

Comment on Fe-Al-Zn (Iron-Aluminum-Zinc)

The tutorial by Prof. D.R. Gaskell¹ in the October 1993 issue of this journal deals with a complex subject in a nicely readable style. It is quite useful in illustrating the application of phase diagrams to the understanding of technological processes. However, recent research has shown that the Fe-Al-Zn diagram that Prof. Gaskell used for explaining the control of the kinetics of the galvannealing of steel is inaccurate. Because of the industrial importance of the galvannealing process, the present comment is submitted to clarify the situation. Much of the explanation offered by Prof. Gaskell for this process, though quite consistent with the diagram being used by him, is inappropriate in fact.

The 450 °C isotherm used by Prof. Gaskell was constructed by Urednicek and Kirkaldy² in the early seventies. Now, it is widely realized by researchers and engineers in the galvanizing industries that the Zn corner of that isotherm is inaccurate. The two most significant inaccuracies are as follows: Fe solubility in molten Zn was

shown as being constant at 0.029 wt.%, and the lower limiting tie-line for the liquid and $\text{Fe}_2\text{Al}_5\text{-Zn}_x$ two-phase region was placed at 0.11 wt.% on the liquid phase boundary. Together, these two errors lead to impossible interpretations of a number of phenomena that occur in galvanizing production.

Contrary to the argument by Cameron and Ormay³ that Fe solubility in molten Zn should decrease with increasing Al content in the melt, Urednicek and Kirkaldy² stated that at 450 °C the Fe solubility in molten Zn was constant at 0.029 wt.%, regardless of Al content. In this regard, Belisle et al.⁴ recently demonstrated that in the region where $\text{Fe}_2\text{Al}_5\text{-Zn}_x$ is in equilibrium with the liquid, Fe solubility decreases with increasing Al content in the molten Zn. Unfortunately, thermodynamic data for the binary Fe-Al compounds instead of the ternary Fe-Al-Zn compounds was used for their calculations. Consequently, Fe solubility in this region was underestimated by a factor of two. Also, the lower limiting tie-line for the liquid and $\text{Fe}_2\text{Al}_5\text{-Zn}_x$ two-phase region was

implicitly placed at 0.07 wt.% Al on the liquid phase boundary.

Due to its importance to industrial applications, the Zn corner was reinvestigated recently by me and my coworkers at Cominco Ltd., Product Technology Centre, Canada. Based on theoretical reasoning supplemented by experimentation, we found that Fe solubility in liquid Zn decreased with increasing Al concentration, as suggested by Cameron and Ormay three decades ago. The functional dependence of Fe solubility on Al content was found to vary with the intermetallic compounds in equilibria with the liquid Zn.^{5,6} It was also established that at 450 °C the lower limiting tie-line for the liquid and $\text{Fe}_2\text{Al}_5\text{-Zn}_x$ two-phase region was located at 0.133 wt.% Al on the liquid phase boundary. A number of observations readily support this conclusion. For example, for galvannealing production, a bath typically contains about 0.13% Al. Technical investigations carried out by Cominco Ltd. for galvanizing customers have positively identified that the equilibrium intermetallic compound in such a bath was δ phase, not $\text{Fe}_2\text{Al}_5\text{-Zn}_x$ as suggested by the isotherm used by Prof. Gaskell. For a full inhibition effect, Horstman⁷ found that the minimum Al was approximately 0.15% at 450 °C. His finding was confirmed recently by Tang and Adams.⁵

For the benefit of the readers, the Zn corner of the 470 °C isotherm of the Fe-Al-Zn ternary phase diagram is shown in Fig. 1. 470 °C was selected because most baths for galvannealing production are kept at this temperature.

