THE ROLE OF INTERFACE ENERGIES IN GALVANIZED COATING DEVELOPMENT*

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A new mechanism is advanced that accounts for the abnormal galvanizing behavior of steels containing silicon. The basis for this model is the influence of interface energies on intermetallic phase formation. High silicon and iron concentrations in the liquid adjacent to the developing coating can trigger liquid phase penetration at various interfaces. This results in abrupt changes in the kinetics of the coating development. Observed microstructures conform well to the proposed mechanism.

1. INTRODUCTION

Galvanizing is an effective means of imparting corrosion protection to steel. The immersion of steel in molten zinc results in a coating that acts both as a physical barrier to the environment and as a sacrificial anode with respect to exposed steel surfaces.

The galvanizing of steels containing silicon involves a number of difficulties. These problems are related to the abnormal growth kinetics and phase morphologies of the Fe–Zn intermetallic layers that form at the interface between steel and molten zinc. Utilization of steels with significant silicon levels is increasing, so this phenomenon is becoming technologically important.

The influence of interface energies on galvanized coating development has not been considered in the past. Variation in the interface energies can have a profound effect on phase nucleation and growth. This is the basis for the proposed new mechanism that accounts for the galvanizing response of steels containing silicon.

2. OBSERVED ANOMALIES IN GALVANIZED COATING DEVELOPMENT

The hot-dip galvanizing of steels with less than 0.03 wt.% Si results in the development of planar layers of the various phases predicted by the equilibrium phase diagram (Fig. 1). Galvanizing is typically performed at about 450 °C, so establishment of a Zn–Fe interface leads to layers of the ζ, δ_1 and Γ phases. A solid solution of zinc (η phase) is also present as the result of the removal of molten metal

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with the substrate. The time dependence of the coating development is parabolic, as would be expected when the coating is formed by diffusion through a surface layer of increasing thickness.
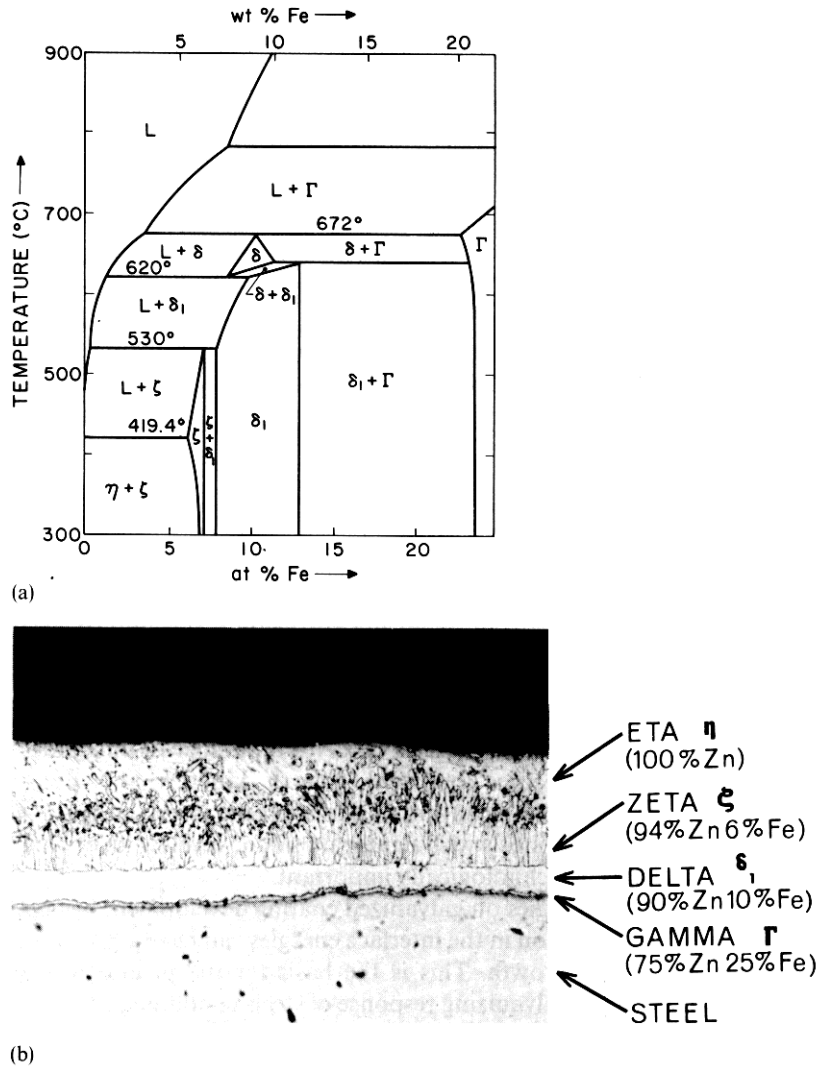

