundation on which to understand the kinetics of precipitation of intermetallic compounds on a steel sheet surface or dross particles in a molten zinc bath. It can be used to estimate the driving force for the formation of dross particles in the molten zinc. This analysis is based upon the CALPHAD modeling as reviewed in previous chapters. This section will focus on the driving force for the nucleation and growth of the \( \text{Fe}_2\text{Al}_5\text{Zn}_x \) and the \( \delta \)-phases in a galvanizing bath.

After inserting the thermodynamic parameters published by Nakano et al. [12] into CALPHAD models of the Fe-Al-Zn system, an isothermal phase diagram in the zinc-rich corner at 460°C was constructed as shown in Figure 23. The boundaries between liquid/\( \zeta \), liquid/\( \delta \) and liquid/\( \text{Fe}_2\text{Al}_5\text{Zn}_x \) correspond to the composition where there is zero driving force for the formation of these intermetallic compounds.
The driving force for the formation of Fe$_2$Al$_5$Zn$_x$ can be determined using CALPHAD parameters applied to equations (46) and (47). The conversion from chemical potential, $\mu_{Fe}^{liq}$, to activity in the liquid, $a_{Fe}$, is defined by:

$$\ln a_{Fe}^{liq} = \frac{\mu_{Fe}^{liq} - \mu_{Fe}^{\infty}}{RT}$$

The parameters provided by Nakano et al. [12], May [16] and Seiersten [17] were used to calculate the values for $a_{Al}$ and $a_{Zn}$. Inserting $a_{Fe}$, $a_{Al}$ and $a_{Zn}$ into equation (47) generated values for $\Delta G$ as a function of the concentration of iron and aluminum in the
bath. Based upon the same concept, the $\Delta G$ for the formation of the $\delta$-phase was able to be calculated using equations (55) and (56). Appendix IV contains two tables listing the driving force for the formation of the Fe$_2$Al$_5$Zn$_x$ phase and the driving force for the formation of the $\delta$-phase. Appendix IV was used to plot the constant $\Delta G$ lines on the 460°C isothermal sections of the Al-Fe-Zn phase diagram displayed in Figure 24.

Figure 24: An isothermal phase diagram with the $\delta$-phase and the $\eta$-phase containing contour lines indicating the driving force for their formation.

The unit for $\Delta G$ given in Figure 24 is J/gram·atom. Figure 24 shows that the driving force for the formation of the Fe$_2$Al$_5$Zn$_x$ phase increases rapidly from 0 to -4kJ/mol when
the concentration of iron in solution increases from 0.007 to 0.100 wt.% for a content aluminum concentration of 0.20 wt.%.. That driving force increases much less rapidly as the iron concentration increases above 0.4 wt%.

Figure 24 reveals an important fact regarding the potential for the nucleation of the Fe$_2$Al$_5$Zn$_x$ phase as opposed to the $\delta$-phase. If a significant supersaturation of iron has formed in the liquid zinc due to rapid dissolution, the driving force for the nucleation of the Fe$_2$Al$_5$Zn$_x$ phase exceeds that for the nucleation of $\delta$-phase even when the effective aluminum content of the bath is below 0.10 wt%.

3.9 Nucleation and Growth of the Inhibition Layer

The precipitation of Fe$_2$Al$_5$Zn$_x$ on a steel sheet surface inherently involves a heterogeneous nucleation mechanism. With limited information regarding values for the relevant interfacial energies, the Fe$_2$Al$_5$Zn$_x$ nuclei are assumed to have a hemispherical shape. The hemispherical nuclei form and grow until they completely cover the surface of the steel sheet. The formation and initial growth of the Fe$_2$Al$_5$Zn$_x$ nuclei are controlled by the rate of diffusivity of aluminum in the molten zinc. Once the inhibition layer completely covers a steel sheet surface and the initially large supersaturation of dissolved
iron is consumed, the further grow of the Fe\textsubscript{2}Al\textsubscript{5}Zn\textsubscript{x} layer is limited by the rate of diffusion of iron in the molten zinc.

