

Reaction between Fe-0.10mass%Si Alloy(s) and Zinc(l)

by

Yasuo Uchiyama* Hideto Koga*

An Fe-0.10mass%Si alloy was immersed in the pure zinc bath for a time up to 6 ks at various temperatures ranging from 713 K to 873 K. The morphology of the alloy layer was observed, and the thickness of the alloy layer and the quantities of iron having reacted with zinc were measured. The total thickness of the alloy layer formed at temperatures ranging from 713 K to 753 K is thicker than that of one formed at higher temperatures. The temperature dependence of the quantity of iron remaining in the alloy layer is similar to that of the total thickness of the alloy layer. An iron mass loss is greater in the temperature range from 713 K to 753 K, and above 813 K, it increases with the immersion temperature.

To obtain information on the silicon reactivity in hot dip galvanizing, the results obtained for the Fe-0.10mass%Si alloy were compared with those obtained for pure iron under the same conditions used in this study. The addition of 0.10mass% Si influences the Fe-Zn reaction in the temperature range from 713 K to 753 K. The alloy layer formed in this temperature range comprises a gamma layer, a delta 1 layer, and a zeta layer. The zeta layer formed in this temperature range is a (zeta+eta) mixture layer, and is composed of granular or columnar zeta crystals. The growth of the zeta layer obeys the linear time law, disobeying the diffusion controlled process. The delta 1 layer formed in the temperature range from 713 K to 753 K is constant. This causes the growth of the zeta layer to obey the linear time law. The rapid reaction between the Fe-0.10mass%Si alloy and liquid zinc in the vicinity of 713 K is the effect of added silicon that allows the formation of the (zeta+eta) mixture layer.

I. Introduction

Hot dip galvanized steel sheet is used for many fields such as auto, building, etc.. Rimmed steel was used for the steel to be galvanized, till continuous casting came into the world. After that, killed steel occupied the place once held by rimmed steel. Being galvanized, killed steel, especially silicon killed steel exhibits an abnormal coating. About the effect of silicon in hot dip galvanizing, Sandelin⁽¹⁾ first reported that silicon of 0.10mass% in steel caused the increase of the quantity of iron having reacted with zinc. As silicon had not been a troublemaker in hot dip galvanizing, the effect of silicon did not attract galvanizers' interest, till silicon killed steel

昭和59年4月28日受理

* : Materials Science and Engineering, Faculty of Engineering,
Nagasaki University, 1-14 Bunkyo-cho, Nagasaki, 852 Japan

was galvanized with the abnormal coating. After the found of the abnormal coating, many investigations on the effect of silicon were performed. Several models that might account for the silicon effect were proposed⁽²⁾⁻⁽⁵⁾. However, there is no unified model without unproven assumption. One of the reasons why an unified model has not yet been proposed is a lack of information about the silicon effect in hot dip galvanizing. Dipping at temperatures higher than conventional galvanizing temperature is considered to be one of the cures for the abnormal coating⁽⁶⁾. Nevertheless, there is only unsatisfactory information about dipping at elevated temperatures.

In this study, to obtain satisfactory information about the effect of silicon on the Fe-Zn reaction, an Fe-0.10mass%Si alloy was immersed in the pure zinc bath at various temperatures from 713 K to 873 K for times from 60 s to 6 ks, and the morphology of the alloy layer was observed, and the thickness of the alloy layer and the quantities of iron having reacted with zinc were measured.

II. Experimental procedure

The Fe-0.10mass%Si alloy (0.04mass%Mn, 0.003mass%P, 0.007mass%S, 0.02mass%Cu, 0.02mass%Ni, 0.02mass%Cr, 0.002mass%Al) was prepared by melting together electrolytic iron and silicon by a high-frequency induction vacuum furnace, and cast into a ingot. Plates 25×20×2mm³ in size were cut out from the ingot. The cut surfaces were abraded with successive grades of emery paper and finally polished with diamond paste. These plates were then annealed at 1173 K for 3.6 ks, furnace cooled, repolished and degreased.