(a)

(b)

Fig. 1. (a) Zinc-rich side of the equilibrium phase diagram for Fe–Zn[1]; (b) the corresponding intermetallic layer formation for a steel with 0.02 wt.% Si galvanized at 450 °C.

For steels containing more than 0.03 wt.% Si that are currently used in structural applications, the process of coating development is somewhat different. Instead of continuous intermetallic layers these coatings have thick regions of disconnected intermetallic crystals. Coating development is much more rapid and has a linear time dependence. The greater reactivity and altered phase structure cause problems in thickness control, mechanical integrity and surface appearance[2].

The relationship between the galvanizing response and silicon concentration is quite complex. At 450 °C there are peaks in reactivity at concentrations of about 0.1 and 0.4 wt.% Si [3], which correspond to differences in the microstructure. For the steel with 0.12 wt.% Si shown in Fig. 2(a) the coating exhibits a wide region of fine discontinuous ζ crystals. The $\zeta-\delta_1$ region is mainly intact. Figure 2(b) is a corresponding micrograph for a steel with 0.54 wt.% Si in which a definite $\zeta-\delta_1$ interface is no longer apparent. The ζ crystals are large and disconnected.

In the galvanizing of steels with less than 0.03 wt.% Si, a kinetic response similar to that of high silicon steels occurs in the temperature range 490–530 °C. A continuous ζ layer does not form, even though this phase is thermodynamically stable. Contact between δ_1 and the liquid leads to rapid dissolution of the steel substrate with a linear time dependence [4].

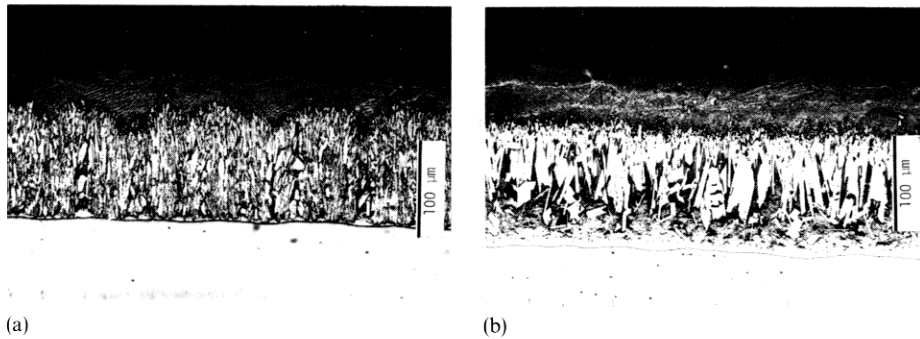(a)   (b)

Fig. 2. Galvanized coatings on steels containing silicon: (a) 0.12 wt.% Si steel galvanized for 3 min at 450 °C in Prime Western zinc; (b) 0.54 wt.% Si steel, galvanized under the same conditions as (a). The steel is at the bottom.

3. A MECHANISM FOR THE EFFECT OF SILICON ON GALVANIZED COATING DEVELOPMENT

Most past explanations for the galvanizing behavior of steels containing silicon are based on the principle that the addition of a third component to a system undergoing phase transformations in a diffusion gradient can lead to non-planar phase boundaries and two-phase regions [5]. For instance, Guttman and Niessen [6] proposed that the low solubility of silicon in the ζ phase leads to the accumulation of silicon at ζ phase boundaries and to the stabilization of liquid in these areas. The presence of continuous liquid paths provides a means for the rapid diffusion of zinc to the growth interfaces. This mechanism does not, however, satisfactorily explain the complex dependence of the kinetics and microstructure on the silicon level; neither can it account for the galvanizing behavior of low silicon steels between 490 and 530 °C.