Based upon an iron supersaturation of 0.56 wt. pct. and an aluminum concentration of 0.20 wt. pct. at 460°C, the time to cover 99% of the surface is 0.0009 second and to cover 99.9% of the surface is 0.0011 second based upon equation (68). The parameters required to assess the initial kinetics are listed in the following:

\[
C^e_{Al}(0.07 \text{ wt.%}) = 160.9 \text{ mol/m}^3
\]

\[
C^a_{Al}(0.20 \text{ wt.%}) = 487.7 \text{ mol/m}^3
\]

\[
C^a_{Al} = 70671.4 \text{ mol/m}^3
\]

\[
D^{\text{liq Zn}}_{Al} = 4.85 \times 10^{-9} \text{ m}^2/\text{s}
\]

Under those conditions the nucleation rate per unit area is estimated to be \(8.0 \times 10^{16} \text{ m}^{-2} \cdot \text{s}^{-1}\) and the critical radius of a nucleus is 0.71nm. The average thickness of the inhibition layer after nucleation and growth of Fe\textsubscript{2}Al\textsubscript{5}Zn\textsubscript{x} to essentially complete impingement is 68nm and the radius of the average particles is 103nm.

After fully covering the surface of the steel sheet, planar growth of the inhibition layer was assessed using by the following parameters:

\[
C^e_{Fe}(0.008 \text{ wt.%}) = 8.0 \text{ mol/m}^3
\]
The inhibition layer thickness as a function of time beginning at the inception of nucleation is displayed in Figures 25 and 26. Figure 25 shows that once nucleation begins it proceeds very rapidly causing the inhibition layer thickness to increase to 68nm in approximately 1 msec.

Figure 25: The thickness of the inhibition layer as function of time for short periods of time after the initiation of nucleation.
Figure 26: The thickness of the inhibition layer as a function of time after initiation of nucleation applied to a long time scale. Triangles represent experimental data from Toussaint et al. [1][3].

When the nucleation kinetics are completed the steel sheet surface is completely covered with Fe$_2$Al$_5$Zn$_x$, the large supersaturation of iron is greatly diminished and planar growth of the inhibition layer occurs at a much lower rate. As shown in Figure 26 the inhibition layer only increases thickness by about 20nm after 4 seconds of planar growth.

3.10 Nucleation and Growth of δ-Phase Particles

With the assumed value of $\gamma_{p/l}$ equal to 0.150 J/m$^2$ it is necessary to have a significant supersaturation of iron in the liquid zinc in order to have a reasonable δ-phase nucleation rate. At 460°C with liquid zinc containing 0.20 wt.% Al, $\Delta G$ for the δ-phase is
-2,605 J/mol of atoms when the iron concentration is 0.50 wt.% based upon equations (55) and (56). Under those conditions the nucleation rate per unit volume is estimated to be $1.3 \times 10^{15} \, \text{m}^{-3} \cdot \text{s}^{-1}$. If the iron concentration is 0.40 wt.%, $\Delta G$ for the $\delta$-phase is -2,425 J/mol of atoms and the nucleation rate per unit volume decrease dramatically to $2.1 \times 10^{11} \, \text{m}^{-3} \cdot \text{s}^{-1}$.

Equation (77) was used to determine the length of time required for the depletion region around each $\delta$ phase particle to occupy a certain fraction of the total volume. The calculations were based upon a temperature of 460°C, as aluminum concentration of 0.20 wt.% and iron concentrations of 0.40, 0.45 and 0.50 wt.%. The following parameters were used:

$$C_{Fe}^{a} (0.40, 0.45 \text{ and } 0.50 \text{wt.\%}) = 469,528 \text{ and } 587 \, \text{mol} / \text{m}^{3}$$

$$C_{Fe}^{c} (0.018 \text{ wt.\%}) = 21.1 \, \text{mol} / \text{m}^{3}$$

$$C_{Fe}^{d} = 15377 \, \text{mol} / \text{m}^{3}$$

$$D_{Fe}^{587} = 1.21 \times 10^{-9} \, \text{m}^{2} / \text{s}$$

The fraction of the total volume consumed by the depletion region is plotted as a function of time in Figure 27. Figure 27 illustrates the extreme dependence of the kinetics of $\delta$-phase particle nucleation and growth on the level of iron supersaturation in the zinc.
bath. With an iron concentration of 0.50 wt.% δ-phase nucleation and growth is complete in less than 0.4 second yielding δ-phase particles with an average diameter of 9.8µm. If the iron concentration level is reduced to 0.40 wt.%, δ-phase nucleation and growth require greater than 6 seconds to reach completion and the resulting δ-phase particles have an average diameters much greater than 22µm.