The methods used for galvanizing, metallographic observation, thickness measurement and the measurement of the quantities of iron having reacted with zinc were described in detail in our former paper⁽⁷⁾.

III. Experimental results

1. Metallographic observation and the growth of the alloy layer

Figure 1 shows the relation between the thickness of the alloy layer and the temperature for a 1.2 ks immersion. For the other immersion times, the temperature dependence curves of the thickness of the alloy layer are similar to those shown in Fig. 1. A gamma layer was formed on the base, but the thickness curve of this layer is excluded from Fig. 1, because of its thinness.

In the temperature range from 713 K to 753 K, the alloy layer comprised mainly a zeta layer composed of small zeta crystals floating in an eta, as shown in Photo.1. The total thickness of the alloy layer in this range is thicker than that of the alloy layer formed at the other immersion temperatures, and has a maximum in the vicinity of 733 K. At 753 K, the zeta layer was composed of columnar zeta crystals,

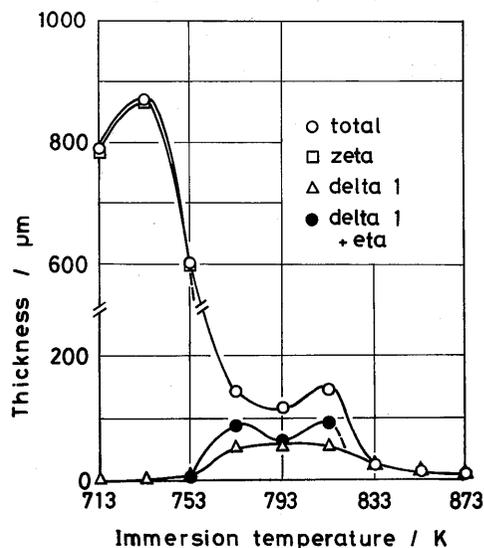


Fig. 1 Relation between the thickness of the alloy layer formed on the Fe-0.10mass%Si alloy (μm) and the temperature (K) for a 1.2 ks immersion.

and a ($\delta_1 + \eta$) mixture was formed in the space among the zeta crystals. In the temperature range from 773 K to 813 K, the alloy layer comprised the δ_1 layer which is thicker than that formed at the other immersion temperatures and the ($\delta_1 + \eta$) mixture layer (Photo.2). In the temperature range from 833 K to 873 K, only the δ_1 layer was formed on the zinc side of the gamma layer, and no other alloy layer was formed on the outer side of the δ_1 layer (Photo.3). The total thickness of the alloy layer in this temperature range is thinner than

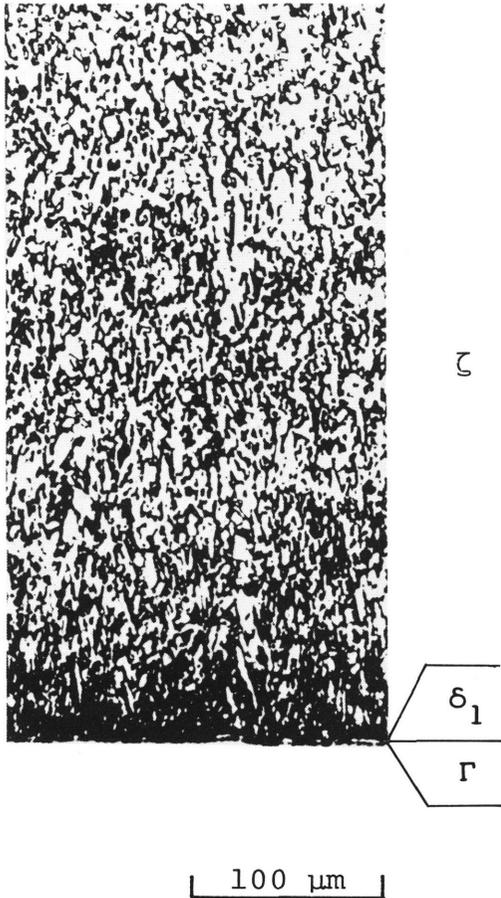


Photo. 1 An optical micrograph showing the cross section of the alloy layer formed on the Fe-0.10mass%Si alloy immersed in the pure zinc bath at 733 K for 6ks.