However, there is experimental support for the basic contention that the linear kinetics are due to liquid penetration between the ζ crystals [7]. If this is accepted, two main questions remain.

(1) How does the penetration of liquid arise?

(2) Why does the contact between liquid and δ_1 persist, when the phase diagram predicts that ζ should form and "heal" the interface?

Horstmann [8] has pointed out that an understanding of the ζ phase nucleation is

the key to answering these questions. Proceeding from the basic principles of nucleation theory and interface behavior, we developed a model that accounts for the various anomalies in the galvanizing behavior.

The driving force for heterogeneous nucleation at interfaces is the decrease in total surface energy. The following approach is taken from Fine[9]. Let us consider a spherical cap of solid phase β which is being formed at the interface between the liquid and non-reactive solid phase α (Fig. 3). The equilibrium contact angle θ is given by

$$\cos\theta = l = \frac{\sigma_{\alpha L} - \sigma_{\alpha\beta}}{\sigma_{\beta L}}$$

where σ denotes the interface energy. The free-energy change to form the critical nucleus will be

$$\Delta F^* = \frac{16\pi\sigma_{\beta L}^3}{3\Delta F_V^2} \frac{2 - 3l + l^3}{4}$$

where ΔF_V is the bulk free-energy change for the transformation liquid (L) $\rightarrow$ β. This compares with

$$\Delta F^* = \frac{16\pi\sigma_{\beta L}^3}{3\Delta F_V^2}$$

for homogeneous nucleation. The following limiting cases are apparent: for case I

$$\theta = 0° \qquad\qquad \sigma_{\alpha L} \geqslant \sigma_{\alpha\beta} + \sigma_{\beta L}$$

$$\Delta F^* = 0$$

and there is no barrier to nucleation; for case II

$$\theta = 180° \qquad\qquad \sigma_{\alpha\beta} \geqslant \sigma_{\alpha L} + \sigma_{\beta L}$$

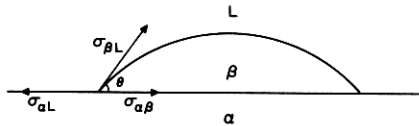and heterogeneous nucleation is not energetically favored.

Fig. 3. Heterogeneous nucleation on a solid substrate.

Strictly, in the above approach it is assumed that the α substrate does not participate in the transformation. However, the basic principles should still be applicable to ζ phase nucleation in galvanizing. The nucleation rate is proportional to the quantity $\exp(-\Delta F^*/kT)$. Thus the observed difficulty in ζ nucleation in low silicon steel above 490 °C is due to an increase in ΔF^*. This can be caused by a decrease in the bulk free-energy change for the transformation, which occurs when the transformation temperature is approached. A second possible cause of the decrease in the nucleation rate is an increase in the contact angle due to changes in

the interface energies. Our work has shown that this contact angle effect is important in ζ phase nucleation.

