Modeling Al Enrichment in Galvanized Coatings

NAI-YONG TANG

Aluminum enrichment in galvanized coatings was shown to be due to the formation of an inhibition layer, consisting of Fe$_2$Al$_3$, at the substrate/coating interface. The formation of the inhibition layer is a two-stage process. The first stage, associated with a high rate of Al uptake, is nucleation controlled, and the successive stage is diffusion controlled. The critical nucleus size is approximately one molecule of the compound Fe$_2$Al$_3$, and the energy barrier for the heterogeneous nucleation is 0.94 eV. Aluminum uptake increases with increasing strip-entry temperature and thickness, because both work to increase the effective temperature for the nucleation and growth processes. A model was proposed in which Al enrichment was shown as a function of bath Al content, bath temperature, strip-entry temperature, strip thickness, immersion time, and coating weight. The model is in good agreement with experimental results available in the open literature.

I. INTRODUCTION

STUDIES of Al partition in continuous galvanizing baths indicated that Al was significantly enriched in galvanized coatings when bath Al contents exceeded a threshold level. For example, recent work by Belisle(10) indicated that Al in the coating remained unchanged at about 0.2 pct of the coating weight for bath Al up to 0.14 pct; further increase in bath Al content led to a rapid increase of Al in the coatings. Such a trend was also noted and reported by other researchers.(2-3) It has been suggested that the mechanism of Al enrichment in coatings was the formation of an inhibition layer, consisting of Fe$_2$Al$_3$. Research work carried out recently by the author and his co-worker(4-5) confirmed the conclusion drawn decades ago by a number of researchers(6-9) that the inhibition layer in galvanized coatings consisted of Fe$_2$Al$_3$ containing Zn in solid solution. The Zn content in the compound was found to increase with increasing immersion time before reaching a saturation level, and the minimum bath Al content for full inhibition was found to be approximately 0.15 pct at temperatures relevant to galvanizing practice.(4-9) These observations are consistent with isotherms of the Zn-Fe-Al ternary phase diagram, revised recently by the present author.(5,10) The currently prevailing 450 °C isotherm was proposed by Urednicek and Kirkaldy(11) in the early seventies, in which the upper limiting tie-line of the δ-liquid two-phase region was placed at 0.11 pct Al along the liquid-phase boundary. After intensive experimentation and thermodynamic calculations, the present author found that the upper limiting tie-line of the δ-liquid two-phase region is actually located at 0.13 to 0.14 pct Al, depending on the bath temperature. This composition corresponds to the change of the thermodynamically stable phase from δ to Fe$_2$Al$_3$. It is easy to understand that the significant enrichment of Al in coatings produced in baths with Al in excess of 0.14 pct is due to the formation of the Fe$_2$Al$_3$ inhibition layer in the coating/substrate interface. The revised isotherms have been proven also to be helpful in providing a better understanding of other processes occurring in galvanizing practice.(3,10,12)

However, the rate of Al uptake in coatings appears puzzling. It has been found to change rapidly with time and to be strongly dependent on the strip-entry temperature. (2-3) Isobe(6) showed that the first 3 seconds, approximately the time required for steel strip to pass through a bath on a continuous galvanizing line, over 80 pct of the total Al uptake at the interface took place in the first second. Faderl et al.(3) found that for a bath containing 0.18 pct Al, the content of Al in the interface increased approximately linearly with the difference between the strip-entry temperature and the bath temperature. On the other hand, research work(13,14) involving long immersion times showed that the overall growth kinetics of the inhibition layer followed a parabolic time law and that bath Fe contents influenced the overall growth kinetics. Aluminum uptake at the interface appeared to be a two-stage process with an initial extremely high rate which then decreased rapidly during the first second of immersion. The present work is intended to disclose the mechanisms by analyzing the nucleation and growth of the inhibition layer. It will be shown that the rate of Al uptake in the coating/strip interface is controlled by continuous nucleation of Fe$_2$Al$_3$, followed by a diffusion-controlled growth process. A model is formulated in which Al uptake is shown as a function of bath Al content, bath temperature, strip-entry temperature, strip thickness, coating weight, pot size, and line speed. This study is part of an overall program on bath chemistry management(5,10,12,15,16) aimed at establishing the optimal Al level and the best practice of Al addition for galvannealing and galvanizing production.