With the inadequacies of the 450 °C isotherm used in his work, it becomes obvious that the explanation offered by Prof. Gaskell is inappropriate. If a dynamic equilibrium state prevails in galvannealing production, the phase that first nucleates on steel strip should be the δ phase, not Fe_2Al_5 . In production, steel strip moves at high speed (typically 2 to 3 m/s) and is exposed to the molten Zn alloy for a short time (ap-

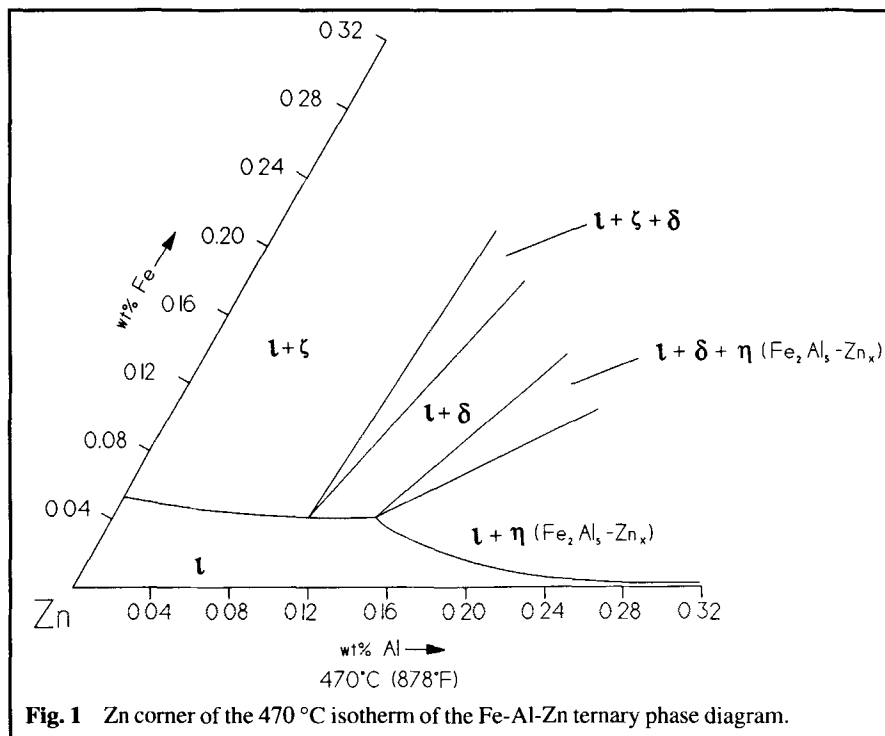


Fig. 1 Zn corner of the 470 °C isotherm of the Fe-Al-Zn ternary phase diagram.

proximately 3 seconds). Therefore, as far as the nucleation of intermetallic compounds is concerned, experimental observation indicated that a thermodynamic equilibrium state was not established. Due to a high Fe activity in the immediate vicinity of the steel strip and also due to high nucleation and growth kinetics, the phase that nucleates first on the steel was found to be mainly ζ .⁸ Due to the fact that it is thermodynamically unstable in the Zn bath with an Al content in excess of 0.10%, further growth of the ζ crystals is hindered, and the thermodynamically stable δ phase nucleates and grows while the portion of the strip where they resided is still in the bath. Simard et al.⁸ found that at 465 °C after 3.5 seconds, approximately the total time the steel strip is submerged in a bath, the average size of the ζ crystals was 4 μm , while the δ crystals had reached an average size of 1 μm .

It should be pointed out that the discussion on the control of the kinetics of galvannealing was also incorrect. It was stated that the "growth of this layer (Fe_2Al_5) causes a decrease in the Al content of the liquid, and when the weight percentage of Al has been decreased to 0.07 (typographic error, should be 0.11), the melt is in equilibrium with both δ_1 and Fe_2Al_5 . Further decrease in the aluminum content of the melt moves the system into the liquid- δ_1 two-phase region, which causes the nucleation and growth of δ_1 on the steel and the dissolution of Fe_2Al_5 . The rate of growth of the initial Fe_2Al_5 layer is significantly lower than the rate of growth of the δ_1 layer, and hence the initial time period during which the Fe_2Al_5 grows can be considered to be an incubation period." Here, Prof. Gaskell believed that the growth of Fe_2Al_5 , the thermodynamically stable phase in the region if one assumes that the old version of the 450 °C isotherm is correct, would cause depletion of Al thereby leading to its own dissolution. It should be pointed out that the Al content in a galvanizing bath is maintained at a predetermined level throughout

production, and therefore the dissolution of a thermodynamically stable compound will not occur. Such an event might happen only when the strip exits the bath and enters the annealing zone where Al supply for the reaction is limited.