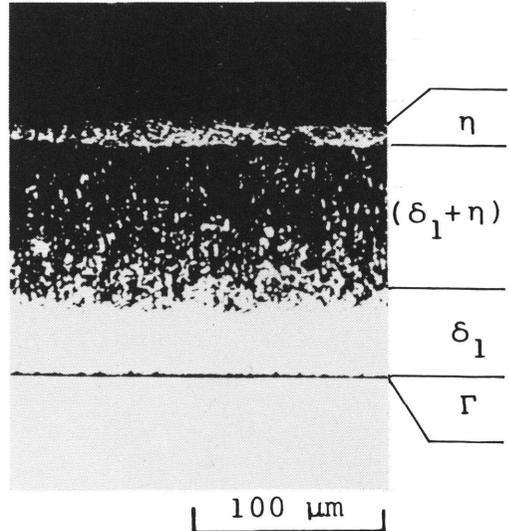


Photo. 2 An optical micrograph showing the cross section of the alloy layer formed on the Fe-0.10mass%Si alloy immersed in the pure zinc bath at 773 K for 600 s.

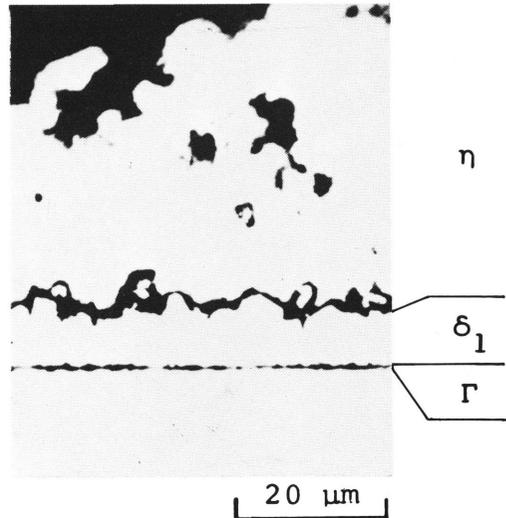


Photo. 3 An optical micrograph showing the cross section of the alloy layer formed on the Fe-0.10mass%Si alloy immersed in the pure zinc bath at 873 K for 600 s.

that of the alloy layer formed at the other temperatures.

The outer portion of the alloy layer dropped off and floated away in the zinc bath.

Figure 2 shows the relation between the thickness of the alloy layer formed at 713 K and the immersion time. The logarithm of the thickness of the alloy layer is plotted against the logarithm of the immersion time. The plots for each alloy layer are roughly on straight lines over

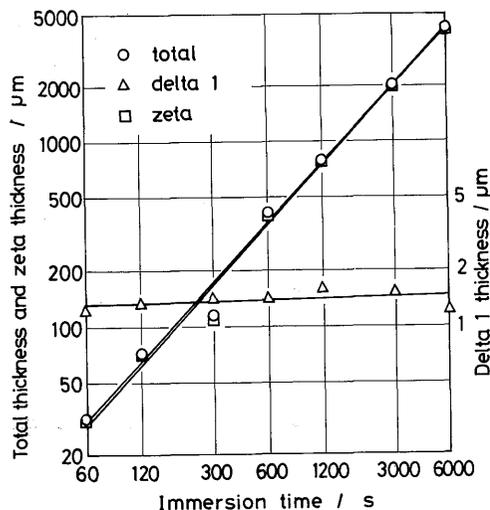


Fig. 2 Relation between the thickness of the alloy layer formed on the Fe-0.10mass%Si alloy immersed in the pure zinc bath at 713 K (μm) and the time (s).

a certain immersion time range. This means that the thickness of the alloy layer (d) is related to the immersion time (t) by the following equation,

$$d = at^m \quad (1)$$

where a and m are constants. The best estimates of a and m for each alloy layer were obtained by the method of least squares for all the immersion temperatures, and are listed in a form of at^m in Table 1. In the range from 713 K to 753 K, the time exponent of the zeta layer and that of the total layer are roughly 1.0, while that of the delta 1 layer is smaller than 0.2. In the range from 773 K to 813 K, the time exponent of the total layer is within the range from 0.6 to 0.7. Above 833 K, it is about 0.2.

