

Control of Silicon Reactivity in General Galvanizing

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In general galvanizing Si dissolved from steels destabilizes the Γ and Γ_1 phases in the alloy layer of the coating. It also alters the morphology of ζ crystallites in the alloy layer thereby exposing the δ layer to the melt. The incompatibility of the liquid phase and the δ phase cause the latter to disintegrate. These changes result in an excessive steel reactivity in general galvanizing. This reactivity can be easily controlled by alloying the Zn bath with metals, such as Ni, if the Si content of the steel does not exceed 0.20%. To combat a fully developed reactivity problem, one has to stabilize the Γ and δ sublayers in the coating. Alloying the bath with suitable metals can generate new equilibrium states to allow the co-existence of the liquid phase and the δ phase thereby preventing its disintegration; the Γ and Γ_1 phases can be stabilized through solid solution of the alloying elements in these phases. The introduction of Al to general galvanizing baths generates new equilibrium states thereby ushering a total new approach to Si reactivity control.

Keywords equilibrium diagram, intermetallics, materials behavior, microstructure, multicomponent, non-equilibrium processes, phase equilibria

1. Introduction

General galvanizing serves as a good example of how the fundamental knowledge of thermo-chemistry and phase equilibria in the Zn-Fe related systems can provide scientific explanations of technical problems encountered by the industry in daily production and provide guidance in seeking practical solutions to these problems.

General galvanizing is to coat a steel article with Zn using a hot-dip process. The typical microstructure of the coating is shown in Fig. 1. Under normal circumstances the coating alloy layer consists of all four binary intermetallic compounds available to the Zn-Fe system, namely the Γ , the Γ_1 , the δ and the ζ phases, as shown in Fig. 2. The coating microstructure suggests that a local equilibrium state has been reached at all interfaces in the coating following the hot-dipping process which lasts typically for several minutes.

2. Si Reactivity Control in General Galvanizing

A small amount of Si frequently exists in structural steels because Si is used as a de-oxidant in the steel making

process. Si is also a low-cost yet very effective strengthening alloying element for steels. It is the key element which affords transformation induced plasticity (TRIP) to steels. However, galvanizing Si-containing steels has been a technical challenge for batch galvanizers.^[2-7] The coatings become abnormally thick and non-uniform. They are brittle and poorly adherent to the steel substrates. The search for practical solutions to this reactivity problem was largely unsuccessful until the development of Technigalva in the 80s of the last century.^[7] However, the effectiveness of this technology is limited to steels containing Si < 0.2%. For structural steels containing higher Si, an economically viable solution still eludes the industry. Consequently, Si is an element which general galvanizers “love to hate.”

3. The Zn-Fe-Si System

Silicon reactivity in general galvanizing has been a never-ending research topic in the last seventy years or so.^[2-17] The problem has been extensively explored and well-described phenomenally. Some practical solutions to the problem have emerged as a result of those investigations, including high temperature galvanizing and the aforementioned Technigalva, that is, Ni addition to the bath.^[7] A literature survey carried out in ILZRO Project ZM-375 cited more than 100 studies, revealing the expanse and depth of the effort devoted to this problem.^[3] In spite of this enormous effort, a scientific explanation of the problem has, however, never fully emerged. To gain a fundamental understanding of the problem, one has to know the detrimental effect of Si on the equilibrium states available in the Zn-Fe system. The phase diagram of the Zn-Fe-Si system was first developed by Köster in 1969.^[9] In the diagram, all phases known at that time were correctly outlined (Γ' phase was not discovered until 1974^[10]). The shortcoming of the diagram is that the solubility limits of Si in the three binary Zn-Fe compounds known at that time, namely, the ζ , the δ , and the Γ phases,

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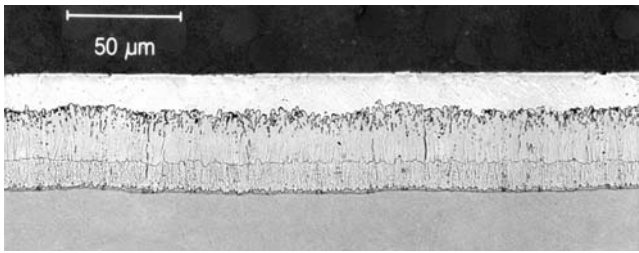


Fig. 1 Typical coating microstructure. Note the existence of all four intermetallic phases available to the binary Zn-Fe system in the coating