II. THEORY

A. Assessment of Nucleation Rate

1. Critical size of nucleus

Following classical nucleation theory, the excess free energy associated with the precipitation of a solid particle of volume $V$ from a liquid onto the liquid/solid interface is given by

$$
\Delta G = (\Delta G_v + \Delta G_s) V + \Sigma A \gamma
$$

[1]
where $\Delta G_s$ is the free energy change per unit volume of solid particle formed, $\Delta G_r$ is the strain energy due to the mismatch of the particle with the substrate, and $\Sigma A_i \gamma_i$ is the sum of surface energy changes due to the precipitation of the solid particle.

The precipitation of $\text{Fe}_2\text{Al}_3$ on a steel surface in contact with a liquid Zn alloy is through the following reaction:

$$2\text{Fe} + 5\text{Al} = \text{Fe}_2\text{Al}_3$$  \[2\]

where the subscripts $f$ and $s$ indicate that the reactants are in the liquid solution of Zn and the product is a solid compound. The free energy change associated with the above reaction as a function of temperature $T$ in kelvin has been given by \[17\]

$$\Delta G = -283,470 + 84.8T \text{ J/mole}$$  \[3\]

At 460 °C (733 K), a temperature commonly employed for galvanizing production, the free energy change due to the formation of 1 mole of $\text{Fe}_2\text{Al}_3$ is $\Delta G = -221 \text{ kJ/mol}$. Research work\[6\] indicated that $\text{Fe}_2\text{Al}_3$ formed at an early stage of immersion almost pure binary Fe-Al compound with little Zn in solid solution. Hence, the theoretical density of the $\text{Fe}_2\text{Al}_3$ compound was calculated as $3.92 \text{ g/cm}^3$, using the lattice constants reported by Chen et al.\[17\]. The free energy change associated with per unit volume of the compound is

$$\Delta G_v = -283,470 + 84.8T \text{ J/m}^3$$  \[4\]

As noted by Chen et al.,\[19\] there is a volume change associated with the formation of $\text{Fe}_2\text{Al}_3$. However, such a change can be easily accommodated by the surrounding liquid, and the strain energy term in Eq. [1] is expected to be negligible.

The nucleation of an $\text{Fe}_2\text{Al}_3$ particle on the substrate surface is heterogeneous in nature. It consumes a small area of the liquid/steel interface and creates an $\text{Fe}_2\text{Al}_3$/steel interface of the same area and an $\text{Fe}_2\text{Al}_3$/liquid interface. For mathematical simplicity, the particle is assumed to be spherical in shape. Then, the surface energy terms associated with the precipitation of the particle can be summarized as

$$\Sigma A_i \gamma_i = \pi r^2 (\gamma_{p\ gamma} - \gamma_s) + 2\pi r^2 \gamma_{p\ liquid}$$  \[5\]

Where $\gamma_{p\ gamma}$, $\gamma_{p\ liquid}$ and $\gamma_{p\ s\ liquid}$ are the surface energy per unit area of the particle/steel interface, the liquid/steel interface, and the particle/liquid interface, respectively. The magnitudes of all three surface energy terms are unknown, and they may well be a function of the size of the particle in view of the nucleus being extremely small. Judging by the fact that the melting point of the compound is similar to that of Fe, $\gamma_{p\ gamma}$ and $\gamma_{p\ liquid}$ are expected not to be markedly different.\[20\] For simplicity, the two terms are assumed to be equal. Also, in general, solid/liquid interfacial energies are only a fraction of those of solid/vapor interfaces. $\gamma_{p\ s\ liquid}$ Direct experiments\[21\] imply that solid/liquid interfacial energy is approximately $0.15 \gamma_{p\ gamma}$, and $0.45 \gamma_s$, the grain boundary energy. The particle/steel interface can be treated as a general grain boundary. Then, for first approximation,

$$\gamma_{p\ liquid} = \gamma_{p\ s\ liquid} = 0.45 \gamma_{p\ gamma}$$  \[6\]

and

$$\Sigma A_i \gamma_i = 1.45 \pi r^2 \gamma_{p\ gamma} = \pi r^2 \Delta \gamma$$  \[7\]

For the present calculation, $\gamma_{p\ gamma}$ is assumed to be $0.835 \text{ J/m}^2$, the grain boundary energy for AISI 304 stainless steel.\[25\] Consequently, $\Delta \gamma$ is equal to $1.21 \text{ J/m}^2$. Substituting Eq. [7] into Eq. [1] and differentiating with respect to $r$, one finds that the critical radius of a semispherical nucleus is given by

$$r^\ast = -\Delta \gamma \Delta G_s$$  \[8\]

Substituting the numerical values of the two terms into Eq. [8] one finds that the critical radius of a nucleus is approximately $3.4 \times 10^{-10} \text{ m}$, which is of the order of the diameter of Fe and Al atoms. The preceding estimation revealed that the critical nucleus contained about one molecule of $\text{Fe}_2\text{Al}_3$.

