ASSESSMENT OF THE FE-SI-SN-ZN SYSTEM AT 450°C: ITS USE IN THE FIELD OF BATCH GALVANIZING [1]

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Abstract

Tin added to the zinc bath has a beneficial effect by minimizing spangling and its role in decreasing the thickness of coating grown on hyper-Sandelin steels has also been pointed out. The work presents an assessment of the Fe-Sn-Zn system which is used for an experimental approach of the Fe-Si-Sn-Zn system. The microstructure of galvanized coatings (Fe-Si alloys dipped in Fe-Sn-Zn baths) is characterized by metallography, scanning electron microscopy (S.E.M.) coupled with X-ray energy dispersive spectroscopy (E.D.S.). Solidification phenomena and coating growth mechanisms during galvanizing are explained by means of equilibria in the ternary and quaternary systems at 450°C. Phase equilibria in the zinc rich corner of the Fe-Si-Sn-Zn system, unknown up to now, are presented together with an optimization at 450°C of the Fe-Sn-Zn diagram. Coherence of the quaternary diagram with the already known Fe-Si-Zn and Fe-Sn-Zn systems was carefully checked. A clear insight into the mechanism of galvanization is thus available. From a more fundamental point of view, tin present in tiny amounts in a zinc bath plays an important role of tracer and corroborates mechanisms previously developed to explain the overthickness of layers observed when galvanizing silicon steels around 0.07 % Si.

Key words: Galvanization; Thermodynamics; Fe-Si-Sn-Zn diagram.

OTIMIZAÇÃO DO SISTEMA FE-SI-SN-ZN A 450°C E UTILIZAÇÃO PARA A GALVANIZAÇÃO A FOGO

Palavras-chave: Termodinâmica; Galvanização; Sistema Fe-Si-Sn-Zn

Introduction

Reactive steels in galvanizing remains a serious problem and several solutions had been previously proposed to overcome the detrimental effect of silicon in steels: formation of a thick, brittle, dull-gray coating with poor surface adhesion. Alloying elements, namely Al, Ni or, more recently, Sn may be added to the zinc bath in order to eliminate the so-called Sandelin effect. The aim of a bath addition is to change the equilibrium between liquid zinc and the ζ phase, which is responsible for the excessive coating thickness. The drawback of nickel is the formation of dross ; the addition of 0.02 to 0.028% Al can lead to a reduction of coating thickness [4] and data about the effect of a Sn addition to the bath [5] are available in the literature. The present work aims to study more systematically the effect of tin additions and to explain the role of tin in the understanding of the solidification process of the galvanized coating.

Experimental procedure

Five steel substrates characterized by their silicon content were used. Steels with 0.07wt.% Si are known as "Sandelin steels". Steel with lower than 0.07wt.% Si and higher than 0.07 wt % Si are referred as "hypo-Sandelin" and "hyper-Sandelin" steels respectively. The samples were dipped at 450°C for 9 minutes in iron saturated zinc baths with 0, 0.5, 1, 1.5, 2 or 5 wt % Sn. Etching in a 4% nital solution for 5 seconds revealed the various layers. The coatings were characterized by optical microscopy, SEM, BSEM, EDX.

Thickness of the coatings

The overall thickness of the coating was evaluated using optical microscopy irrespective of the chemical nature of the galvanizing bath or the type of sample. Samples which were batch galvanized in a pure zinc bath saturated with iron were used as reference samples. Figure 1 shows the Sandelin effect, characterized by an overthickness of the coating around 0.07 wt % Si.

Tin has no effect on the thickness of coatings and on the microstructure of the hypo-Sandelin steels. For the Sandelin steels, a high tin content (5%) leads to the disappearance of the coating overthickness. For hyper-Sandelin substrates, the outcome is similar, but lower tin additions lead to minor modifications of thicknesses compared to no addition at all. Increasing tin content does not seem to continuously diminish the thickness of the coating for Sandelin and hyper-Sandelin steel substrates (figure 1), although the literature mentions that tin is known to diminish the Sandelin effect [5, 7].

Coating microstructure

For all samples, the galvanized coating consists of three layers.

- Two layers are formed by the intermetallic compounds δ-FeZn$_7$ close to the steel substrate and ζ-FeZn$_{13}$. The third layer is composed of η-Zn. (figure 2).