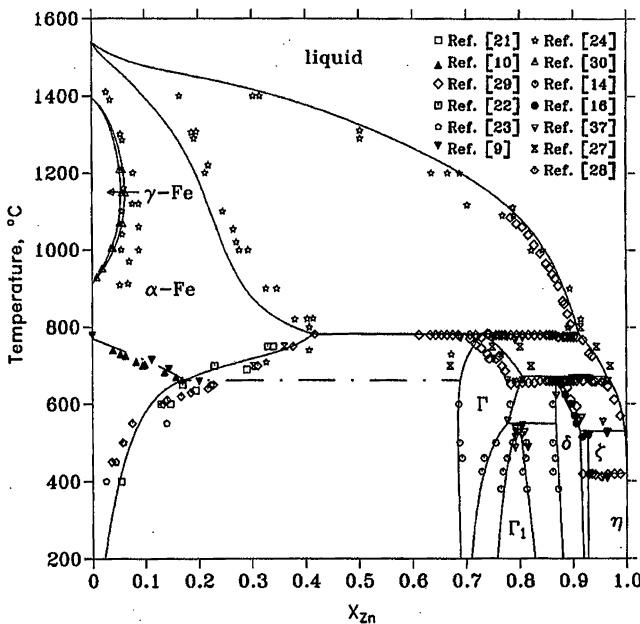


Fig. 2 The binary Zn-Fe phase diagram^[1]

and in the liquid phase were not addressed. This shortcoming has severely limited the applicability of the phase diagram in the interpretation of the Si reactivity problem. Foct and his co-workers^[11,12] were among the few who made an effort to explain the problem based on the availability of phase equilibrium states. The observation that ζ crystallites frequently exist at locations remote to the coating/substrate interface in coatings with a fully developed reactivity problem led these researchers to believe that the equilibrium between the liquid and the ζ phase was not available in the Zn-Fe-Si system. They concluded that the root cause of Si reactivity is that the FeSi phase and the ζ phase cannot co-exist in the system. They revised the Zn-Fe-Si phase diagram to include an equilibrium state between the liquid, the δ , and the FeSi phases. However, their proposal is in contradiction to a well-documented experimental observation that the δ phase disintegrated into a phase mixture referred to as diffused δ when it was exposed to the Si-containing liquid phase.^[13]

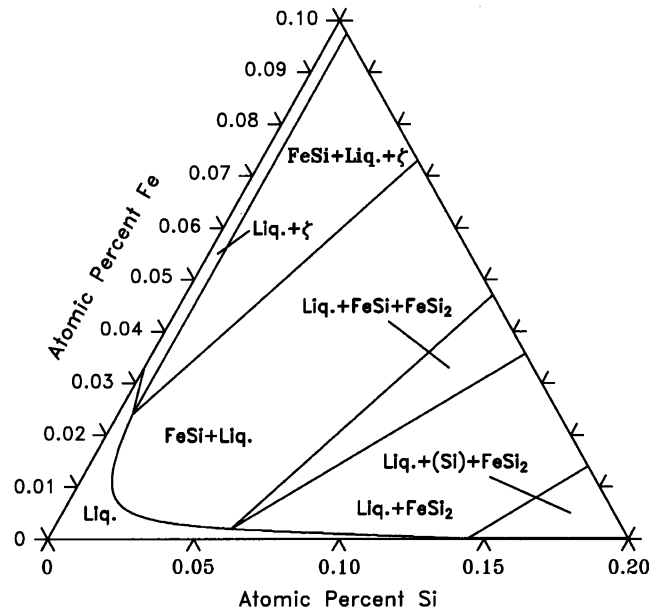


Fig. 3 The Zn-rich corner of the 450 °C isothermal section of the Zn-Fe-Si phase diagram.^[5] Note the co-existence of the liquid and δ phases is thermodynamically prohibited

In view of its importance to the galvanizing industry, the Zn-Fe-Si system was revisited by Su et al.^[5] These researchers explored the Zn-rich corner in great detail and confirmed all phase equilibrium states originally proposed by Köster.^[9] The Zn-rich corner of the 450 °C isothermal section of the Zn-Fe-Si system, proposed by Su et al., is reproduced in Fig. 3; their main conclusions are reiterated here:

- (1) The ζ phase can co-exist with the FeSi phase in the system. However, an equilibrium state between the δ phase and liquid Zn was found to be impossible.
- (2) Si is almost insoluble in the Γ , and ζ phases. Its solubility in the Γ_1 and δ phases was estimated to 0.3 at.%, and 1 at.%, respectively.
- (3) Fe solubility in liquid Zn decreases significantly with an increase in the Si content of the liquid.

The above findings are important for the understanding of Si-induced steel reactivity problem in general galvanizing.

To better explain how various alloying additions afford the control of the steel reactivity in general galvanizing, the Si reactivity problem is briefly reiterated here. The problem is normally subdivided into two categories based on its severity. When the Si content in the steel is 0.20% or less, the reactivity is frequently referred to as the Sandelin Peak^[2,3] as the coating becomes thicker and non-uniform. In general, a well-defined alloy layer still exists in the coating, which consists of three sub-alloy layers. However, close examinations of the alloy layer revealed that its integrity was compromised. The ($\Gamma + \Gamma_1$) layer is thinner in general and non-continuous at locations; the δ layer is thinner too; the ζ layer is no longer compact with gaps between the

crystallites. In addition, outbursts of ζ crystallites can be seen in the Zn overlay at numerous locations. These outbursts are the main cause of a thick and non-uniform coating. The typical microstructure of such a reactive coating is shown in Fig. 4. When steel contains Si higher than 0.20%, a continuous alloy layer no longer exists in the coating; pockets of a phase mixture, referred to as diffused δ , appear near the coating/substrate interface. The reactivity is referred to as the Niessen-Guttman Plateau by some researchers^[3] to honor the pioneering work of these two researchers of Cominco Ltd.^[13] The morphology of ζ crystallites totally changed from columnar to dendritic. Some δ phase containing Si frequently survive at the coating/substrate interface; however, the ($\Gamma + \Gamma_1$) layer no longer exists. The microstructure of such a coating is shown in Fig. 5a. The coating is totally grey in color and extremely brittle; its adhesion to the steel substrate is totally lost. Consequently, the coating can be easily removed from the steel surface.