Prof. Gaskell also believed that the growth of Fe_2Al_5 was significantly slower than the δ_1 phase. However, research work published by a number of authors did not support such a supposition. The study carried out at the Iron & Steel Research Laboratory, Kawasaki Steel⁹ revealed that at a bath temperature of 470 °C and with Al content in the bath less than 0.14%, the time of immersion has practically no effect on Al uptake by the steel. On the other hand, with bath Al content in excess of 0.15%, Al uptake by the strip increased linearly with immersion time. Faderl et al.¹⁰ reported that at 470 °C the amount of Al in the steel-coating interface layer remained unchanged for bath Al levels up to 0.14%, and with Al in excess of 0.14%, it increased linearly with increasing Al content in the bath. These observations are consistent with the conclusions that at 470 °C the lower limiting tie-line for the liquid- Fe_2Al_5 two-phase region is located at 0.138% Al, the dominant intermetallic compounds in galvannealing are ζ and δ phases, and the growth rate of Fe_2Al_5 is probably comparable to, if not faster than, that of δ phase.

In summary, the intermetallic compound that forms first in a galvannealing bath is the ζ phase. It is thermodynamically unstable in a Zn bath with an Al content in excess of 0.10%, and its further growth is hindered. The sluggish growth kinetics of the δ phase makes the control of the kinetics of galvannealing of steel possible. It should be reiterated that the tutorial is an excellent article. The misinterpretation of the reactions in the Fe-Al-Zn system stems mainly from the use of an obsolete isotherm. Prof. Gaskell's article illustrates how the

knowledge of phase equilibria as functions of composition and temperature can be utilized to generate useful practical information. The present comment is in no way intended as a criticism of Prof. Gaskell but is written because it is vital for researchers and engineers in the galvanizing industry to possess accurate information about the Fe-Al-Zn ternary system and to understand the mechanisms at work.

Cited References

1. D.R. Gaskell, "Tutorial: The Practical Use of Phase Diagrams," *J. Phase Equilibria*, 14(5), 543-556 (1993).
2. M. Urednicek and J.S. Kirkaldy, *Z. Metallkd.*, 64, 419-427 (1973).
3. D.I. Cameron and M.K. Ormoy, *Proc. The Sixth Annual Conference on Hot Dip Galvanizing*, London, ZDA, 276-331 (1962).
4. S. Belisle, V. Lezon, and M. Gagne, *J. Phase Equilibria*, 12(3), 259-265 (1991).
5. N.Y. Tang and G. Adams, "Studies on the Inhibition of Alloy Formation in Hot-Dip Galvanized Coatings," *The Physical Metallurgy of Zinc Coated Steels: Processing, Structure and Properties*, TMS Annual Meeting, San Francisco, 41-54, 1994.
6. N.Y. Tang, "450 °C Isotherm of the Zn-Fe-Al Phase Diagram," *Mater. Sci. Technol.*, to be published.
7. D. Horstman, in *Proc., The 7th International Conference on Hot Dip Galvanizing*, Pergamon, 146 (1964).
8. A. Simard, G. L'Esperance, and J. L'Ecuyer, *Proceedings, Galvanizers' Association Meeting*, Baltimore, Maryland, October, 1993.
9. M. Isobe, *CAMP-ISIJ*, Vol.5, 1630 (1992) in Japanese.
10. J. Faderl, M. Pimminger, and L. Schonberg, *Proceedings, 2nd International Conference on Zinc and Zinc Alloy Coated Steel Sheet (Galvatech '92)*, Verlag Stahleisen, Amsterdam, 194-198.

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