In all samples, the δ phase layer is thin, more particularly in the case of hyper-Sandelin samples where it is the thinnest. This is consistent with previous observations [3]. The ζ phase and the η-Zn phase layers generally present greater thicknesses for hypo-Sandelin and Sandelin samples, irrespective to the substrate, the chemical nature of the bath, the immersion time or the bath temperature. Larger crystals of ζ phase and a thicker layer of ζ phase are observed for hyper-Sandelin

samples when compared to hypo-Sandelin and Sandelin samples (figure 3). For higher silicon content, a two phase layer of δ and FeSi appears (figure 4). It has been called "diffuse Δ" [3, 8] and the E.D.S. analysis confirms this result.

Tin phase

B.S.E./S.E.M. micrographs show the presence of a tin phase which appears in white, given its atomic number compared with atomic numbers of iron, zinc and silicon (figure 5). The tin phase never appears in the δ phase layer but is present in both η-Zn and ζ layers. In the latter case it is located at the grain boundaries of columnar crystals (figure 2).
Some 'particles' located in η-Zn phase, and appearing in relief after etching, present strange grey and white contrasts (figure 5). They may originate from Fe-Zn dross which is trapped in the tin phase of the bath and probably not, from eutectics because of the coarsened structure.

Phase diagrams assessments

Calphad method [6] and various data [9-12] were used for the assessment of binary phase diagrams namely: Fe-Sn, Fe-Zn [13] and Sn-Zn [14], then for the Fe-Sn-Zn ternary diagram at 450°C (figure 6). When the tin content of the liquid phase increases, the equilibria liquid-ζ, liquid-δ, liquid-FeSn are successively observed. Equilibrium between δ and FeSn prohibits any equilibrium between Γ (Γ_1 or Γ_2) and liquid [7]. Zn rich corner of the quaternary Fe-Si-Sn-Zn phase diagram (Figures 6d and 6e) has been checked to be consistent with ternary phase diagrams Fe-Si-Sn (figure 6c), Fe-Sn-Zn (figure 6b) and Si-Sn-Zn (figure 6a).
According to the microstructures of coatings depicted in figure 1b, it can be suggested that an addition of 5%Sn to the bath changes the nature of the phases in equilibrium with the liquid.
For Sandelin steel substrates dipped in a bath without tin, δ phase is in equilibrium with liquid (point 3) and for Sandelin steel substrates dipped in a bath with 5% Sn, it is ζ phase which is in equilibrium with liquid (point 3').
For hyper-Sandelin steel substrates dipped in a bath without tin, FeSi phase is in equilibrium with liquid (point 4) and for Sandelin steel substrates dipped in a bath with 5% Sn, it is δ phase which is in equilibrium with liquid (point 4').

Effect of tin addition and mechanism of solidification

In the η-Zn phase layer, the tin phase is characterized by a rounded morphology. This is consistent with the facts. Firstly, tin has no solubility in zinc (figure 5) and thus tin is rejected by zinc during solidification. Secondly, tin has the lowest melting point, 232°C. It is the last phase to solidify. This has been found in a previous study [14].
Literature data mention that the surface tension of tin is quite low [5] and some authors have suggested that a tin layer appears around the intermetallic compounds of Fe-Zn [5]. The tin layer would then prohibit the diffusion of iron and zinc, which limits the growth of intermetallic compounds. The hypothesis seems to be proved by figure 7. In the present study, tin is never detected in the δ layer. It would be surprising if it were, because the chemical affinity of tin for iron is greater than the chemical affinity of zinc for iron. But it can be accounted for by other factors which can explain the phenomenon:
- on the one hand, the concentration of tin in the bath is lower than that of zinc and,
- on the other hand, the first layer which is formed is ζ phase layer [15].

For hypo-Sandelin steel substrates, the δ phase is formed from the ζ phase layer and diffusion of iron from the substrate [3]. The ζ phase layer pushes tin into the η-Zn phase.

In the case of hyper-Sandelin steel substrates, tin behaves as a tracer. It permits the confirmation of the solidification mechanism of galvanized coatings on these substrates proposed in previous studies [2, 3, 16, 17]. The ζ phase is the first compound which is formed. But, according to previous studies on the FeZnSi ternary system [3, 15], only a very small amount of Si is soluble in the ζ phase. Silicon plays the role of inhibitor towards the development of ζ close to the substrate when the Si content is too high. ζ crystals appear in the liquid phase where the Si content is low. Between the substrate and the ζ phase, a zone of liquid zinc sursaturated in silicon and eventually rich in tin (because the chemical affinity of tin for iron is greater than the chemical affinity of zinc for iron) remains.