2. Quantity of iron having reacted with zinc

Table 1 Experimental expression of the thickness of the alloy layers (μm) for the immersion time (s) at various temperatures (K).

Temp. (K)	Total	Zeta	Delta 1	Mixture
713	$0.369t^{1.07}$	$0.348t^{1.08}$	$1.206t^{0.02}$	***
733	$0.466t^{1.06}$	$0.441t^{1.07}$	$0.867t^{0.15}$	***
753	$0.649t^{0.97}$	$0.567t^{0.98}$	$2.046t^{0.09}$	—
773	$1.630t^{0.67*}$	***	$0.428t^{0.73*}$	$1.231t^{0.64*}$
793	$1.421t^{0.71*}$	***	$0.657t^{0.63*}$	$0.799t^{0.75*}$
813	$2.076t^{0.60**}$	***	$0.802t^{0.58**}$	$1.149t^{0.62**}$
833	$9.495t^{0.17}$	***	$0.495t^{0.17}$	***
853	$5.147t^{0.18}$	***	$5.147t^{0.18}$	***
873	$2.723t^{0.19}$	***	$2.723t^{0.19}$	***

Range of immersion time (s) :

*:(60-600), **: (60-1200), no mark: (60-6000)

*** : not appeared

Mixture : (delta 1+eta)

— : not determined

The relation between an iron mass loss and the immersion temperature is shown in Figure 3. The iron mass loss is large in the temperature range from 713 K to 753 K, but it is small at 773K and 793 K. As the immersion temperature increases above 813 K, it increases with the immersion temperature. The temperature dependence of the quantity of iron remaining in the alloy layer is similar to that of the total thickness of the alloy layer; the quantity of iron remaining in the alloy layer is large in the temperature range from 713K to 753K, and is small at higher temperatures. The quantity of iron dissolved into the zinc bath is small up to 813K, while, at and above 833K, it increases rapidly with the immersion temperature.

Figure 4 shows the time dependence of the quantity of iron having reacted with zinc. It is clear from Fig. 4 that the quantity of iron having reacted with zinc (Δw) is related to the immersion time(t) by the following equation,

$$\Delta w = bt^n \quad (2)$$

where b and n are constants. The best estimates of b and n were also determined by the least square fits, and are listed in Table 2. The time exponent of the iron mass loss is about 1.0 in the range from 713K to 753K. Above 773K, it is in the range from 0.6 to 0.9. The time exponent of the quantity of iron remaining in the alloy layer is also about 1.0 in the range from 713 K to 753 K, while, above 813 K, it is below 0.2. The time exponent of the quantity of iron dissolved into the zinc bath is greater than 0.8 under all the immersion temperatures.

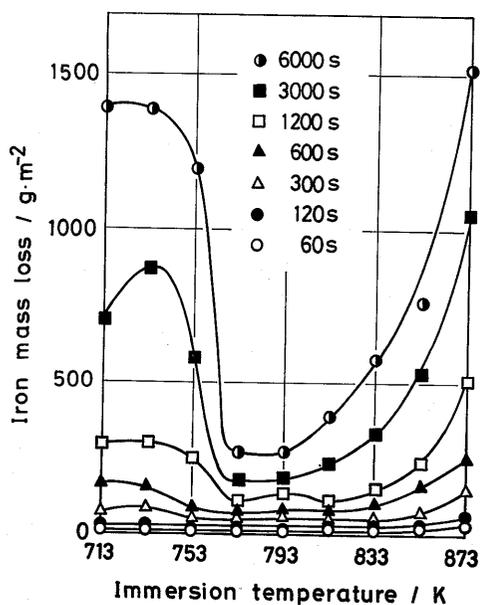


Fig. 3 Relation between the iron mass loss of the Fe-0.10 mass%Si ($\text{g}\cdot\text{m}^{-2}$) and the immersion temperature (K) for various times (s).