Figure 27: The volume fraction depleted of iron due to the precipitation of δ-phase as a function of time for three concentrations of iron in liquid zinc containing 0.20 wt.% aluminum at 460°C.

Figure 27 indicates the kinetics associated with the precipitation of δ-phase under the conditions of a given initial supersaturation of iron in the zinc bath that diminishes as the δ-phase particles nucleates and grows. However, a galvanizing bath presents a more
dynamic environment with regard to the concentration of iron. As sheets of steel continuously pass through the zinc bath, a constant flux of iron enters the bath. The calculation was made that 0.127 g/m² of iron are consumed by the rapid formation of an inhibition layer 68nm thick. If it is assumed that an equal amount of dissolved iron is transferred into the bath, i.e., 0.127 g/m², and steel sheet 1.5m wide is traveling through the bath at 2m/s, 0.762g/s is the rate at which iron continuously enters the bath. A mass balance for iron based upon 1 second of time leads to the following:

\[ \frac{4}{3} \pi r_p^3 N_T \rho_{Fe} = 0.762 \quad \text{(in units of grams)} \]  

where \( r_p \) is the average \( \delta \)-phase particle radius after 1 second of nucleation and growth, \( N_T \) is the total number of \( \delta \)-phase particles created in 1 second and \( \rho_{Fe} \) is the number of grams of iron per unit volume of the \( \delta \)-phase, i.e., 858,750 g/m³. The value for \( N_T \) is obtained from the following:

\[ N_T = \int_0^t N V_{\text{bath}} (1 - f) \, dt \]  

where \( N \) is the nucleation rate; \( V_{\text{bath}} \) is the volume of the bath, i.e., 22m³ and \( f \) is the volume fraction consumed by the depleted regions as indicated in equation (77). The total volume of the depleted regions, \( V_d \), is given by:

\[ V_d = V_{\text{bath}} f = V_{\text{bath}} \left( 1 - \exp \left( -\frac{1}{2} N m t^{5/2} \right) \right) \]  

The average radius of a \( \delta \)-phase particle, \( r_p \), is given by the following:
\[ r_p = \left[ \frac{3(0.5) C_{Fe}^0 - C_{Fe}^\delta}{4\pi C_{Fe}^\delta - C_{Fe}^0} \bar{V}_d \right]^{1/3} \]  

(85)

where the concentration parameters \( C_{Fe}^0 \) and \( C_{Fe}^\delta \) are the same as those previously given for the \( \delta \)-phase at 460°C and 0.20 wt.% Al in molten zinc; \( C_{Fe}^\delta \) is the unknown concentration of iron required to enable 0.762g of iron to precipitate out of the liquid zinc per second and \( \bar{V} = V_d / N_T \). Solving equation (82) for \( C_{Fe}^\delta \) after insertion of equations (83), (84) and (85) resulted in a value of 0.35 wt.% iron. At that level of iron supersaturation \( 1.9 \times 10^{10} \) particles of \( \delta \)-phase with an average diameter of 3.3\( \mu \)m would be created in 1 second causing 0.762 g of iron to precipitate out of the liquid zinc. The relatively high iron supersaturation required to achieve the necessary amount of \( \delta \)-phase precipitation indicates that the activation barrier employed for the calculation was too large. One way to lower the activation barrier for the formation of the \( \delta \)-phase is to have heterogeneous nucleation on pre-existing oxide particles dispersed in the galvanizing bath.
Conclusions

A model is proposed to describe dynamic reactions associated with hot-dip galvanizing that involves 1.) dissolution of iron from the surface of an automotive steel sheet and 2.) homogeneous and heterogeneous nucleation and growth of intermetallic phases, i.e., Fe₂Al₅Znₓ and the δ-phase. The modeling was validated by comparison with experimental data in the literature for short time galvanizing treatments.