Iron diffuses into this liquid layer and some intermetallic compounds such as δ and FeSi (diffuse Δ) – because of the dissolution of the excess of silicon in the δ phase - develop. Some tin is detected in diffuse Δ (figure 4). Excess of silicon is dissolved in δ phase. A tin phase which is not soluble in the δ or the ζ phase (see galvanized hypo-Sandelin steels) is rejected from the δ phase at the interface between δ and ζ. Figure 8 shows that a large amount of tin phase occurs at this interface compared with hypo-Sandelin steels, irrespective of the tin content in the bath (figure 3). Moreover some tin is detected between ζ crystals and in η phase.

For Sandelin steels, the mechanism is the same as for hyper-Sandelin steels.

Figure 9 depicts the mechanism of solidification of coatings on hypo-Sandelin, Sandelin and hyper-Sandelin steel substrates.

Conclusions

The present work confirms the mechanisms of solidification for Sandelin substrates previously proposed [3]. The marker role played by tin is important in this interpretation.

Aknowledgments

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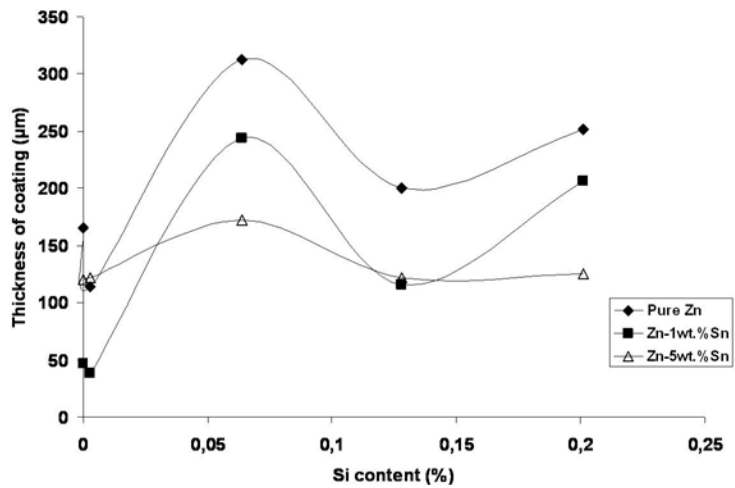
Figure 1: Effect of Si content of steel on the thickness of galvanized coatings.
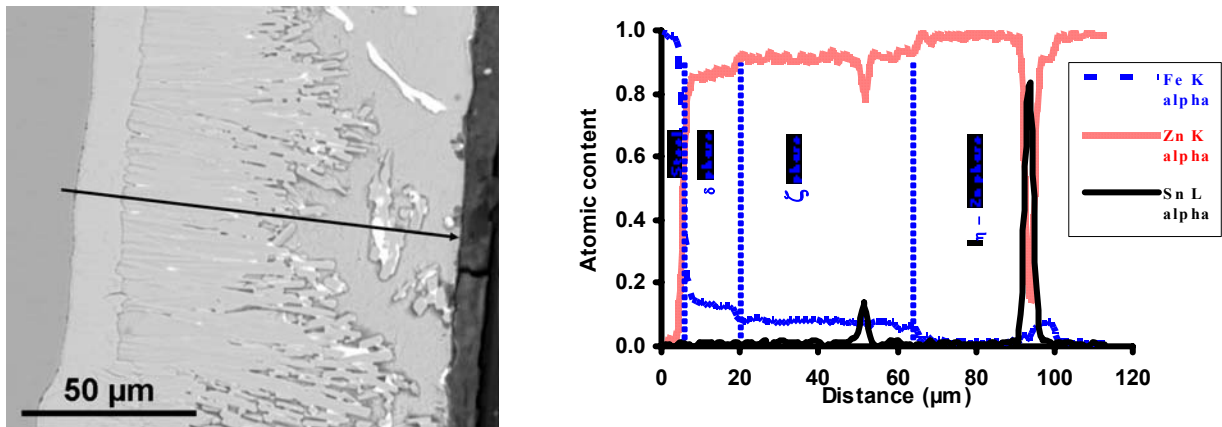

