

Practical Applications of Phase Diagrams in Continuous Galvanizing

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(Submitted February 10, 2006; in revised form May 31, 2006)

Zn-Fe based high-order phase diagrams have found a wide range of applications in continuous galvanizing. With the development of computer software DEAL (Determine Effective Aluminum), the Zn-rich corner of the Zn-Fe-Al phase diagram is being used daily for scientific interpretation of bath assays. Computer software PAL (Predict Aluminum Level), also developed by Teck Cominco Metals Ltd., assesses transient equilibria between the steel substrate and the liquid galvanizing alloy for the estimation of Fe dissolution and Al consumption in galvanizing. Aluminum deportment in galvanizing baths has been scientifically described based on the fact that bath assays corresponding to different locations and depths of a galvanizing bath formed one tie-line in the liquid-Fe₂Al₅ two-phase field of the Zn-Fe-Al phase diagram. Zn-Fe based high-order phase diagrams also afford a better understanding of the mechanisms for a number of industrial phenomena. These practical applications of the Zn-Fe based phase diagrams are detailed in the article.

Keywords invariant, isothermal section, practical applications, ternary phase diagram, Zn-Fe-Al system

1. Introduction

Phase diagrams are concise representations of the states of equilibrium available to materials systems. They clearly illustrate the influence of changes in composition, temperature, and pressure on the equilibrium states. However, their complexity increases exponentially with the number of components present in a system. If binary phase diagrams are frequently used by researchers and engineers to understand experimentation and production practices, ternary diagrams are a luxury for a privileged few. The mention of ternary phase diagrams in undergraduate texts is universally brief and limited to the simplest systems. Ternary phase diagrams available in the open literature are frequently too sketchy for applications in industrial process control.

The development of high-order phase diagrams is mainly driven by practical needs and, to a lesser degree, by the scientific curiosity of devoted researchers. In recent years, a large number of ternary and partial quaternary phase diagrams evolved from the binary Zn-Fe system have been developed.^[1-10] These developments are the results of the rapid increase in production capacity in the galvanizing industry, the increasingly stringent quality requirements from end users, and the dedication of researchers in the Zn in-

dustry who strive to serve the galvanizing industry better. As a result, the Zn-rich corners of these ternary phase diagrams mostly possess a high accuracy. The partial quaternary phase diagrams are presented in the form of liquid domain, a perspective presentation of the Zn corner of the phase diagram. Due to the complexity of the diagrams, they are largely schematic at present, and a complete isothermal tetrahedron of a quaternary phase diagram has yet to be developed.

2. Zn-Fe-Al Ternary System

During the hot dip galvanizing process, Fe constantly dissolves from the steel being coated, and intermetallic compounds form at the interface between the steel and the coating. The amount of Fe dissolved from the steel is always more than the amount taken out by the coating, resulting in Fe saturation of the coating bath and the formation of dross. Experimental results, shown in Fig. 1, indicate that the time period for a continuous galvanizing bath to become Fe-saturated is only about 10 h.

Calculations indicated that the Fe dissolution rate was initially greater than 1 g/m² of coated steel strip. The rate decreased with time and leveled off at about 0.4 g/m² when Fe was saturated in the bath containing 0.04%Al at 470 °C.

Continuous galvanizing baths always contain a small amount of Al, frequently less than 0.3%, to mitigate the reaction between the molten Zn alloy and the coated steel. The Al content of the bath can be as high as 55% if a super corrosion resistance of the coating is required. Consequently, the continuous galvanizing bath is essentially a Zn-Fe-Al alloy of the ternary system. The bath Al content for processing a certain type of product is dictated by the law of economics: to produce a product with the highest quality at the lowest possible cost, thereby maximizing the

This article is based on a presentation made at the Galvanizers Association Ninety-Seventh Meeting held in Lexington, KY, from Oct 17 to 19, 2005.

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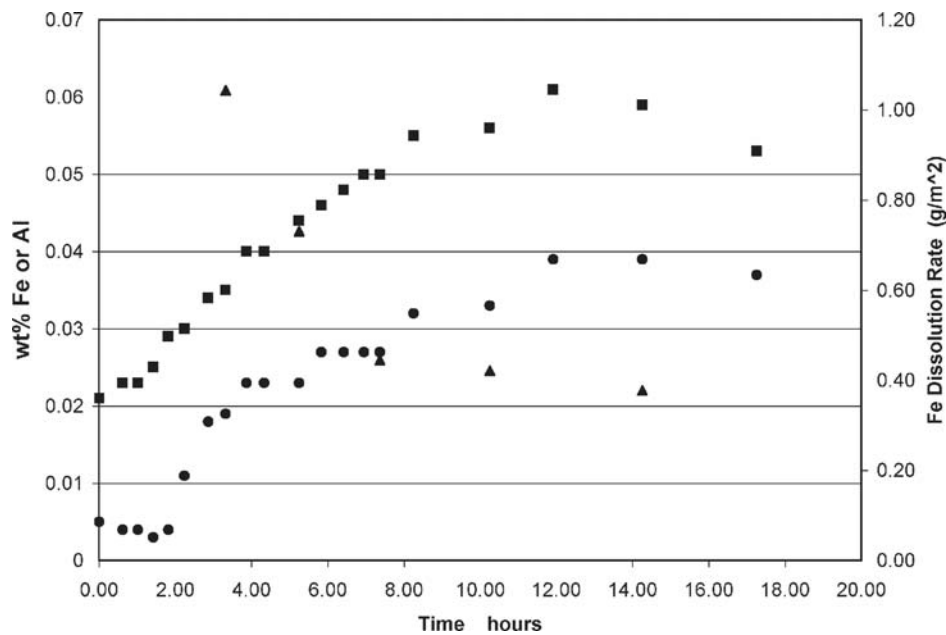