Apparently, the introduction of Si into the Zn-Fe system disturbs the phase equilibrium states in the Zn-Fe binary system and creates a number of new equilibrium states. As a result, a compact alloy layer is no longer able to form in the coating. The Γ' phase ($\text{Fe}_5\text{Zn}_{21}$) is an electron compound

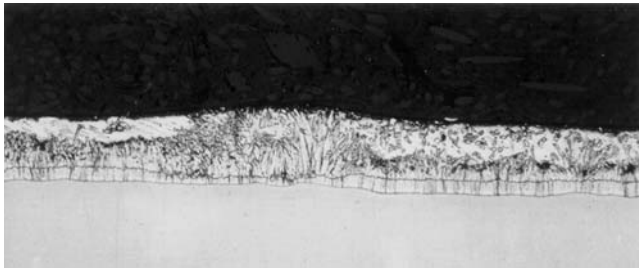


Fig. 4 Microstructure of reactive coating developed on Si-containing steel. The outbursts of the ζ phase are the main contributor to the anomaly of coating thickness

which possesses a fixed atom/electron ratio (13:21). The Γ phase is similar to the Γ' phase in this regard. Si atoms possess too many valence electrons and can easily upset the atom/electron balance within the Γ phase. As a result, the Γ layer cannot exist in the coating when the steel contains a high level of Si. Although it can tolerate a small amount of Si in solid solution, the Γ' phase does not form immediately during hot dipping. It is most likely transformed from the existing Γ phase because its lattice parameter is exactly twice that of the Γ phase. The Γ' phase exists between the Γ layer and the δ layer frequently as tiny discrete particles although it may exist as an extremely thin layer as well. That is why it was not positively identified until 1974.^[10] Without the existence of the Γ layer, the coating's adhesion to the steel is largely lost. In a reactive coating the morphology of the ζ crystallites has changed, resulting in the formation of liquid channels between these crystallites. Consequently, the δ sublayer is now exposed to the liquid phase, resulting in a state prohibited in the Zn-Fe-Si system. As a result, the δ sublayer disintegrates, and the ductility of the coating deteriorates because diffused δ is porous in solid state. X-ray diffraction studies of a coating flake removed from a steel containing Si in excess of 0.34 at.% indicated that there was no Γ layer in the coating/substrate interface. Shown in Fig. 5b is a diffraction pattern taken from the inner side of the coating flake. It can be seen that only the ζ and δ phases were detected.

Guttman and Niessen^[13] elegantly demonstrated that in the initial stage of hot dipping, <1 min to be more precise, an alloy layer consisting of the ζ , the δ , and possibly the Γ phase still formed and grew to a certain thickness in the coating on a steel containing Si as high as over 0.4%. The coating microstructure appeared normal for samples hot-dipped for 60 s and less. However, when the dipping time increased to over 2 min, the ζ crystallites atop the δ phase became bulky and failed to form a compact layer, thereby exposing the δ phase to the liquid Zn. The δ phase started decomposing and transformed into so-called diffused δ , a mixture of ζ , FeSi, and liquid coexisting with surviving δ crystallites. The thickness of the diffused δ layer increased with the dipping time. Concurrently, the morphology of the

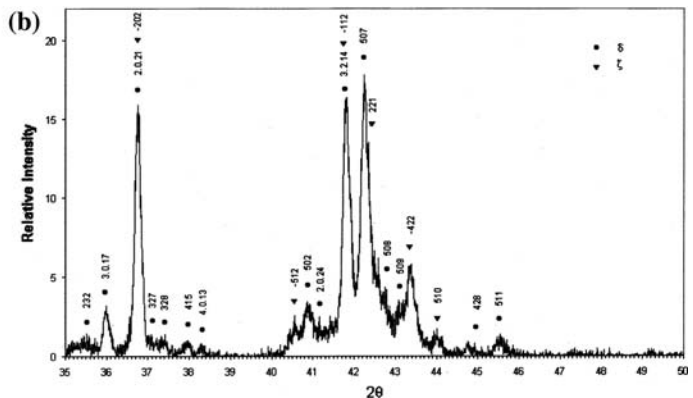
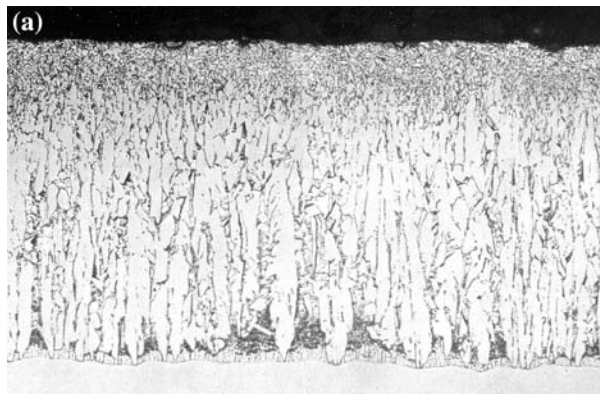


Fig. 5 (a) Reactive coating developed on steel containing 0.35% Si. Pockets of diffused δ developed in the coating/substrate interface. (b) An X-ray diffraction pattern generated from the inner side of a coating flake. Note there is no trace of the ($\Gamma + \Gamma_1$) sublayer

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ζ phase changed from columnar to dendritic, and the dendrites increased in size with time.