Figure 2: Example of BSE/SEM micrograph of a galvanized coating on substrate 3 (bath of Zn-5wt.%Sn, 9 minutes, 450°C) and chemical analyses line profile across the coating (EDS/SEM). It shows that the coating consists of three layers (δ, ζ and η-Zn phases). Tin (white phase) appears at the interface between δ and ζ, between ζ crystals and in the η-Zn phase).
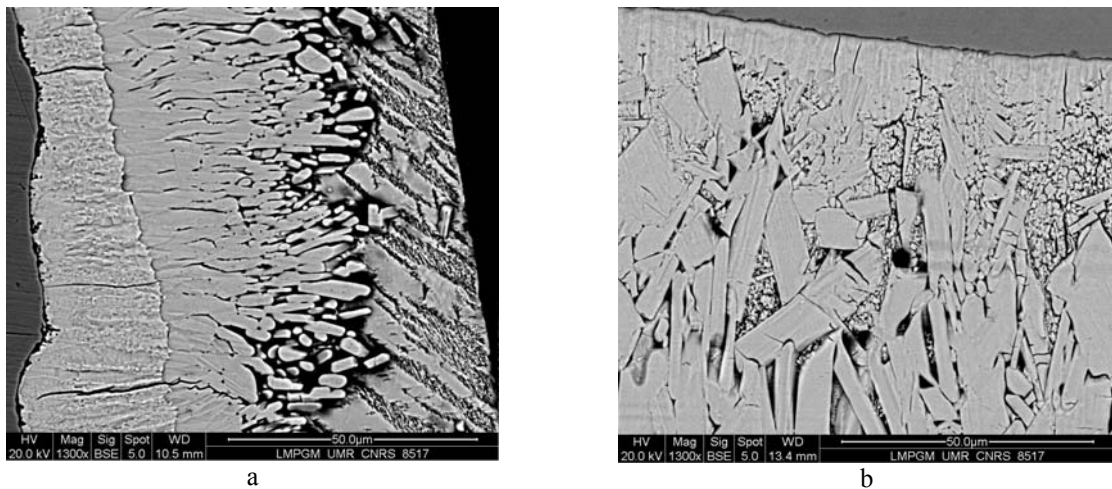
Figure 3: Galvanized coatings in a pure Zn bath (BSE/SEM) : a) galvanized substrate 2 and b) galvanized substrate 6. It shows that ζ crystals are larger for hyper-Sandelin steels.
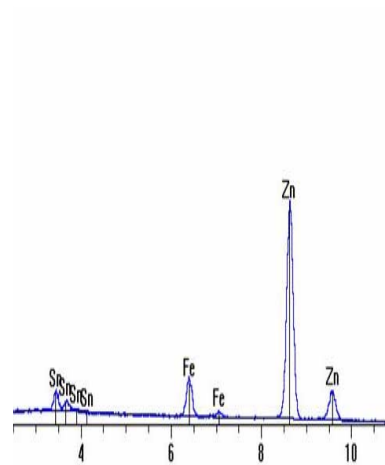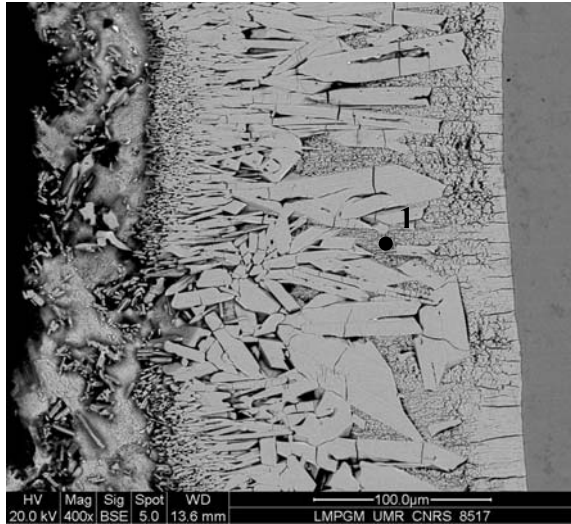