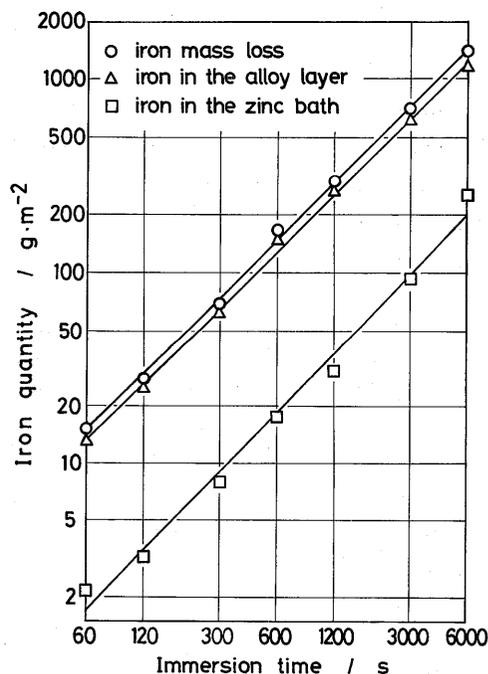


Fig. 4 Relation between the quantity of iron having reacted with zinc of the Fe-0.10 mass%Si alloy ($\text{g}\cdot\text{m}^{-2}$) and the time (s) for a 713 K immersion.

Table 2 Experimental expression of the quantity of iron having reacted with zinc ($\text{g}\cdot\text{m}^{-2}$) for the immersion time (s) at various temperatures (K).

Temp. (K)	Fe (total)	Fe (alloy)	Fe (zinc)
713	$0.255t^{0.99}$	$0.234t^{0.98}$	$0.024t^{1.04}$
733	$0.257t^{1.00}$	$0.248t^{0.99}$	$0.012t^{1.10}$
753	$0.178t^{1.02}$	$0.168t^{1.00}$	$0.018t^{1.10}$
773	$1.054t^{0.64}$	$1.391t^{0.53}$	$0.098t^{0.84}$
793	$0.251t^{0.92*}$	$0.316t^{0.81*}$	$0.135t^{0.85}$
813	$1.109t^{0.67}$	$5.686t^{0.23}$	$0.153t^{0.89}$
833	$0.744t^{0.76}$	$4.772t^{0.17}$	$0.183t^{0.93}$
853	$0.923t^{0.78}$	$2.387t^{0.20}$	$0.586t^{0.84}$
873	$1.285t^{0.84}$	$3.966t^{0.09}$	$0.896t^{0.87}$

Range of immersion time (s):

*: (60-600), no mark : (60-6000)