Fig. 1 Increase in Fe content (squares) of a bath during the early stage of production. The pot made of Fe was initially loaded with special high grade (SHG) Zn only and the bath temperature was kept at 470 °C. The Fe content in the bath reached 0.02% before the commissioning of the line. The bath was saturated with Fe after less than about 10 h into the production. Calculations indicated that the Fe dissolution rate (triangles) decreased with time and leveled off at about 0.4 g/m² when Fe was saturated in the bath. Also shown is the evolution of Al content (solid circles) of the bath.

financial return for the producer. After more than a decade of intensive research and development, the optimum Al content of a coating bath can now be scientifically defined based on the product and pot specifics: the invariant point corresponding to the liquid- δ (FeZn₁₀)- η (Fe₂Al₅) three-phase equilibrium in the Zn-Fe-Al system has been used as the reference bath composition in continuous galvanizing production.

The complexity of the problem increases exponentially when one tries to better understand how an alloying addition to the steel would affect the optimum bath Al level and the coating properties. It is well known that a small amount of P and/or Si in the steel has a strong bearing on the galvanizing temperature and the final structure and properties of the coatings.^[11,12] To fully understand the underlying mechanisms, one must possess some knowledge of the relevant quaternary systems, the Zn-Fe-Al-P and Zn-Fe-Al-Si systems.

The situation is similar when one tries to improve the performance of bath hardware. While pot rolls are frequently made of 316L stainless steel, bearings for these rolls are made of complex engineering alloys frequently containing Co and other transitional metals. To interpret the performance of pot rolls, one needs a basic knowledge of the Zn-Fe-Al-Cr quaternary system. Additionally, to understand the performance of bearings made of Stellite, one needs to know the interplay of Co with the Zn-Fe-Al ternary system. The sections that follow provide detailed explanations on how the Zn-Fe-Al ternary phase diagram has been developed to better equip line engineers to meet the challenges arising from their daily work.

3. Determination of Effective Al

In the early 1990s, galvanneal coatings (GA) became the material of choice for exposed automobile body panels. The production of high-quality GA requires a precise control of bath effective Al. However, the analysis and control of Al is complicated by the fact that it exists in two forms in the bath: in solution of the molten Zn and in intermetallic particles. It is the Al in liquid solution, commonly referred to as “active” or “effective” Al, which performs its main function of inhibiting the Fe-Zn reaction. Due to the dynamic and turbulent nature of the bath metal, avoiding the entrapment of intermetallic particles in bath samples has proven challenging if not impossible.^[13] At that time, most galvanizers relied on empirical formulas developed by major integrated steel producers to calculate the effective Al based on bath assays of total Al and Fe. These formulas have no scientific basis^[14] and failed to provide meaningful data in GA production. At that time, several research groups^[13-16] engaged in the refinement of the Zn-Fe-Al phase diagram to accurately describe the liquid phase boundaries, referred to as Fe solubility curves in the galvanizing industry, for the development of a scientific method for the determination of the effective Al content of a bath.

Among the few sets of isothermal sections proposed by those researchers,^[13-18] only the one proposed by Tang^[17,18] has survived the rigid tests of galvanizers.^[19] Tang and his coworkers have repeatedly revised and refined the Zn-Fe-Al phase diagram through a combination of experimentation and thermodynamic modeling,^[6,17,18] thereby ensuring that the phase diagram possesses accuracy compatible with the

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quality-control practices in GA productions. The Zn-rich corner of the 465 °C isothermal section of the Zn-Fe-Al system is shown in Fig. 2. It can be seen that the system is quite complicated. With the Al content of the liquid phase increasing from 0 to 0.136%, the equilibrium intermetallic compound changes in rapid succession from the ζ -FeZn₁₃ phase to the δ -FeZn₁₀ phase and to the η -Fe₂Al₅ phase. With further increases in Al content, the θ -FeAl₃ emerges.