Figure 4: Diffuse Δ (galvanized substrate 5, Zn-0,5wt.%Sn bath) (BSE/SEM) and EDS analysis of point 1 located in diffuse Δ (8.21 at.%Fe, 89.39 at.%Zn, 1.18 at.% Si, 1.22 at.%Sn).
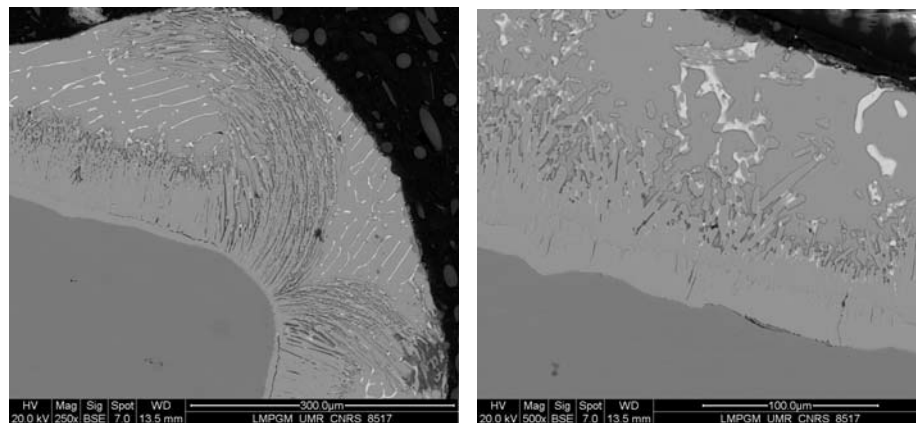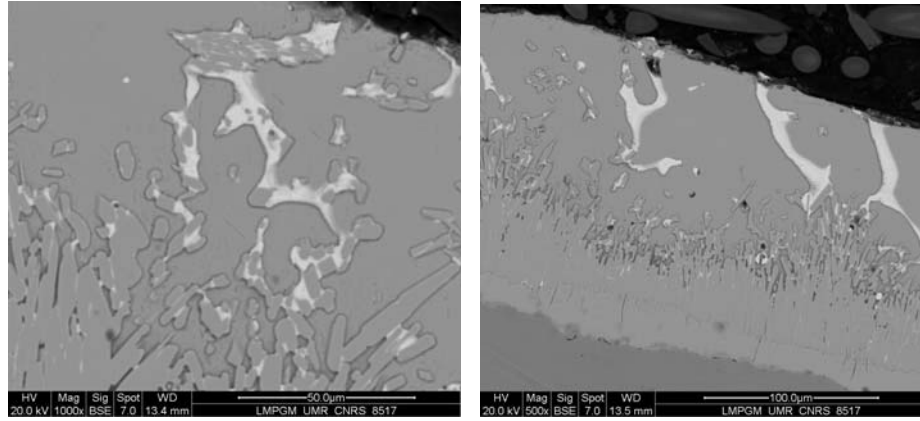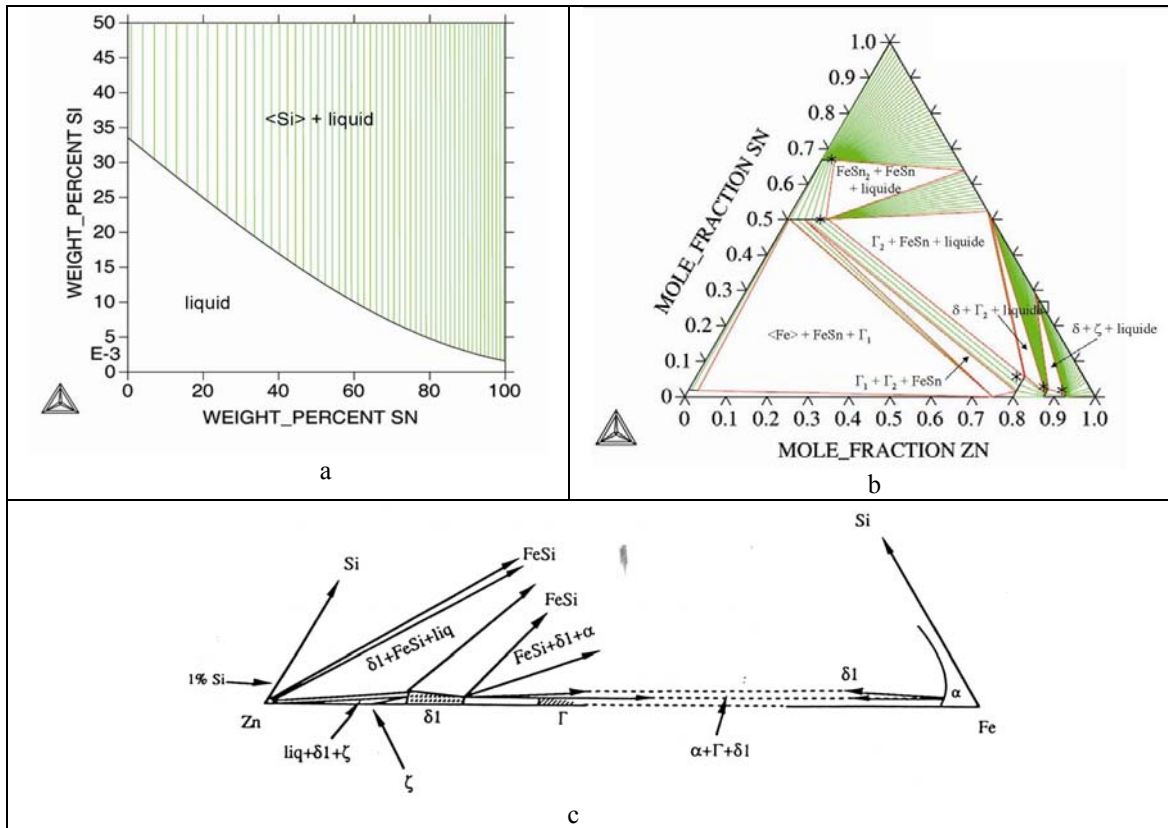
Figure 5: Examples of BSE/SEM micrographs of galvanized coating on substrate 2 (Zn-1wt.%Sn bath, 9 minutes, 450°C). The white phase is tin.
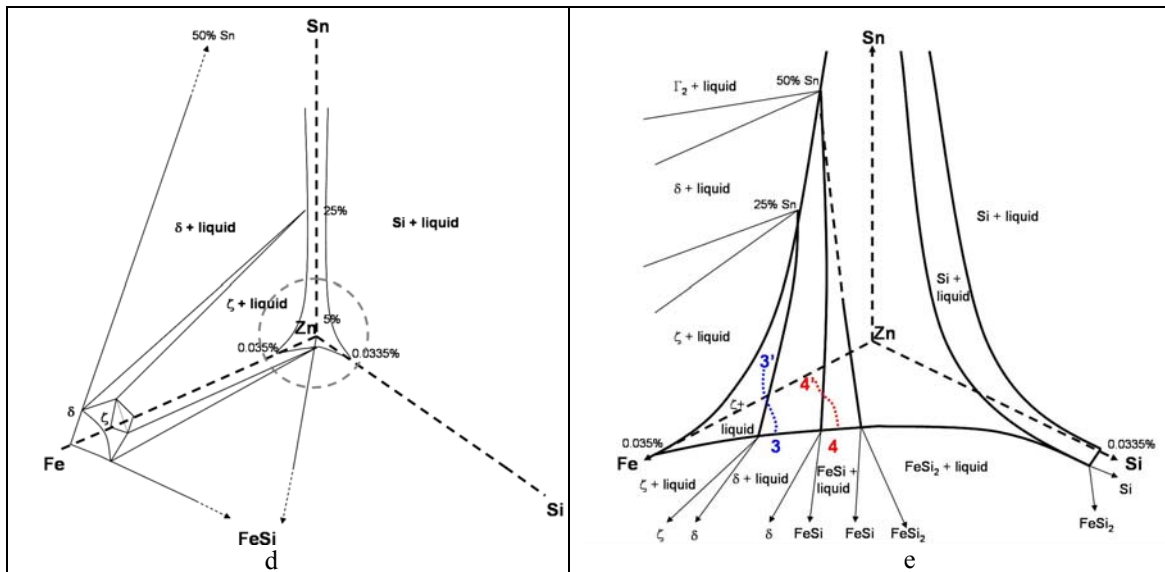
Figure 6: Assessment of Si-Sn-Zn phase diagram (a), of Fe-Sn-Zn phase diagram (b), of Fe-Si-Zn phase diagram according to [3] (c) and the Zn-rich corner of the Fe-Si-Sn-Zn phase diagram (d and e) at 450°C.
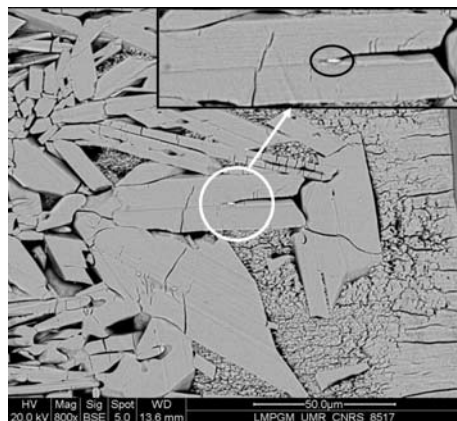