A model was generated that is capable of estimating the concentration profile of iron in the boundary layer adjacent to a steel/liquid zinc interface. Other models were used to calculate the zinc-rich corner of the Fe-Al-Zn isothermal phase diagram. The formation of the intermetallic compounds is highly dependent upon the value used for the interfacial energy between a particle and the liquid zinc. The value assumed in this study for the nucleation of the δ-phase (γ_p,i = 0.150 J / m²) requires a high supersaturation of the iron in the zinc bath (>0.40wt.%). Adjustment to the model needs data regarding the level of iron supersaturation present in baths during the δ-phase nucleation in commercial galvanizing baths. Another refinement of the model for the precipitation of the δ-phase would include the possibility of heterogeneous nucleation on oxide particles found in commercial galvanizing baths.
Appendix I: CALPHAD Parameters Used in Modeling

The magnetic contribution to the Gibbs free energy is defined as following equation. [9]

\[
\text{mag } G_m = RT \ln(\beta + 1) f(\tau), \tau = T / T_C
\]

for \( \tau < 1 \Rightarrow f(\tau) = 1 - \frac{1}{A} \left[ \frac{79\tau^{-1}}{140p} + \frac{474}{497} \left( \frac{1}{p} - 1 \right) \left( \frac{\tau^3}{6} + \frac{\tau^9}{135} + \frac{\tau^{15}}{600} \right) \right]
\]

for \( \tau \geq 1 \Rightarrow f(\tau) = -\frac{1}{A} \left( \frac{\tau^{-5}}{10} + \frac{\tau^{-15}}{315} + \frac{\tau^{-25}}{1500} \right)
\]

where \( A = \frac{518}{1125} + \frac{11692}{15975} \left( \frac{1}{p} - 1 \right) \), \( T_C \) is the Curie temperature and \( \beta \) is the mean atomic moment express in Bohr magnetons \( \mu_B \). The value of \( p \) depends on the structure, \( p = 0.4 \) for a bcc phase and \( p = 0.28 \) for a fcc phase.

Liquid: (Fe,Zn,Al)_1

\[ L_{\text{Fe,zn}}^{\text{liq}} = +58088 - 23.665T^a \]
\[ L_{\text{Fe,zn}}^{\text{liq}} = +92219 - 55.584T^a \]
\[ L_{\text{Fe,zn}}^{\text{liq}} = +13570^a \]
\[ L_{\text{Fe,zn}}^{\text{liq}} = +20696.5073^b \]
\[ L_{\text{Fe,zn}}^{\text{liq}} = +14782.0192 - 8.9768T^b \]
\[ L_{\text{Fe,zn}}^{\text{liq}} = -11266.6992 + 7.3942T^b \]
\[ L_{\text{Al,Fe}}^{\text{liq}} = -91976.5 + 22.1314T^c \]
\[ L_{\text{Al,Fe}}^{\text{liq}} = -5672.58 + 4.8728T^c \]
\[ L_{\text{Al,Fe}}^{\text{liq}} = +121.9^c \]
\[ L_{\text{Al,Fe}}^{\text{liq}} = +10465.5 - 3.39259T^d \]
BCC: (Fe,Zn,Al)$_{(Va)}_3$

\[
\begin{align*}
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\end{align*}
\]

\[\begin{align*}
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\end{align*}\]

\[\begin{align*}
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\end{align*}\]

\[\begin{align*}
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\end{align*}\]

\[\begin{align*}
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
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\end{align*}\]

\[\begin{align*}
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\delta &: \text{Fe}_{0.058}(\text{Al},\text{Fe},\text{Zn})_{0.180}\text{Zn}_{0.525}\text{Zn}_{0.237} \\
\end{align*}\]
FeAl$_2$:FeAl$_2$(Va,Zn)$_3$

\[ \Delta G_{FeAl_2}^{FeAl_2} = 5 \Delta G_{Fe}^{fcc} - 2 \Delta G_{Fe}^{hpc} - 3 \Delta G_{Fe}^{hcp} = -277947 + 121.95T^a \]

\[ \Delta G_{FeAl_3}^{FeAl_3} = 5 \Delta G_{Al}^{fcc} - 2 \Delta G_{Al}^{hpc} = -228576 + 48.99503T^c \]