In principle, the determination of effective Al content of the bath is to determine the Al activity in the system. It involves the construction of a tie-line passing through the point that represents the bath sample composition in the Gibb's composition triangle. The tie-line connects two-phase compositions in equilibrium. Its intersection with the liquid phase boundary corresponds to the effective bath Al level. The lever rule is then used to determine the amount of solid intermetallic particles entrapped in the bath sample. If the bath composition falls into a three-phase region, as it

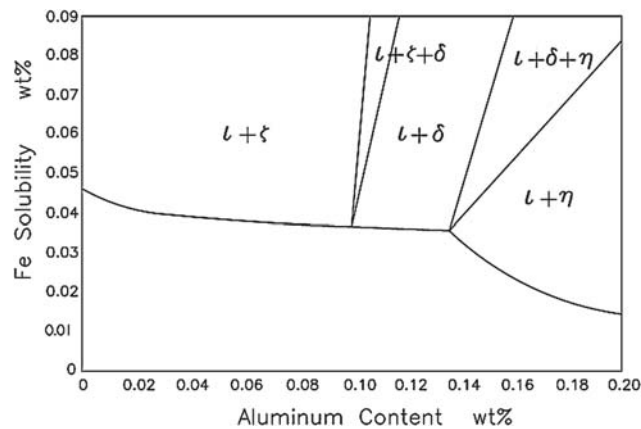
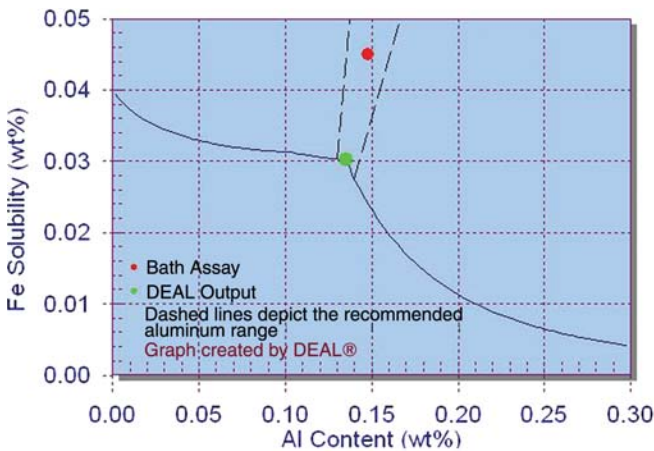


Fig. 2 The Zn-rich corner of the Zn-Fe-Al ternary system at 465 °C



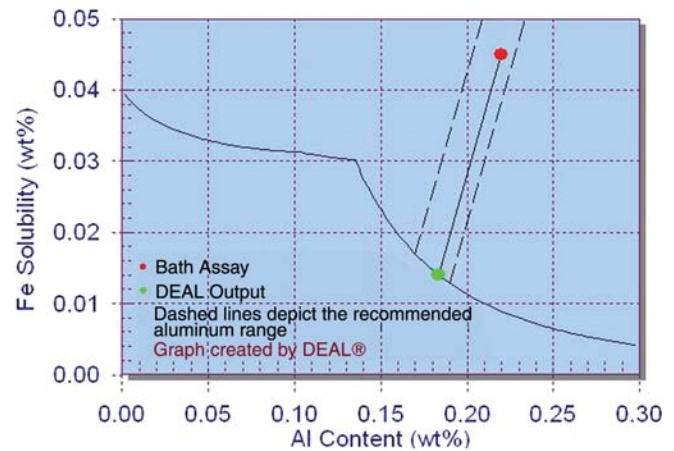
(a)

frequently does in GA production, then determination of the effective Al becomes much easier. Despite the fact that bath sample compositions can vary within the full expanse of this triangle, Gibb's phase rule dictates that the effective Al level remains the same and is a function of temperature only.

To facilitate the practical applications of the phase diagram, computer software DEAL (Determine Effective ALuminum) (Teck Cominco Metals Ltd., Mississauga, Ontario, Canada) was written^[14] using an event-driven programming technique to ensure its user-friendliness. DEAL has been accepted by galvanizers with great interest and has become the standard tool for the daily management of bath chemistry. Some galvanizers have even incorporated DEAL into their line control systems. On these galvanizing lines, bath temperature and bath assays are fed directly into DEAL, and a recommendation on bath chemistry adjustment is issued directly by the line controlling system. Figure 3 illustrates how DEAL is used to calibrate bath assays in productions of (a) GA and (b) GI (galvanized coatings).

Scientific interpretation of bath assays is only one practical application of the Zn-Fe-Al ternary phase diagram. The selection of an optimum effective Al level for GA production is an even more important application of the phase diagram.

In GA production, bath Al control is extremely critical for the following reasons. Coating thickness for automotive applications is limited to less than 10 μm . Hence, the reaction between the molten coating alloy and the steel substrate should be largely inhibited in the hot dip stage to prevent the growth of Zn-Fe intermetallic compounds in the coating. Otherwise, coating weight control would be a problem. On the other hand, the inhibition layer in the interface should be uniform and thin enough so that it will be broken down easily and uniformly during the annealing stage. These two conflicting requirements dictate that the invariant point corresponding to the liquid- δ - η three-phase equilibrium is the reference composition for GA production.