Fe (total) : iron mass loss

Fe (alloy) : iron remaining in the alloy layer

Fe (zinc) : iron dissolved into the zinc bath

IV. Discussion

The growth of the alloy layer formed on iron generally obeys eq.(1)⁽⁶⁾. when the time exponent m is 0.5, the reaction between iron and zinc is a diffusion controlled one. The increase of the quantity of iron having reacted with zinc obeys eq.(2)⁽⁹⁾. Recently, Wakamatsu et al.⁽⁹⁾ investigated the formation and growth kinetics of intermediate phases in the reaction between solid iron and solid or liquid zinc in more detail. They reported that the growth curve of the intermediate phases roughly obeyed eq. (1), but did not obey correctly eq. (1) with a single m value, and that the rate-determining process in hot dip galvanizing reaction should be discussed from another standpoint. Their opinion is concerned with such reaction that the outermost portion of the alloy layer does not dissolve in liquid zinc. In this study, the outermost portion of the alloy layer can dissolve in the zinc bath, because the pure zinc bath is used. Furthermore, it dropped off and floated away in the zinc bath. Assuming the growth of the alloy layer obeying the parabolic time law and the dissolution of the alloy layer obeying the linear time law, Gellings⁽¹⁰⁾ discussed the Fe-Zn reaction, and reported the parabolic law; the m value was in the range from 0.5 to 1.0. The present authors reported that the m value was in the range from 0.0 to 1.0, in the case that the growth of the alloy layer obeyed the parabolic time law and the alloy layer dropped off and floated away in the zinc bath (11).

As discussed above, to clarify the mechanism of such reaction that the alloy layer dropped off and floated away in the liquid phase, eq. (2) should be discussed in connection with eq.(1).

The alloy used is essentially Fe-Si binary alloy. The effect of the other elements on the Fe-Zn reaction, therefore, could be negligible, if any. Hence, the effect of silicon addition on the morphology and thickness of the alloy layer and the quantity of iron having reacted with zinc is discussed by comparing the consequence obtained for the Fe-0.10mass%Si alloy with that ob-

tained for pure iron under the same condition used in this study⁽⁷⁾. Figures 5 and 6 show the effect of addition of 0.10 mass% Si on the thickness of the alloy layer and the quantity of iron having reacted with zinc. The consequence obtained for the Fe-0.10mass%Si alloy differs from that obtained for pure iron in the temperature range from 713K to 753 K. In this temperature range, the growth of the alloy layer formed on pure iron and the increase of the quantity of iron having reacted with zinc obeys the parabolic time law. Thus the reaction between pure iron and liquid zinc is a diffusion controlled one. On the other hand, in the case of the Fe-0.10mass%Si alloy, the growth of the alloy layer and the increase of the quantity of iron having reacted with zinc obey the linear time law, as shown in Tables 1 and 2. Since the values b and n for the iron mass loss are equal to those for the quantity of iron remaining in the alloy layer, the formation of the alloy layer is a main reaction between the Fe-0.10mass%Si alloy and liquid zinc. Since the immersion time dependence of the growth of the zeta is similar to that of the iron mass loss, the growth of the zeta layer is a rate-determining process in the reaction between the Fe-0.10-mass%Si alloy and liquid zinc. In the case of pure iron, the zeta was composed of columnar crystals and stratified. In this case, the δ_1 formed on the iron side of the zeta layer was not contact with liquid zinc, and the δ_1 layer grew with the parabolic time law. On the other hand, in the case of the Fe-0.10mass%Si alloy, the zeta is composed of granular crystals and the zeta layer is correctly the (zeta+eta) mixture layer, then the δ_1 formed on the steel side of the zeta layer is contact with liquid zinc. The δ_1 layer in this case does not grow. Therefore, a transfer rate of iron through the δ_1 layer is constant. This causes the growth of the zeta layer to obey the linear law.

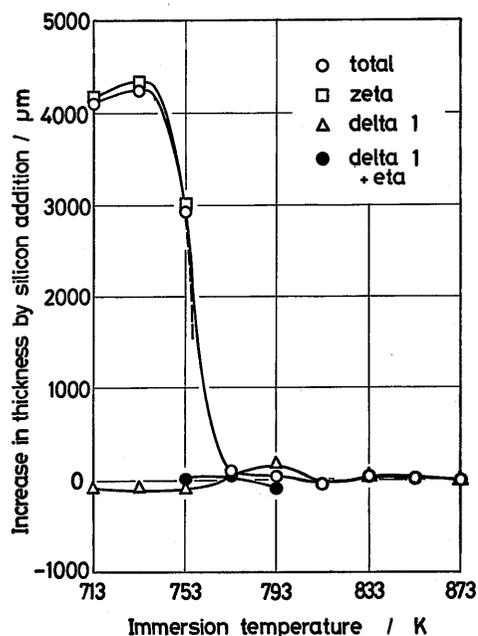


Fig. 5 Effect of addition of 0.10mass% Si on the thickness of the alloy layer (μm) as a function of the temperature (K) for a 6 ks immersion.