$^a$ Parameters adopt from [12]

$^b$ Parameters adopt from [13]

$^c$ Parameters adopt from [17]

$^d$ Parameters adopt from [14]
Appendix II: Chemical Potential of Zinc in the $\zeta$ Phase on Different Sublattices

The zeta ($\zeta$) phase in the binary Fe-Zn system is represented as $(Fe, Va)_{0.072} (Zn, Va)_{0.072} Zn_{0.856}$ where zinc occupies two possible sublattices, the second and the third. To maintain the minimum free energy, the filling of sublattices one and two will occur as $(Fe, Va)_{0.072} Zn_{0.072} Zn_{0.856}$ for an iron fraction between 0 and 0.072 and $Fe_{0.072} (Va, Zn)_{0.072} Zn_{0.856}$ for an iron fraction between 0.072 and 0.0776.

To verify whether the chemical potential of zinc in the second sublattice is the same as it is in third sublattice, a thermodynamic model using interaction parameters cited Nakano et al. [12] calculates the chemical potential of zinc at various sites. This model applied the high precise function with Wolfram Mathematica® software.

The molar free energy of the zeta $\zeta$ phase is given by equation (86).

$$G^\zeta_n = y^1_{Fe} y^2_{Va} G^\zeta_{Fe, Va: Zn} + y^1_{Fe} y^2_{Zn} G^\zeta_{Fe, Va: Zn} + y^1_{Va} y^2_{Va} G^\zeta_{Va, Va: Zn} + y^1_{Va} y^2_{Zn} G^\zeta_{Va, Va: Zn} + 0.072 \times RT \left[ y^1_{Fe} \ln y^1_{Fe} + y^1_{Va} \ln y^1_{Va} + y^2_{Va} \ln y^2_{Va} + y^2_{Zn} \ln y^2_{Zn} \right]$$  \hspace{1cm} (86)

The relationship between the iron mole fraction and site fraction is defined by equation (87).

$$X_{Fe} = \frac{n_{Fe}}{n_{Fe} + n_{Zn}} = \frac{y^1_{Fe}(0.072)}{y^1_{Fe}(0.072) + 0.856 + y^2_{Zn}(0.072)}$$  \hspace{1cm} (87)

The chemical potential of the compound Va:Va:Zn is given by equation (88).
\[ \mu_{V_a Va Zn}^Z = G_m^Z + \frac{\partial G_m^Z}{\partial y_{Va}^Z} - y_{Fe}^1 \frac{\partial G_m^Z}{\partial y_{Fe}^1} - y_{Va}^1 \frac{\partial G_m^Z}{\partial y_{Va}^1} - y_{Zn}^2 \frac{\partial G_m^Z}{\partial y_{Zn}^2} \] (88)

\[ = 0.856 G_{Zn}^{hcp} + 14T + y_{Fe}^1 y_{Zn}^2 [5370.91 - 17.816T] + 0.072RT \left[ \ln y_{Va}^1 + \ln y_{Zn}^2 \right] \]

Dividing by 0.856 yields one mole of atoms of zinc in the third sublattice.

\[ \mu_{Zn}^3 = \frac{1}{0.856} \mu_{V_a Va Zn}^Z \] (89)

\[ = \frac{1}{0.856} [0.856 G_{Zn}^{hcp} + 14T + y_{Fe}^1 y_{Zn}^2 [5370.91 - 17.816T] + 0.072RT (\ln y_{Va}^1 + \ln y_{Zn}^2)] \]

The chemical potential of zinc in the second sublattice is defined by equation (90).