2. Energy barrier for nucleation

The energy barrier for the formation of such a semispherical nucleus is given by

$$\Delta G^\ast = 2/3 \pi r^\ast \Delta G_s + \pi r^\ast 2 \Delta \gamma$$

$$= \pi 3 \Delta \gamma \Delta G_s$$

$$= 1.51 \times 10^{-19} \text{ J (or 0.94 eV)}$$  \[9\]

Following classic nucleation theory, the number of embryos that have reached the critical size is given by

$$n = \Omega \exp (-\Delta G^\ast /kT)$$  \[10\]

where $\Omega$ is the area density of Fe atoms in the interface, equal to $1.92 \times 10^{19} \text{ atoms/m}^2$, $k$ the Boltzmann constant, and $T$ the temperature in kelvin.

B. Rate of Al Uptake

The addition of one more Al atom to each cluster will convert the embryo into a stable nucleus. If one assumes the sticking efficiency of Al atoms to be unity, i.e., every atom bumping into an embryo will be captured, then the heterogeneous nucleation rate $N$ is given by

$$N = fC_{Al} \Omega \exp (-\Delta G^\ast /kT)$$  \[11\]

where $f$ is a complex function that depends on the vibration frequency of the atoms, the activation energy for Al diffusion in the molten Zn, and the surface of the nucleus, and it is frequently treated as a constant equal to $10^{13}$\[22\] and $C_{Al}$ is the molar fraction of Al in the melt/nucleus interface. Should a strip be constantly exposed to fresh melt, $C_{Al}$ will be a constant related to the concentration of Al in the melt, $C_{Al}$\text{initial}. However, in continuous galvanizing production, the strip travels at a high speed, typically 2 to 3m/s. Fluid mechanics dictates that a boundary layer be developed between the fast-moving strip and the molten Zn alloy, and the thickness of this boundary layer increases with time. This boundary layer is quite stagnant with respect to the strip. This leads to the decrease in $C_{Al}$ due to the fact that Al atoms, consumed by continuous nucleation of $\text{Fe}_2\text{Al}_3$, cannot be totally replenished by the liquid-state diffusion process. Hence, $C_{Al}$ itself is a function of time $t$. Since the consumption rate of Al is proportional to its concentration, $C_{Al}$ is an exponential function of time $t$:

$$C_{Al} = C_{Al}^{initial} \exp (-\alpha t)$$  \[12\]

where $C_{Al}^{initial}$ is the initial interfacial molar fraction of Al.
The heat-transfer coefficient can be evaluated using the following procedure. Using an equation proposed by Sparrow and Gregg\(^{21}\) for liquid metals with uniform wall temperature as a boundary condition, the Nusselt number is approximated by

\[
\text{Nu}_u = \sqrt{\text{Re} \cdot \text{Pr} \cdot \frac{0.564}{1 + 0.90 \sqrt{\text{Pr}}}}\]

where Pr is the Prandtl number for molten Zn and Re, is the Reynolds number. The heat-transfer coefficient h is related to the Nusselt number, the length of the strip L, and the heat conductivity of the steel \(\tau\), through the following equation:

\[
\text{Nu}_u = \frac{hL}{\tau}\]

The average heat-transfer coefficient h was found to be approximately \((0.5 \sim 1.5) \times 10^4 \text{ W/m}^2\text{°C}\).

Nucleation of the Fe\(_2\)Al\(_3\) compound takes place on the steel substrate, and its temperature changes rapidly after entering a bath. Consequently, the nucleation rate of the compound also changes rapidly.

The temperature drop of immersed strips of different thicknesses is shown as a function of immersion time in Figure 1. The calculations were carried out assuming a thermal transfer coefficient of 15,000 W/m\(^2\) °C, a strip-entry temperature of 480 °C, a bath temperature of 460 °C, and an activation energy of 91 kJ/mol. It can be seen that the overall rate of temperature drop decreases with increasing strip thickness. It takes about 1 second for a strip, 1-mm thick, to reach a temperature within 1 °C of the bath temperature. Also indicated in the figure are effective temperatures of the strips, which were calculated using the concept of the kinetic strength of a thermal cycle, proposed by Ion et al.\(^{24,25,26}\) The effective temperature of the 1-mm-thick strip during the transient is approximately 467 °C. In other words, during the first second of immersion, the strip can be treated as one with a constant temperature of 467 °C as far as Al uptake in the interface is concerned.