(b)

Fig. 3 (a) Bath assay calibration using DEAL in GA production. The bath sample composition falls within the tie-triangle, and the effective bath Al level is the invariant composition (0.135% Al at 460 °C). (b) The tie-line passing through the assay point (0.220%Al/0.045%Fe) intersects the liquid phase boundary at the green dot that indicates an effective bath Al level of 0.184%. The volume fraction of Fe₂Al₅ particles entrapped in the sample is 0.13%.

The greatest contribution of the researchers at Teck Cominco to the prosperity of the galvanizing industry is the precise determination of the invariant composition. An earlier study reported that the Al composition of this invariant point was 0.12% at 450 °C.^[20] Tang^[17,18] pinpointed the composition to 0.134% at this temperature. He further predicted that the position of this variant is a weak function of temperature. With an increase in temperature of 1 °C, the corresponding Al composition of the invariant point increases by 1 ppm only. Such a prediction has been proven accurate by data collected using Al sensors in galvanizing. When a galvanizing bath operates at the invariant point, the Al reading of the sensor increases by 10 ppm with a 10 °C increase in the bath temperature with no Al added to the bath. On the other hand, if the bath operates at an effective Al level higher than the invariant composition, the sensor output increases by 70 ppm. In these cases, the increase in bath Al level is afforded by the dissolution of η -Fe₂Al₅ particles, referred to in the industry as top dross, when the bath temperature increases.

The accuracy of the phase diagram and the versatility of the DEAL program have also been proven in numerous practical applications. A few case studies are detailed here.

3.1 Case 1—Predicting Bath Temperature

Three bath samples, 3.8 cm in diameter and 4.6 cm long, were provided by one galvanizer for chemical analyses. Such big samples are not recommended because the cooling rate of the samples was slow and intermetallic particles, rejected from the solidification front, were found to segregate in the center of the samples. When chips are taken from the samples by drilling, erratic assays are frequently reported.^[13]

Three sets of chips were drilled from the surface layer, the middle, and the center of each sample. Chemical analyses revealed that the total Al and Fe in the samples increased with the depth from which the chips were taken. The assay results of samples 1 and 2 are listed in Table 1. Before using DEAL for the determination of the effective Al of the bath, the temperature of the bath must be estimated because the bath temperature was not given (only a range of 450 to 460 °C was mentioned).

The bath temperature was estimated based on the following facts:

- The metal in the outside layer must have been cooled down relatively quickly due to the direct contact with the mold. Hence, chips taken from this layer can be considered a true representation of the bath chemistry.
- Metallographic examination of a cross section of sample 2 revealed that there were few dross particles near the surface layer of the sample.
- The total Fe and Al in the outside layer of sample 2 were 0.025% and 0.132%, respectively. This composition falls on the liquid boundary at 453 °C.

Hence, it was concluded that the bath temperature when sample 2 was taken could not have been higher than 453 °C. Otherwise, the bath would have been unsaturated in Fe, a

Table 1 Bath nominal compositions (wt.%) and effective Al determined using DEAL

Sampling location	Sample 1		Sample 2	
	Al _{tot} /Al _{eff}	Fe _{tot} /Fe _{sol}	Al _{tot} /Al _{eff}	Fe _{tot} /Fe _{sol}
Outside	0.137/0.135	0.025/0.023	0.132/0.131	0.025/0.023
Middle	0.139/0.134	0.035/0.023	0.133/0.131	0.030/0.023
Center	0.143/0.134	0.047/0.023	0.135/0.131	0.035/0.023
Average	0.140/0.134	0.036/0.023	0.133/0.131	0.030/0.023
STD	0.003/0.0006	0.011/0.000	0.0015/0.000	0.005/0.000

situation not realistic for a line in constant operation and plagued by excessive bottom dross formation. It was later confirmed that the temperature of the bath was 451 °C when the bath samples were taken.

The assays were calibrated using DEAL, and the bath effective Al was found to be unique for each sample regardless of the assays used for the calibration (see data listed in Table 1). If the empirical formula, $Al_{eff} = Al_{tot} - Fe_{tot}$, proposed by a major steel producer,^[14] was used, the effective bath Al for sample 1 would vary from 0.112 to 0.096%.

3.2 Case 2—Predicting Characteristics of Intermetallics

The galvanizing industry has witnessed rapid technology advances in almost every sector of a galvanizing line. However, quite a few lines that were built in the 1960s are still being used. The galvanizing pots on these Sendzimir lines are typically small in capacity, and a high strip entry temperature is used to provide heat to the galvanizing pot. Frequently, the bath temperature is abnormally high by modern standards. As a result, bath chemistry management on these lines is a challenge. A bath sample was provided by one such galvanizer to determine the bath effective Al in relation to the nature, size, and distribution of dross particles in the bath sample. The bath temperature was 482 °C at the time of sampling. This should be compared with the normal bath operating temperature of about 460 °C on modern galvanizing lines.