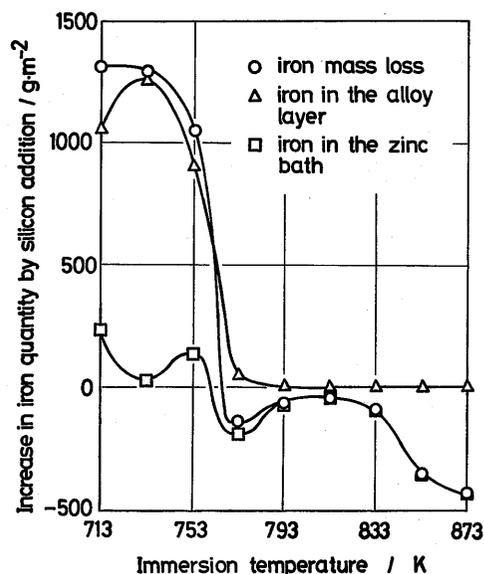


Fig. 6 Effect of addition of 0.10 mass% Si on the quantities of iron having reacted with zinc ($\text{g}\cdot\text{m}^{-2}$) as a function of the temperature (K) for a 6 ks immersion.

This way of thinking that the added silicon influences the formation of the zeta layer agrees with that of Sedzimir et al. ⁽²⁾ and that of Horstmann et al. ⁽³⁾.

V. Conclusion

The reaction between the Fe-0.10mass%Si alloy and liquid zinc was studied for the time up to 6ks at various temperatures in the range from 713 K to 873 K. An information was obtained on the silicon reactivity in hot dip galvanizing.

The addition of 0.10mass% Si influences the Fe-Zn reaction in the temperature range from 713K to 753K. The alloy layer formed in this temperature range comprises the gamma layer, the delta 1 layer and the zeta layer. The zeta layer formed in this temperature range is the (zeta+eta) mixture layer, and is composed of granular or columnar zeta crystals. The growth of the zeta layer obeys the linear time law, disobeying the diffusion controlled process. The delta 1 layer formed in the temperature range from 713 K to 753 K is constant. This causes the growth of the zeta layer to obey the linear time law. The rapid reaction between the Fe-0.10mass%Si alloy and liquid zinc in the vicinity of 713K is the effect of added silicon that allows the formation of the (zeta+eta) mixture layer.

Reference

- 1) R. W. Sandelin: Wire and Wire Products, **15** (1940), 655 and 721.
- 2) J. Sedzimir and H. Szymanke: Neue Hütte, **14** (1969), 176.
- 3) H. Guttman and P. Niessen: Canadian Metallurgical Quarterly, **11** (1972), 609.
- 4) D. C. Pearce: Proc. of Semin. on Galvanizing Silicon containing Steels, International Lead and Zinc Research Organization, New York, (1975), 32.
- 5) L. P. Devillers, H. Guttman and P. Niessen: *ibid.*, (1975), 48.
- 6) E. Varady: *ibid.*, (1975), 21
- 7) H. Koga, Y. Uchiyama and T. Aki: Trans. JIM, **20** (1979), 290.
- 8) D. Horstmann and F.K. Peters: Proc. of 9th Intern. Conf. on Hot Dip Galvanizing, Industrial Newspapers Ltd., London, (1971), 75.
- 9) Y. Wakamatsu and M. Onishi: Tetsu-to-Hagané, **68** (1982), 1808.
- 10) P. J. Gellings: Proc. of Semin. on Galvanizing Silicon containing Steels, International Lead and Zinc Research Organization, New York, (1975), 69.
- 11) H. Koga, Y. Uchiyama, and T. Aki: J. Japan Inst. Metals, **42** (1978), 136.