It should be mentioned that the finding that a reactive coating microstructure does not develop on steels containing a high level of Si within the first 30 s or so of hot dipping was also reported by Amistadi et al.,^[14] researchers at the former St. Joe Minerals Co. In a recent study carried out in the author's laboratory, such a phenomenon was confirmed again.^[15] As shown in Fig. 6a and c, the microstructures of the coating formed on steels containing 0.02 at.% Si and 0.34 at.% Si are similar within the first second or so of hot dipping. However, the coating on the steel containing 0.34 at.% Si developed into a reactive one after only 30 s of hot dipping (Fig. 6d).

The above observations indicate that the reactivity problem can be avoided by limiting the hot dipping time to a few seconds. In practice, this solution is only applicable to long products with a relatively small cross section, such

as wire and mesh-grade rebar, which can be galvanized continuously. In fact, continuously galvanized high-strength steel wires in pure Zn baths have never experienced any reactivity problems in spite of their high Si content.

This initial transient in which a normal coating microstructure forms on steels containing Si well over 0.2% is worth exploring. Calculation of the metastable equilibrium of liquid Zn with α -Fe at 450 °C indicated that the transient Fe solubility in the vicinity of the coating/steel substrate could reach 5 at.%, higher than the equilibrium Fe solubility of 0.030% in the molten Zn at this temperature by two orders of magnitude. In the experiment, the steel sample was only heated to about 120 °C to preserve the flux. As a result, the transient Fe solubility is slightly below 2 at.%. The Fe dissolution process will introduce Si into the coating/substrate interface region. A simple calculation indicated that the transient Si concentration in this region is 0.008 at.% if the steel contains 0.4 at.% Si. The fact that a thin compact