The bottom surface of the bath sample was turned on a lathe to obtain material for chemical analysis. The total Fe and Al were found to be 0.078 and 0.172%, respectively. A DEAL calibration indicated that the bath effective Al was 0.141% with soluble Fe of 0.052%, very close to the invariant point of 0.138% Al at 482 °C. In view of the unavoidable uncertainty in the chemical analyses and temperature measurement, and the dynamic nature of a small coating bath, it was believed that the sample could contain two types of intermetallic particles, that is, the δ and the η phases with the majority being the latter compound. Metallographic examination carried out later confirmed the above prediction. As can be seen in Fig. 4, both δ (gray) and η (black) particles were present in the bath sample.

3.3 Case 3—Clarifying Confusion in Bath Assays

In the early 1990s, there was no scientific method for determining the bath effective Al level. Different galvaniz-

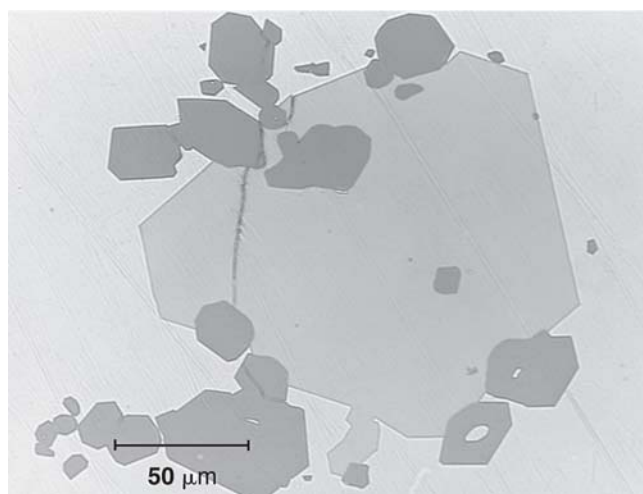


Fig. 4 Two types of intermetallic particles, δ (gray) and η (black), coexisted in the bath. Source: Ref 18

Table 2 Effective bath Al level (wt.%) determined using DEAL, Japanese, and IRSID formulas

Laboratory	Samples	Total		Effective aluminum		
		Al	Fe	DEAL	Japan	IRSID
A	1	0.198	0.099	0.135	0.101	0.116
	2	0.151	0.055	0.135	0.106	0.119
	3	0.144	0.050	0.135	0.106	0.119
	4	0.152	0.058	0.135	0.104	0.118
	5	0.143	0.046	0.135	0.109	0.121
	Average				0.135	0.105
	STD			0.000	0.003	0.0018
B	1	0.149	0.049	0.135	0.112	0.123
	2	0.135	0.043	0.130	0.105	0.120
	3	0.141	0.040	0.135	0.115	0.118
	4	0.157	0.049	0.135	0.114	0.124
	5	0.126	0.040	0.123	0.100	0.115
	Average				0.132	0.109
	STD			0.0048	0.0065	0.0037

ers used different methods for this purpose. One European galvanizer carried out a study to evaluate the reliability of empirical formulas and the capability of its two analytical laboratories. The galvanizer used two calibration methods, one proposed by Japanese researchers and the other by IRSID.^[16] The bath was sampled every 4 h in a GA production campaign, and the calibrated bath assays indicated that over a 16 h period, the bath effective Al content constantly changed. The bath assays were calibrated using the empirical formulas, and rather confusing results were obtained. Assay calibrations based on the analyses carried out by laboratory A indicated that the effective Al level changed within a range from 0.101 to 0.109% according to the Japanese formula and from 0.116 to 0.121% using the IRSID formula (Table 2). The results obtained by the two laboratories suggested that the effective Al sometimes varied significantly even within a bath sample. After the data were

reported at the Inaugural Meeting of the Galvanizing Bath Management Task Force, organized by the International Lead Zinc Research Organization (ILZRO) in 1994, Teck Cominco volunteered to process the data using DEAL. The results indicated that its control over bath Al content was excellent. Over the 16 h period, the bath effective Al remained unchanged at 0.135%. Although the total Al and total Fe reported by the two laboratories varied significantly for sample 1 because the analyzed material was taken from different locations of the sample, hence the amount of intermetallic particles entrapped in the material was significantly different, the bath effective Al was found to be unique. A thorough analysis of the data suggests that the analyses carried out by laboratory B were less reliable than those carried out by laboratory A. Bath effective Al contents determined by DEAL are also listed in Table 2.