Figure 7: Coating obtained on substrate 5 from galvanizing in a Zn-0.5wt.%Sn bath (BSE/SEM). Tin seems to impede the growth of intermetallic compounds.
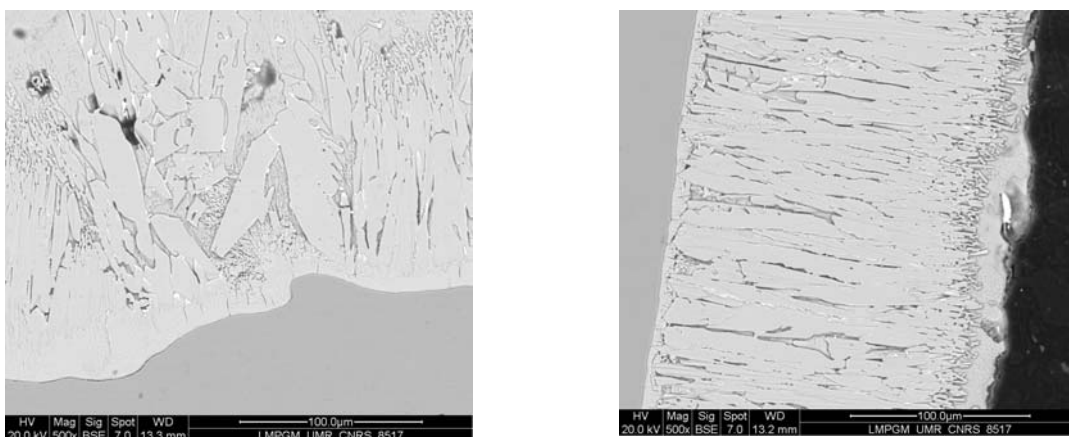