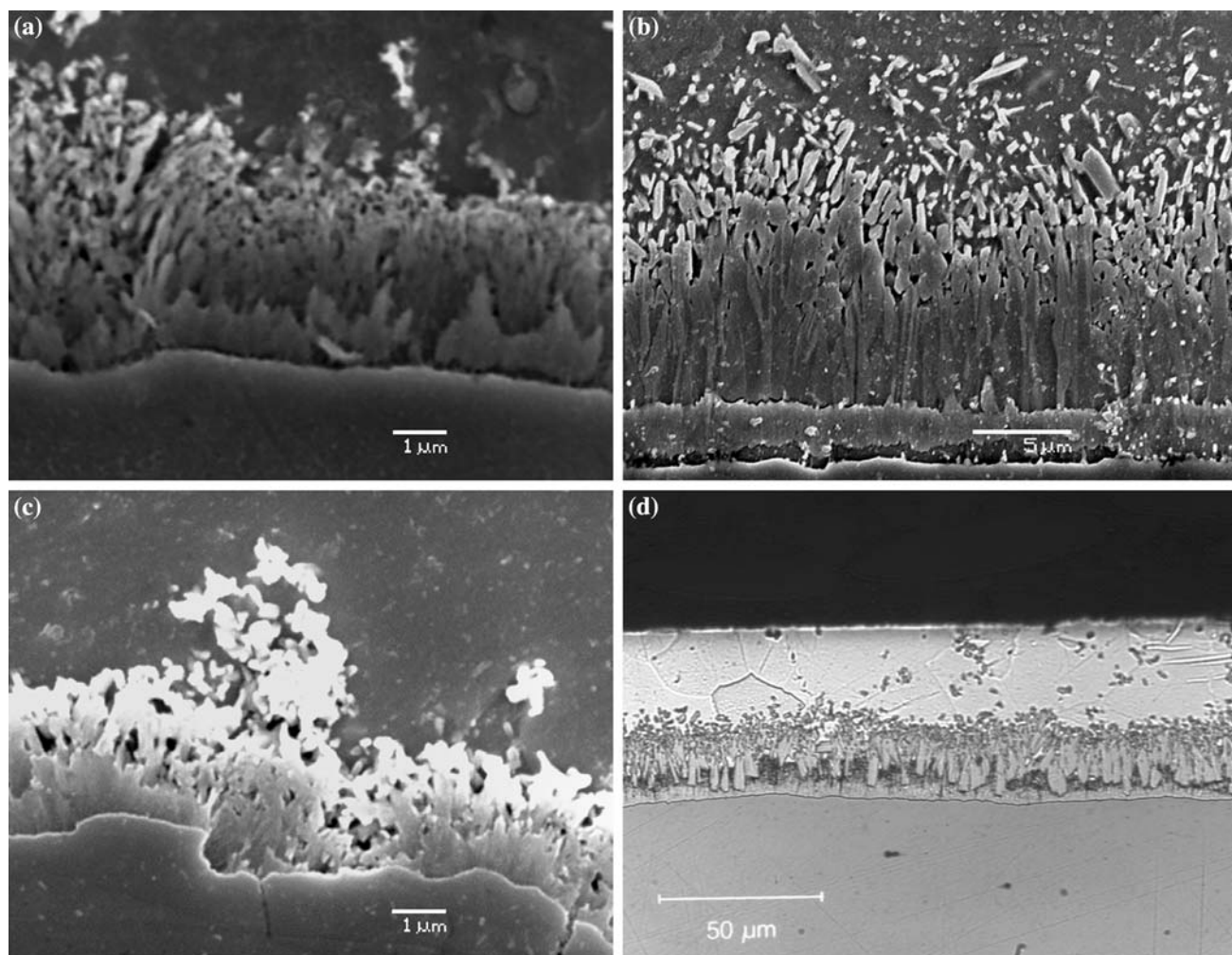


Fig. 6 The evolution of the alloy layers in coatings during hot-dip galvanizing. A continuous alloy layer could form and grow in the early stage of hot dipping (dipping time 1 s) regardless of the Si level in the steels (0.02% Si in a and b, and 0.34% Si in c and d). The δ phase continued to grow on the low Si steel, as shown in b, but started to disintegrate when the dipping time exceeded 30 s or so for the high Si steel, as shown in d. Bath temperature was 450 °C, and all samples were water quenched immediately following the hot dipping process

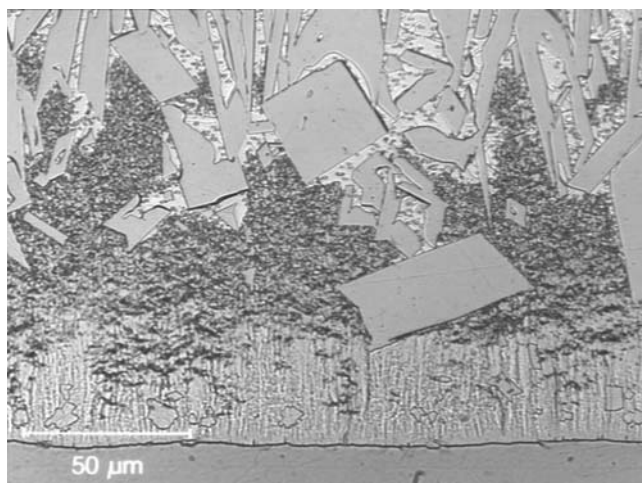


Fig. 7 Diffused δ consists of mainly fragmented fine δ particles, ζ crystallites and FeSi particles existing in a liquid Zn matrix. Note the existence of ζ crystallites in the disintegrating δ layer. Steel contains 0.34% Si and dipped in special high-grade Zn at 450 °C for 5 min

alloy layer can grow on such steel suggests that a normal coating can form in a bath containing <0.01 at.% Si. This suggestion is substantiated by the Zn-rich corner of the Zn-Fe-Si phase diagram shown in Fig. 3. However, Si is accumulated at the coating/substrate interface and is also enriched in the melt with further dissolution of the steel during the hot-dipping process. Since the ζ phase practically cannot contain any Si in solid solution, Si is rejected laterally by the growing ζ crystallites and enriched in the melt at their outskirts. This stabilizes the liquid between the crystallites and results in the formation of so-called liquid channels in the alloy layer. Consequently, the ζ crystallites fail to form a compact protective layer for the δ phase, and the latter is exposed to the liquid metal and starts disintegrating. The disappearance of the just-formed Γ layer and the disintegration of the δ phase lead to a full-blown reactivity problem.

A close examination of the microstructure of the diffused δ layer is important to the understanding of the reactivity problem. Shown in Fig. 7 is typical diffused δ , a mixture of liquid Zn, newly formed ζ crystallites, tiny FeSi particles and surviving δ particles. The microstructure of the diffused δ substantiates the existence of the liquid- ζ -FeSi three-phase equilibrium state in the Zn-Fe-Si ternary system. The formation of the diffused δ suggests that the coating is adopting an equilibrium state following the exposure of the δ layer to the liquid phase. Measurements carried out at the author's laboratory indicated that an Fe composition gradient existed in the surviving δ layer. The part close to the steel substrate contained about 12 at.% Fe and the part exposed to the liquid Zn contained only about 8 at.% Fe. The fragmented δ particles in the diffused δ region contained an even lower Fe content, close to that in the ζ phase (7 at.%), revealing their metastable nature.