4. Managing Dross Generation

Precise determination of the invariant composition has brought practical solutions to a number of industrial problems. At the beginning of the last decade, all then newly built lines produced mainly GA products and were plagued with excessive bottom dross accumulation in the production that negatively affected not only line operating efficiency but also product quality. One line had to be stopped for bottom dross removal every week or so. By maintaining the effective Al content of the bath at a level marginally higher than the invariant composition, intermetallic particles produced in the bath are all iron aluminide, lighter than the molten metal. As a result, bottom dross accumulation is no longer a problem. The beneficial effect of using DEAL was realized immediately by these GA producers. For example, one galvanizer generated 7 to 9 tons of bottom dross every 2 weeks before a Teck Cominco service engineer recommended DEAL to the line engineers. After abandoning the empirical formula they had relied on for bath assay calibration and using the DEAL program and its built-in recommendation on the Al range for GA production, the bottom dross produced in the pot was reduced to 5 to 6 tons every 3 weeks after just a couple of months. With further tuning up of the bath addition practice, the line never requires stoppage for the sole purpose of bottom dross removal.

Because of its importance to galvanizing production, the liquid- δ - η invariant has been dubbed the knee point by galvanizers.

5. Characterization of Galvanizing Bath

A clear understanding of the characteristics of galvanizing baths would not be possible without the Zn-Fe-Al phase diagram. Working with former Inland Steel, engineers and researchers from Teck Cominco sampled the bath at 21 locations at three depths and experimentally determined the distribution of bath composition and temperature. The results were published in the proceedings of the 1996 Galvanizers Association meeting.^[22] It was shown that effective Al is more or less uniformly distributed in the pot. However

a scientific description of the bath characteristics emerged only after the present author reanalyzed the results and plotted all assay data onto the Zn-Fe-Al phase diagram. As shown in Fig. 5, points representing bath assays formed a tie-line in the phase diagram, indicating clearly that the bath metal is well mixed due to the rapid movement of the strip, and that the distribution of bath effective Al in a pot is a function of bath temperature distribution only.^[23]

The above conclusion serves as the foundation for computer modeling of Al department in galvanizing baths.

6. Predicting Al Consumption

Knowledge of transient Fe solubility is critical for predicting Al consumption in galvanizing, and the estimation of transient Fe solubility in the vicinity of steel strip when it is first exposed to the molten Zn-Al alloy also relies on the information contained in the phase diagram. Iron solubility at the coating/substrate interface is dictated by the equilibrium between the liquid and the outermost intermetallic compound in the alloy layer covering the steel surface. This compound is the ζ phase in general galvanizing and the η phase in continuous galvanizing. However, when the strip is initially exposed to the melt, there is no intermetallic compound covering the steel surface, and the bare steel momentarily coexists with the liquid. The transient Fe solubility in the immediate vicinity of the strip surface is, at this time, determined by the metastable equilibrium between the steel and the molten coating alloy. This transient Fe solubility is much higher than the equilibrium value. It is more than two orders of magnitude higher than the equilibrium value if the liquid consists of pure Zn, as shown in Fig. 6, and it is about one order of magnitude higher than the equilibrium Fe solubility when the molten Zn contains a small amount of Al. The amount of Al consumed in galvanizing the steel strip is mainly determined by the amount of Fe dissolved from the

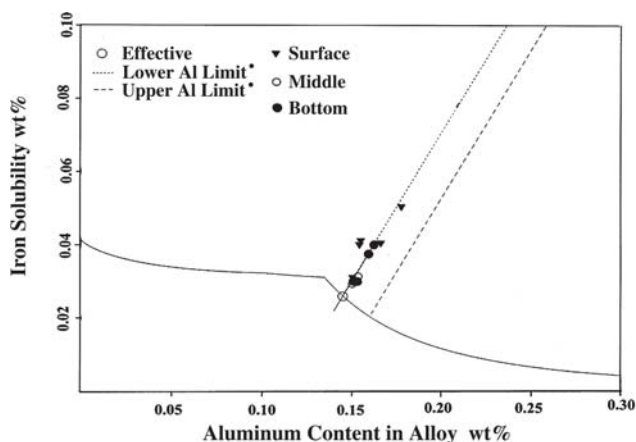


Fig. 5 Bath samples were taken from 21 locations at three depths of a pot. When plotted onto the Zn-Fe-Al phase diagram, these assays formed a tie-line in the liquid- η two-phase region. This finding indicates that the bath is a two- or three-phase mixture, and the distribution of bath effective Al is a function of bath temperature distribution only (Ref 23)

strip during this transient. In galvanizing production, the dissolved Fe will all convert into the η phase, either as the interfacial inhibition layer or as top dress particles. In galvannealing, the dissolved Fe could either be transformed into the η phase and/or the ζ phase, depending on the bath effective Al level. Teck Cominco has developed computer program PAL (Predict Aluminum Level) (Teck Cominco Metals Ltd., Mississauga, Ontario, Canada) to accurately calculate the amount of Fe dissolved from the strip and the bath feed requirement in the production.