C. Growth of Fe\(_2\)Al\(_3\)

For galvanizing production, where bath Al content is maintained below 0.2 pct, the rate-controlling step for the growth of the inhibition layer was found to be long-range diffusion of Al in the bath.\(^{10,11,14}\) Treating the whole inhibition layer as a plate growing on the substrate surface and using the simplified approach originally due to Zener,\(^{22}\) the growth rate of the inhibition layer is given by

\[
v = \frac{\Delta X_0}{2(X_s - X_0)} \sqrt{\frac{D}{t}}\]

where \(X_s\) is the molar fraction of Al in Fe-Al\(_3\), compound, \(X_0\) is the molar fraction of Al in the liquid in equilibrium with the Fe-Al\(_3\) compound, \(\Delta X_0 = X_0 - X_s\) is the supersaturation of Al prior to precipitation, \(X_s\) is the molar fraction of Al in the liquid in front of the interface prior to precipitation, \(D\) is the diffusivity of Al in the liquid Zn alloy, and \(t\) is the time.

Equation [17] reveals that the growth rate of the inhibition layer is linearly proportional to the level of Al supersaturation in the liquid. For liquid in equilibrium with the Fe-Al\(_3\) compound, the Al supersaturation level is directly...
proportional to the level of Fe supersaturation. This is the reason why Borzillo and Hahn observed that the growth rate of Fe$_2$Al, increased with increasing Fe content in baths.\(^{12}\) For galvanizing production, the total immersion time is approximately 3 seconds. During this transient, the total amount of Fe dissolved from a strip is expected to be more than that deposited back into the inhibition layer. For example, Yamaguchi and Hisamasu\(^{28}\) reported that the ratio of the total amount of Fe dissolved to that in the alloy layer in the coatings, produced in baths containing Al in the vicinity of 0.2 pct, was approximately 1.5. Their results suggested that Fe was supersaturated in the interface. A direct measurement on an Fe-Zn couple heat-treated at 450 °C using a transmission electron microscope\(^{29}\) indicated that Zn in contact with the ζ phase was indeed supersaturated with Fe at 3.5 wt pct. Perrot \textit{et al.}\(^{10}\) reported that Fe supersaturation in the Zn contiguous to Zn-Fe alloy layers was 0.5 at. pct in a coating produced in an Al-containing Zn alloy. However, quantifying the Fe supersaturation level maintained in front of the inhibition layer is not an easy task. There appears to be no reports on direct measurements available in the open literature. Observations by the present author and his co-workers\(^{8,12}\) suggested that the level of Fe supersaturation maintained in the front of the inhibition layer was a fraction of the equilibrium Fe solubility limit. Iron solubility limits with respect to stable and metastable ζ, δ, and Fe$_2$Al, are shown in Figure 2. Also shown is the proposed Fe content in the front of the inhibition layer as a function of bath Al content. For the present study, ΔX$_{\text{Fe}}$ is estimated to be one-half of the Fe solubility limit X$_{\text{Fe}}$ at a given bath Al content. The instantaneous rate of Al uptake at the interface is illustrated in Figure 3. For the calculation, the Al diffusivity in Zn was assumed to be equal to the Zn self-diffusivity because no data was available, and the two are expected to be similar. Superimposed in Figure 3 is the instantaneous rate of Al uptake due to continuous nucleation. It can be seen that the rate of Al uptake due to nucleation was extremely high initially. However, it decreased quickly due to Al exhaustion and fell below the rate due to the diffusion-controlled growth process.