It is known that steel reactivity increases with its Si content up to 1.5%, thereafter, the reactivity decreases with a further increase in Si content.^[18] At about 4.5% Si, the

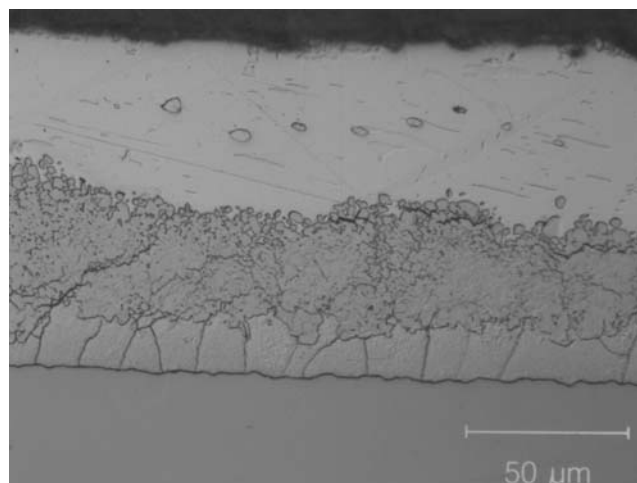


Fig. 8 The alloy layer developed in a coating on an electrical steel containing 3% Si consists of two sublayers. Dipping time was 6 min and bath temperature was 455 °C. The coupon was preheated to 130 °C before the hot dipping

steel reactivity is lower than that of pure Fe. The alloy layer in the coating on such a high Si steel possesses a high compaction.^[2] This compact alloy layer serves as a barrier layer, preventing the direct contact of the molten Zn with the steel substrate. As a result, the steel reactivity is well curtailed. Shown in Fig. 8 is the coating structure developed on an electrical steel plate containing 3%Si. It can be seen that the alloy layer in the coating consists of two sublayers. The identities of phases in the alloy layer are yet to be determined.

4. Practical Solution for Steel Reactivity Control

Control of Si reactivity in the Sandelin Peak region is a relatively easy task. As mentioned earlier, the alloy layer in the coating is still reasonably compact, and the defects in the coating are limited and localized. The main problem is that the coating is abnormally thick at some locations and non-uniform in coating thickness in general. At thick spots the coating appears grey. The root cause of this type of reactivity is that the integrity of the alloy layer in the coating was compromised because of the existence of Si. Due to the existence of defective sites in the alloy layer, the liquid Zn is in direct contact with the steel substrate at locations. This direct contact between the liquid and the steel allow the liberation of Fe atoms from the substrate. When reaching the coating surface, this Fe flux converts to clusters of ζ crystallites in the free Zn layer of the coating. A much-reduced Fe solubility in the now Si-containing free Zn exacerbates the problem. This conversion can consume most of the free Zn, changing a bright coating surface to grey.

As mentioned earlier, the most popular solution to control the reactivity is to alloy the Zn bath with a small amount of Ni.^[7] This is because that Ni addition at ~0.055% introduces to the system a ternary phase, the T

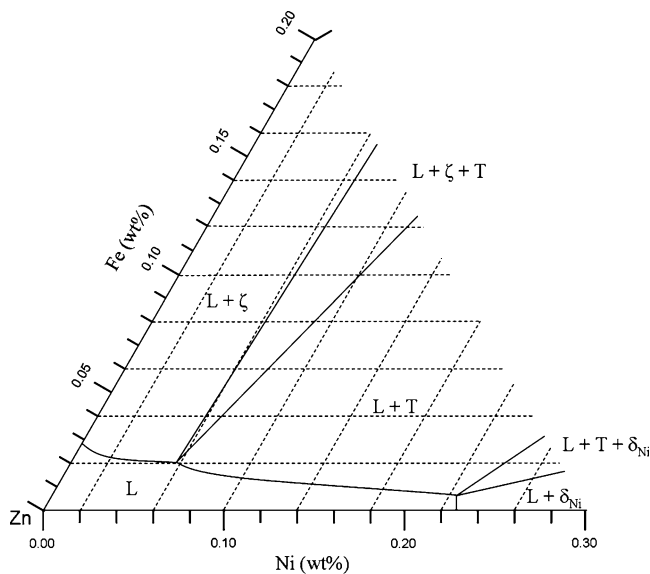


Fig. 9 The Zn-rich corner of the Zn-Fe-Ni ternary phase diagram at 450 °C. Note the ζ phase is no longer stable when the Ni content of the bath exceeds 0.06%

phase, as shown in Fig. 9, which replaces the ζ phase as the equilibrium intermetallic compound in the bath. As a result, out-bursting of ζ crystallites in the free Zn layer is no longer a thermodynamically favored process. The coating thickness becomes normal, and the coating surface remains bright. Studies conducted by Tang et al.^[16] indicated that Ni has a significant solid solubility in the Γ (over 11%) and Γ' (close to 4%). Examinations of coating microstructure obtaining in Ni containing baths suggest that Ni can repair the defect in the coating alloy layer on Si-containing steels.