7. Conclusions

In the early 1990s, GA coatings became the material of choice for exposed automobile panels. The production of high-quality GA coatings requires accurate control of the Al

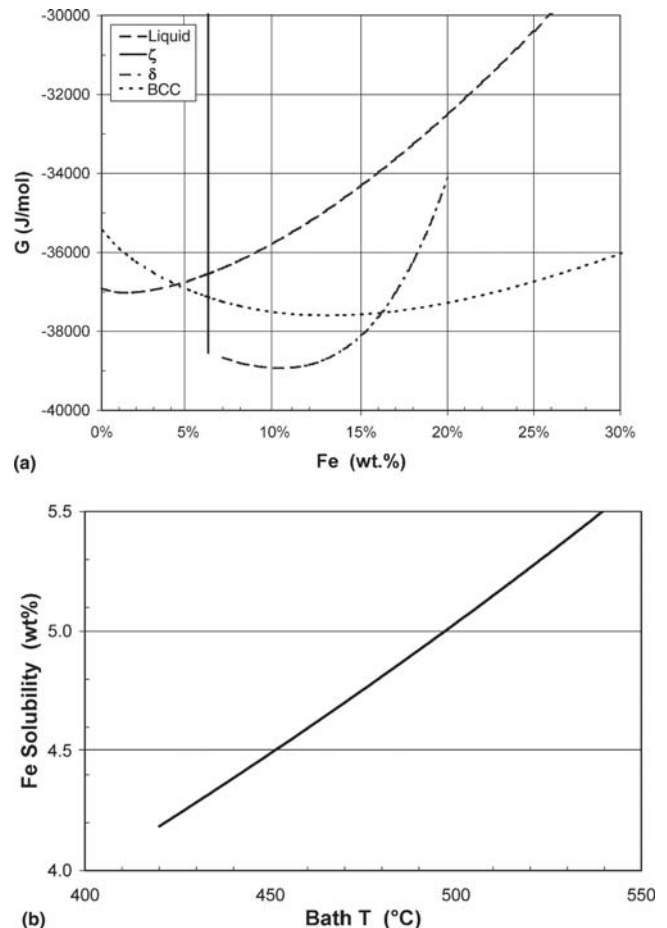


Fig. 6 (a) The free energies of the relevant phases in general galvanizing. The liquid is momentarily in equilibrium with the bcc phase when the steel is just exposed to the molten Zn. The data plotted here are generated using ThermoCalc and the database created in the assessment of the Zn-Fe system by Su et al. (Ref 21). (b) The transient Fe solubility in the immediate vicinity of the strip submerged in pure molten Zn as a function of temperature. The data plotted here are generated using ThermoCalc and based on the work of Su et al. (Ref 21)

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content in the bath. As a result, empirical formulas, developed by large integrated steel companies for calculation of bath effective Al level, became inadequate and even misleading. There was an urgent need for scientific tools for bath assay interpretation and for process improvement. With the concerted efforts of scientists and engineers from the industries and academia, the Zn-Fe-Al ternary phase diagram with a great accuracy was developed and numerous applications of the phase diagram have since been devised. It should be emphasized here that the development of these applications would be impossible without the availability of low-cost yet powerful computers due to the complexity of the technical tasks involved in these applications. With the development of computer software DEAL, the Zn-rich corner of the Zn-Fe-Al phase diagram has been used daily for scientific interpretation of bath assays. Computer software PAL assesses transient equilibria between the steel substrate and the liquid galvanizing alloy for the estimation of Fe dissolution and Al consumption in galvanizing, thereby making automation of bath chemistry control possible. Aluminum deportment in galvanizing baths has been scientifically described based on the fact that bath assays corresponding to different locations and depths of a galvanizing bath formed one tie-line in the liquid-Fe₂Al₅ two-phase field of the Zn-Fe-Al phase diagram. The successful applications of the Zn-Fe-Al ternary phase diagram in continuous galvanizing have demonstrated clearly that multicomponent phase diagrams are useful tools in industrial process design and control.

Acknowledgments

The author is grateful to Dr. Yihui Liu for plotting Fig. 6(a) and (b), Mr. Artur Filc for drawing the phase diagram, and Mrs. Angeline M. Prskalo for editorial assistance in the preparation of the manuscript.