To further demonstrate the transition from a nucleation-controlled to a long-range diffusion-controlled Al uptake process, the amount of Al in the interface in units of grams per square meter is plotted in Figure 4. The amount of Al enriched in the interface due to continuous nucleation and growth was calculated through integrating Eq. [13] and [17], respectively, over the immersion time, assuming a bath temperature of 470 °C and a bath Al content of 0.16 pct. It can be seen that Al uptake was mainly due to continuous nucleation. It increased rapidly to approximately 0.2 g/m$^2$ in less than 1 second; thereafter, the rate diminished to a negligible level, and long-range diffusion-controlled growth took over. Also shown in the figure are experimental data taken from a number of publications.\(^{1,2,31,32}\) Although there is considerable scatter in the reported data, the predicted values are in general agreement with the experimental data. It is worthwhile noting that the curve runs almost parallel to the set of data reported by Isobe,\(^{21}\) revealing that the present theory describes the transition in the dominant mechanism very well.
The effect of strip-entry temperature on Al uptake is illustrated in Figure 5. For the sample calculation, the bath temperature is assumed to be 470 °C, the effective bath Al is assumed to be 0.16 pct, and the strip thicknesses are 0.75 and 1.5 mm. It can be seen that the effect of strip-entry temperature is augmented by a thicker strip. The predicted curves show the same trend reported by Faderl et al., but they were asymmetrical with respect to the original and their slopes smaller than that portrayed by these researchers. The discrepancy stems most likely from the fact that the data were generated from a production line over a wide range of strip thicknesses and bath temperatures.

Total Al in galvanized coatings Al₁ (wt pct) consists of two parts: one, Al₁ in g/m², being tied up in the Fe₅AI₃ compound in the interface, and the other, Al₂ in g/m², in the coating itself, being linearly related to the coating thickness, t, in micrometers. In general, Al content in the Zn overlay is expected to be slightly lower than the effective Al content in the bath, Alₑ (wt pct), as observed by Dubois. This is because of the Al gradient in front of the interface and further growth of the inhibition layer after the strip exits the bath. For the present calculation, such a difference is ignored. Consider Al₁ in 1 m² coating,

\[ Al₁ = \frac{Alₑ}{\rho} \]  
and

\[ Al₁ = \frac{Alₑ}{\rho} + Al₃ \]

where \( \rho \) is the specific weight of the coating, 7.13 g/cm³. Equation (19) indicates that for galvanizing production, the amount of Al required to maintain a targeted bath Al content is inversely related to the coating thickness and always higher than the targeted bath Al level. Assuming an Al uptake in the interface of 0.15 g/m², a coating thickness of 12 μm (G-60 coating), and a targeted bath Al content of 0.15 pct, the Al content in the charge should be at least 0.33 wt pct. If an 18-μm-thick (G-90) coating is produced, the Al content in the charge could be 0.06 pct less. The minimum Al content in continuous galvanizing grade (CGG) alloy to maintain a bath at 0.15 pct Al for galvanizing production is shown as a function of coating weight in Figure 6.

It should be mentioned here that there is a threshold of bath Al content below which no Fe₅Al₃ can form. For aluminum killed deep drawing quality (AKDQ) steels, this threshold is close to 0.14 pct, slightly higher than the Al content corresponding to the lower limiting tie-line composition for the Fe₅Al₃-liquid two-phase region. For an interstitial free (IF) steel, the threshold can be even higher if the ratio of Ti/C, an indicator of free Ti in the steel, is much higher than 4. The strong affinity of Ti to Al will reduce the effective Al content in the vicinity of the interface. When bath Al contents are below the threshold, the alloys formed in the interface are a mixture of \( \xi \) and \( \delta \) particles, containing little Al. Consequently, Al uptake in the interface is insignificant. With bath Al contents increased from 0.14 to 0.15 pct, the fraction of Fe₅Al₃ in the interface increases exponentially, resulting in a dramatic increase in Al uptake. Also, it should be recognized that steel compositions, steel surface conditions, and bath additions can all shift the threshold. However, these are beyond the scope of the present study.

III. CONCLUSIONS

A model is proposed in which Al uptake at the coating/steel interface is shown to be a two-stage process. The initial high rate of Al uptake is due to continuous nucleation of Fe₅Al₃. The critical nucleus size was found to be approximately one molecule of the compound. The initial rate of Al uptake in the interface was only limited by the availability of Al atoms in front of the interface. Aluminum is quickly depleted in this region, and growth of the inhibition layer is limited by the supply of Al through long-range diffusion in the liquid. Aluminum uptake is expected to increase with increasing strip-entry temperature and thickness, because both work to increase the effective temperature of a strip for the formation of Fe₅Al₃ at the interface. Coating weight does not affect the Al uptake in the interface, but alters the weight percentage of Al in the coating because molar fractions of Al in the interface and in the coating are substantially different. Variations in line speed
and pot size lead to variations in total immersion time of a strip. However, the rate of Al uptake is relatively low after the first second of immersion, and thus, for normal commercial continuous galvanizing lines, the effects of line speed and pot size on Al uptake are insignificant.

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REFERENCES