In fact, any alloy addition which introduces a new equilibrium phase into the Zn-Fe system can afford controllability of Si reactivity in the Sandelin Peak region. Laboratory trials carried out at Teck Cominco's Product Technology Centre indicated that Ti, Mn, Cr and Co, when added in small amounts, all alleviated Si reactivity problem in general galvanizing.^[15]

When the Si content in the steel exceeds 0.2%, the damage to the Γ sublayer in the coating is beyond repair. This sublayer practically does not exist anymore. It should be realized that this sublayer is critical to the coating adhesion. Without this sublayer, coating adhesion to the steel is totally lost! Furthermore, the δ sublayer has disintegrated to so-called diffused δ which is porous in the solid state because the liquid portion of the mixture shrinks when the coating solidifies. These pockets of diffused δ are located near the substrate/coating interface, making them more damaging to the coating ductility and adhesion.

However, although the nature of Si reactivity is well understood, devising a practical solution to curtail the reactivity of high Si steels is not an easy task. Economical consideration and environmental concern frequently prevent the acceptance of a practical solution. For example, Si reactivity can be controlled by alloying the Zn with a sufficient amount of Sn, especially when it is combined with

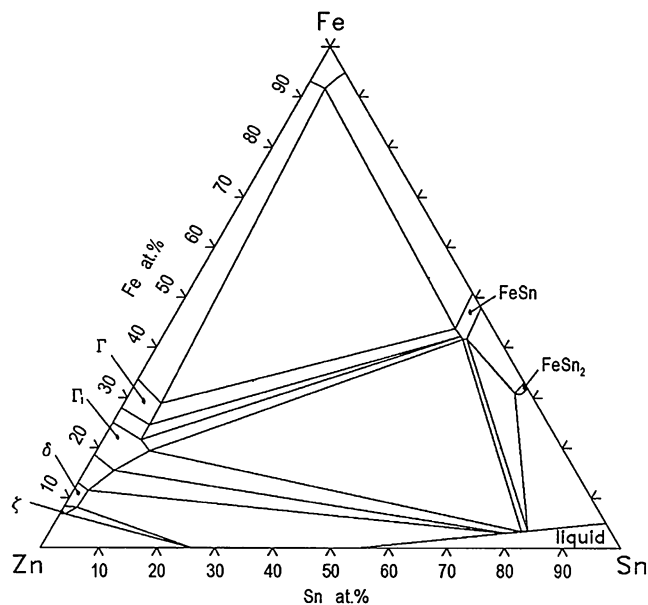


Fig. 10 The Zn-Fe-Sn system at 450 °C. Note the existence of Sn enables the co-existence of the liquid phase and the δ phase. The Sn also stabilizes the Γ and Γ_1 phases.^[17]

V.^[6] The science behind such a solution was unraveled by the recent study of the Zn-Fe-Sn system by Tang and his co-workers.^[17]

As shown in Fig. 10, Sn addition to the molten Zn enables the liquid to coexist with the ζ , the δ , and the Γ_1 phases with an increase in Sn content. Sn addition also stabilizes the Γ phase substantially through solid solution. As a result, when high Si steels are galvanized in a bath containing a sufficient amount of Sn, the reversion of the δ phase formed at the early stage of hot dipping does not occur anymore and the ($\Gamma + \Gamma_1$) layer can also survive well in the coating. Unfortunately, galvanizing kettles, frequently made of industrial Fe, are found to erode at a much faster rate when the Zn is alloyed with Sn. Furthermore, the relatively high level of Sn (>1%) which is needed to effectively control high Si levels can contribute to cracking of structural steel units with a high residual stress during galvanizing. Last, but by no means least, government regulation has limited the amount of alloying elements one could add to a galvanizing bath. All these factors have limited the acceptance of Sn as a universal solution in steel reactivity control in general galvanizing.

Sb, Pb, and Bi work in a similar way in stabilizing the δ layer in coatings on Si-containing steels. However, due to their rather limited solubility in the Γ and Γ' , those alloying elements are not capable of retaining the Γ layer in an otherwise typical reactive coating. As such, although a bright coating with a reasonable thickness can be obtained, the adhesion of such a coating is poor.^[15]

If an alloying element in the bath introduces new intermetallic compounds which serve as a barrier layer preventing the direct contact of molten Zn with the steel substrate, it affords a new solution for resolving Si-induced reactivity. The discussion of this option is carried out in the next section.

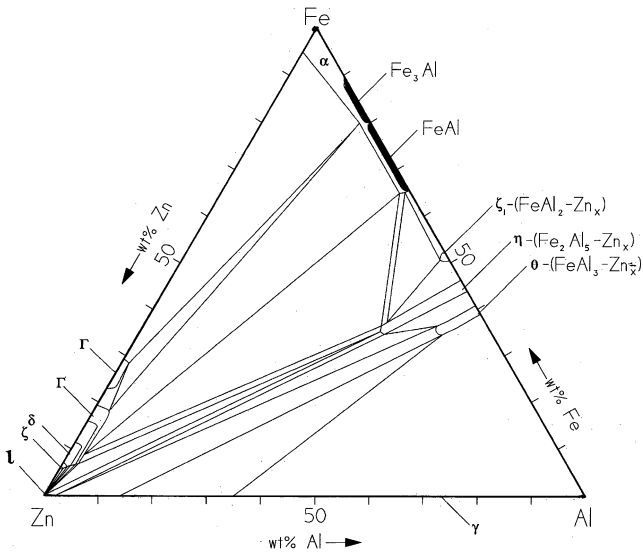


Fig. 11 The addition of Al into the Zn-Fe system creates two important Fe aluminides for Si reactivity control^[22]