References

1. N.-Y. Tang, X.P. Su, and X.B. Yu, The Zn-Rich Corner of the Zn-Fe-Co System at 450 °C, *Z. Metallkd.*, 2003, **94**(2), p 116-121
2. N.-Y. Tang, X.P. Su, and X.B. Yu, A Study of the Zn-Rich Corner of the Zn-Fe-Sn System, *J. Phase Equilibria*, 2003, **24**(6), p 528-532
3. X.P. Su, F.C. Yin, Z. Li, N.-Y. Tang, and M.X. Zhao, Thermodynamic Calculation of the Fe-Zn-Si System, *J. Alloy. Compd.*, 2005, **396**, p 156-163
4. N.-Y. Tang and X.B. Yu, Study of the Zinc-Rich Corner of the Zn-Fe-Cr System at Galvanizing Temperatures, *J. Phase Equilibria Diffus.*, 2005, **26**(1), p 50-55
5. X.P. Su, N.-Y. Tang, and J.M. Toguri, 450 °C Isothermal Section of the Fe-Zn-Si Ternary Phase Diagram, *Can. Metall. Q.*, 2001, **40**(3), p 377-384
6. N.-Y. Tang, 450 °C Isotherm of Zn-Fe-Al Phase Diagram Update, *J. Phase Equilibria*, 1996, **17**(5), p 396-398
7. X.P. Su and N.-Y. Tang, The Zinc-Rich Corner of the Zn-Fe-Ni-Si Quaternary System at 450 °C, *J. Phase Equilibria*, 2002, **23**(5), p 424-431
8. N.-Y. Tang, Y.H. Liu, and K. Zhang, Development of High Order Phase Diagrams for Practical Applications in Galvanizing, in Proceedings, *44th Mechanical Working and Steel Processing (MWSP) Conference* (Orlando, FL), Sept 8-11, 2002, p 815-821
9. G. Reumont and P. Perrot, Fundamental Study of Lead Additions in Industrial Zinc, in Proceedings, *18th International Galvanizing Conference, Intergalva 97* (Birmingham, UK), June 8-11, 1997, European General Galvanizers Association, p 4/1-7
10. G. Reumont, T. Gloriant, and P. Perrot, The Zinc Rich Corner of the Fe-Zn-Ni-Ti Quaternary System at 450 °C, *J. Mater. Sci. Lett.*, 1997, **16**, p 62-65
11. J. Faderl, J. Strutzenberger, and W. Fischer, Galvannealed Steel Sheet: 10 Years of Experience on Product and Process Improvement, Proceedings, *Galvatech'01* (Brussels, Belgium), June 2001, Verlag Stahleisen GmbH, Düsseldorf, 2001, p 385-392
12. J.-S. Kim and J.-H. Chung, Galvannealing Behaviour of High Strength Galvanized Sheet Steels, Proceedings, *Galvanised Steel Sheet Forum-Automotive*, The Institute of Materials, London, UK, May 2000, p 103-108
13. M. Gagne, H. Guttman, J. L'Ecuyer, G.G. Brummitt, G.L. Adams, and D. Kleimeyer, The Analysis and Control of Aluminum in Galvanizing Baths, Proceedings, *82nd Galvanizers Association Meeting* (Niagara Falls, NY), Oct 22-25, 1990, p 126-145
14. N.-Y. Tang, G.R. Adams, and P.S. Kolisnyk, Determination of Effective Aluminum in CGL Baths, Proceedings, *Galvatech'95* (Chicago, IL) Sept 17-21, 1995, ISS, p 777-782
15. P. Biele, Determination of the Active Al and Fe Contents in the Zinc Bath and Their Influence on Alloy-Layer Formation in the Hot-Dip Galvanizing Process, Proceedings, *Galvatech'95* (Chicago, IL) Sept 17-21, 1995, ISS, p 769-776
16. M. Dauszat, F. Stouvenot, and T. Moreau, Zinc Rich Corner of the Fe-Zn-Al Revised Phase Diagram, Proceedings, *Galvatech'92* (Amsterdam, The Netherlands), Sept 1992, Verlag Stahleisen, Düsseldorf, 1992, p 449-454
17. N.-Y. Tang, 450 °C Isotherm of the Zn-Fe-Al Phase Diagram, *Mater. Sci. Technol.*, 1995, **11**, p 870-873
18. N.-Y. Tang, Determination of Liquid Phase Boundaries in Zn-Fe-Mx Systems, *J. Phase Equilibria*, 2000, **21**(1), p 70-77
19. M.-L. Giorgi, J.-B. Guillot, H. Biaisser, and R. Nicole, Assessment of the Zinc-Aluminum-Iron Phase Diagram in the Zinc-Rich Corner, Proceedings, *Galvatech'01* (Brussels, Belgium), June 26-28, 2001, Stahleisen GmbH, Düsseldorf, 2001, p 179-186
20. M. Uredniecek and J.S. Kirkaldy, An Investigation of the Phase Constitution of Iron-Zinc-Aluminum at 450 °C, *Z. Metallkd.*, 1973, **64**(6), p 419-427
21. X.P. Su, N.-Y. Tang, and J.M. Toguri, Thermodynamic Assessment of Zn-Fe System, *J. Alloy. Compd.*, 2001, **325**(1-2), p 129-136
22. G.N. Anderson, N.-Y. Tang, and R.S. Patil, Aluminum Distribution in a CGL Bath, Proceedings, *Galvanizers Association 88th Meeting* (Chicago, IL), Oct 20-23, 1996, p 44-62
23. N.-Y. Tang, Characteristics of Continuous Galvanizing Baths, *Metall. Mater. Trans. B*, 1999, **30B**, p 144-148