\[ \mu_{Zn}^2 = \mu_{Zn}^3 - \mu_{Va}^2 = \frac{1}{0.072} \left[ \frac{\partial G_m^Z}{\partial y_{Zn}^2} - \left( \frac{\partial G_m^Z}{\partial y_{Va}^1} \right) \right] \] (90)

\[ = \frac{1}{0.072} [0.072 G_{Zn}^{hcp} + 808.7 - 14.102T + y_{Fe}^1 (-5370.91 + 17.816T)] \]

The chemical potentials of zinc in these two sublattices should conform to equation (91).

\[ \mu_{Zn}^2 = \mu_{Zn}^3 \] (91)

The difference between the chemical potentials of zinc on the second and the third sublattices are shown as a function of the site fraction of iron on the first sublattice in Figure 28. Figure 28 contains three lines based upon zinc concentrations in the second sublattice of 0.99, 0.99999 and 0.99999999. As previously indicated the zeta (\(\zeta\)) phase should exhibit the stoichiometry composition \((Fe, Va)_{0.072} Zn_{0.072} Zn_{0.856}\) as the iron fraction varies from 0 to 0.072. In reality, zinc does not fully occupy the second sublattice.
The second sublattice must contain a low concentration of vacancies (<0.01) under equilibrium conditions.

The same need for vacancies appears when the arrangement of zinc Fe\textsubscript{0.072}(Va,Zn)\textsubscript{0.072}Zn\textsubscript{0.856} occurs for iron fractions from 0.072 to 0.078. Figure 29 contains three lines corresponding to iron concentrations in the first sublattice of 0.99, 1 - 1 \times 10^{-27} and 1 - 1 \times 10^{-62}. As the Zn site fraction in the second sublattice varies between 0 and 1, the concentration of Fe in the first sublattice will have to change along with the vacancy content in order to maintain thermodynamic equilibrium.
Figure 29: The energy difference between zinc in the second and the third sublattices of the $\zeta$-phase as a function of site fraction of iron in the first sublattice.

Figures 28 and 29 reveal two points: 1.) the chemical potentials of zinc in the second and the third sublattice are the same, and 2.) equilibrium is only obtained when the proper vacancy concentrations are maintained on the first and the second sublattices.
Appendix III: Iron Dissolution from Steels Galvanized at the POSCO Gwangyang Works

Table A1 lists the amount of iron dissolution that occurred when steel strip was processed through the commercial galvanizing lines at the POSCO Gwangyang Works. Data for 120 coils of steel are contained in Table A1. The amount of iron dissolution is given in units of mass per unit area of a steel strip. For each coil its width (mm), strip line speed (m/min), strip entry temperature (°C), galvanizing pot temperature (°C) and effective aluminum concentration in the galvanizing pot (wt. pct.) are listed in Table A1. The value for \( k_M \) calculated using equation Table A1 based upon the amount of iron dissolution and an assumed iron dissolution time of 0.1 second for each coil also is included in Table A1.

### Table A1

<table>
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<tr>
<th>Coil Width [mm]</th>
<th>Line Speed [m/min]</th>
<th>Strip Entry Temp. [°C]</th>
<th>Pot Temp. [°C]</th>
<th>Effective Al [%]</th>
<th>Fe Dissolution [mg/m²]</th>
<th>( k_M \times 10^6 ) [m/s]</th>
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<td>291.9361</td>
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</tr>
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<td>453</td>
<td>0.12</td>
<td>311.2023</td>
<td>6.01</td>
</tr>
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Appendix IV: The Driving Force for the Formation of the Fe$_2$Al$_5$Zn$_x$ and δ-Phases

Two tables are contained: the driving force of precipitate of Fe$_2$Al$_5$Zn$_x$ and the δ-phase, respectively.

Table AIV-I
\( \Delta G \) of Formation for the η-Phase (Fe$_2$Al$_5$Zn$_{1.32}$) (J/mole of atoms)

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Table AIV-II

ΔG of Formation for the δ-Phase (Fe$_{0.1288}$Al$_{0.0667}$Zn$_{0.8045}$) (J/mole of atoms)

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<td>Fe wt.%</td>
<td>ΔG(J/mol)</td>
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Bibliography