5. Phase Equilibria in the Zn-Fe-Al-Si System

The effect of Al additions to the galvanizing bath in countering Si reactivity has been well known for over three decades.^[19] It was found that the formation of the Zn-Fe alloy layer in the coating can be totally inhibited over periods of time that are compatible with general galvanizing, provided the Al content of the bath is above a threshold level which varies with the Si content of the steel. As little as 0.05% Al is effective with steels containing 0.4% Si and higher.^[19] However, due to the incompatibility of an Al containing bath with the existing flux and due to the difficulty in coating weight control this approach did not receive enough attention until recently. Under the influence of ILZRO R&D activities in this area, a renewed interest in using Al addition for Si reactivity control has emerged.

If Si is an element which the general galvanizers love to hate, it is purposely introduced into molten Zn-Al alloys to mitigate the reaction kinetics between the steel and the coating alloys in continuous galvanizing, in other words, for reactivity control! It is well known that Galvalume alloy contains 1.5% Si otherwise the steel strip cannot survive the hot dipping process. Some European galvanizers add Si to their Galfan bath to improve coating uniformity. Si, and P as well, are also intentionally added to steels for an increased strength and an improved coating adhesion after galvanizing treatment.^[20] As such, the fundamental of the interactions between the four elements, namely, Zn, Al, Fe, and Si are reasonably well understood by researchers in the continuous galvanizing industry.^[21] Such knowledge can be readily transferred to the general galvanizing industry. The addition of Al into a molten Zn bath introduces two important intermetallic compounds, namely Fe_2Al_5 and $FeAl_3$, as shown in Fig. 11. When the bath Al level exceeds approximately 0.14% at 450 °C, these compounds can form at the coating/substrate interface as an inhibition layer,

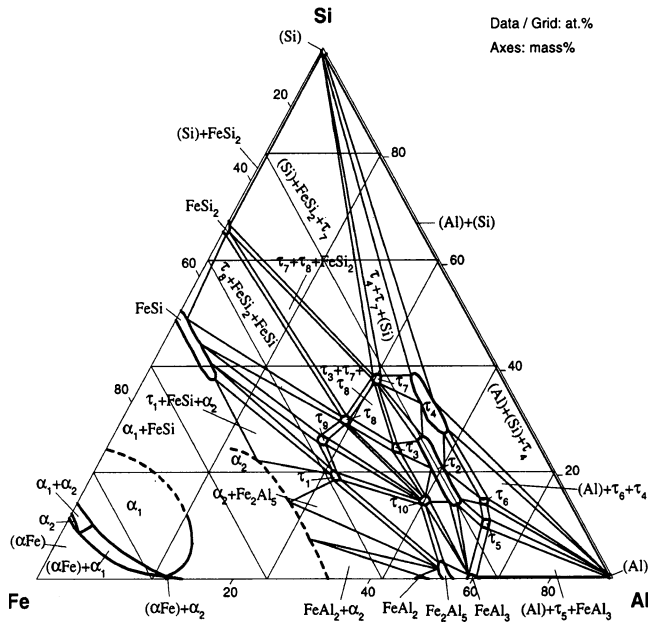


Fig. 12 The incorporating Si into the inhibition compounds could significantly change the nature of these compounds^[23]

which prevents the direct contact between the molten Zn and the steel substrate and substantially reduces the rate of inter-diffusion of Fe and Zn, thereby preventing Si-induced steel reactivity. On the other hand, Si contained in the steels is incorporated into the two compounds thereby stabilizing the inhibition layer and prolonging the survival time of the inhibition layer. If Si is added to the bath in sufficient amount, it can transform the binary Fe aluminides to ternary Fe-Al-Si compounds, such as τ_5 as shown in Fig. 12.^[23]

Due to the existence of a stable inhibition layer, the formation of Fe-Zn compounds in the coating becomes difficult or impossible. As a result, the coating thickness achievable in an Al containing bath is frequently only about 20 μm , much below the minimum coating thickness demanded by some users. In addition, Al containing Zn melt is much more corrosive to the kettle and submerged hardware. As such, research and development work have to be carried out to resolve these technical challenges before the general galvanizing industry can embrace this new galvanizing technology.

6. Summary

The mechanism of Si caused steel reactivity problem in general galvanizing is mostly understood following studies of the thermodynamic equilibrium states available in the Zn-Fe and Zn-Fe-Si systems and through the exploration of the transient nature of the formation of a reactive coating microstructure. Ni addition to the Zn bath has become a standard industrial practice for control of the reactivity of steels containing less than 0.2% Si. However, devising a solution to combat a fully developed Si reactivity problem is

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still a challenge due to the complexity of the problem. In addition is a promising new technology. However, research and development work has to be carried out to resolve technical issues induced by this promising new technology, including its incompatibility with the existing galvanizing technologies and equipment and an increased difficulty in coating weight control and bath chemistry management.

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