Figure 8: Galvanized substrate 5 (Zn-2wt.%Sn bath). Sn content between ζ and δ is more important for hyper-Sandelin substrates than for hypo-Sandelin substrates (see figure 5).
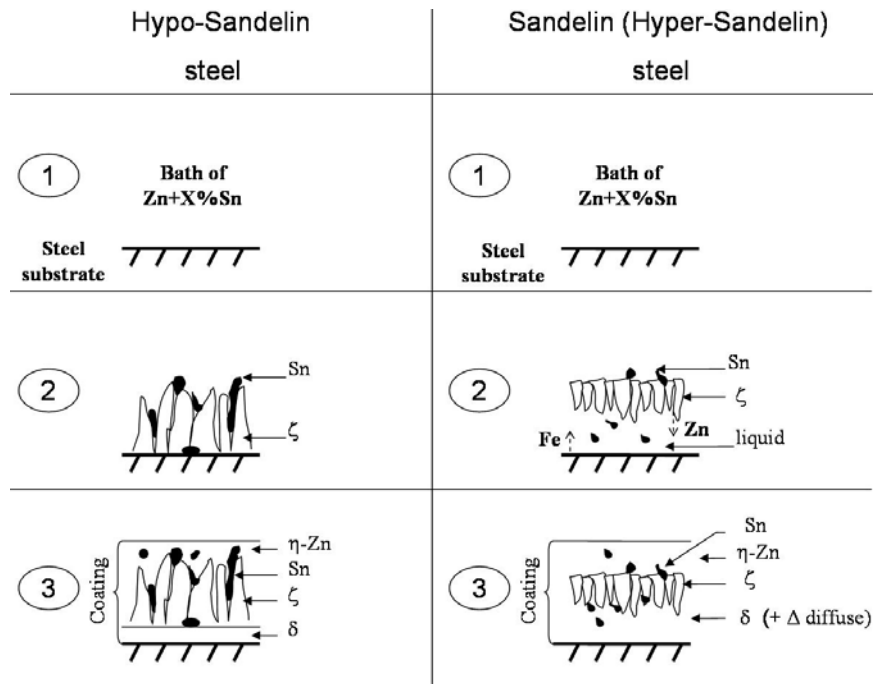
Figure 9: Proposal for a mechanism of solidification for galvanized hypo-Sandelin, Sandelin and hyper-Sandelin steels.