The following experiment was performed. Samples of low silicon steel were first galvanized at 450 °C to develop the continuous intermetallic layers. They were then quenched and reimmersed in molten zinc at a series of higher temperatures. As shown in Fig. 4, there is extensive penetration of the liquid between ζ crystals at 490 °C and some severing of the δ_1–ζ interface at 510 °C. As the ζ phase is thermodynamically stable at these temperatures, the effect is apparently the result of changes in interface energies.
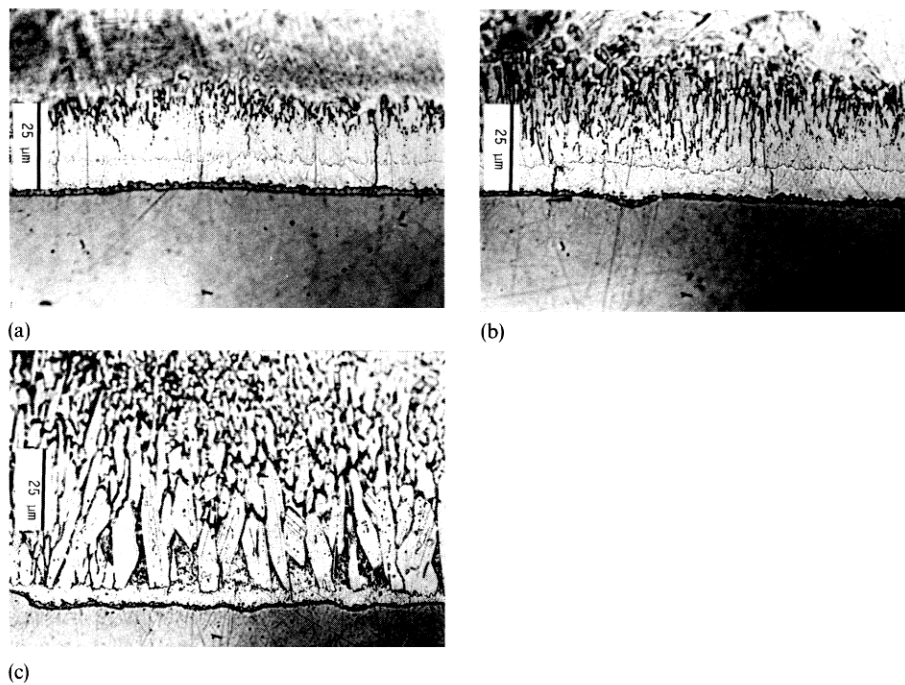

(a)

(b)

(c)

Fig. 4. Two-step procedure for galvanizing a steel with 0.02 wt.% Si after a first immersion at 450 °C for 3 min and (a) a second immersion at 480 °C for 1 min (the ζ phase is mainly intact), (b) a second immersion at 490 °C for 1 min (the liquid appears to be penetrating the ζ grain boundaries) and (c) a second immersion at 510 °C for 1 min (the ζ phase layer is discontinuous and the interface between ζ and δ_1 is only partially intact).

The solubility of iron in molten zinc is strongly temperature dependent. It changes from 0.03 wt.% at 450 °C to 0.10 wt.% at 500 °C [10]. Thus, liquid zinc adjacent to the ζ phase will be much richer in iron at higher temperatures. As a general rule, the energy of the interface between two phases becomes smaller as the compositions of the two phases approach each other. This is intuitively obvious, since the interface energy is the result of chemical and structural differences between the two phases. Passerone et al.[11] demonstrated that this is indeed the case in the eutectic systems Zn–Sn and Zn–Sn–Pb. For the Fe–Zn system it is apparent that the reduction in $\sigma_{\zeta L}$ is at least a major cause of the difficulty in heterogeneous nucleation of ζ above 490 °C.

We propose that the presence of silicon affects coating development in a similar manner. Silicon in the melt adjacent to the developing coating lowers the liquid–solid interface energies by increasing the iron content of the liquid. Silicon and iron have a strong tendency to form intermetallic compounds. In liquid zinc this manifests itself in the impossibility of maintaining a significant iron level in the melt when silicon is also present and vice versa[12]. In the galvanizing of steels containing silicon there will be a tendency for Fe–Si intermetallics to form in the liquid adjacent to the coating. However, nucleation of these phases takes time. When the steel is first immersed in the galvanizing bath, the melt immediately adjacent to it builds up an iron level higher than it would if silicon were not present, because of the strong positive interaction between iron and silicon. As a result, the energies of the interfaces between liquid and solid phases decrease, as discussed above.

Microstructurally this effect can be manifested by liquid phase penetration between ζ crystals. This will occur when

$$\sigma_{\zeta\zeta} \geqslant 2\sigma_{\zeta L}$$

At higher silicon levels the build-up of iron in the liquid can eventually lead to severing of the δ_1–ζ interface. This will happen if

$$\sigma_{\delta_1\zeta} > \sigma_{\zeta L} + \sigma_{\delta_1 L}$$

These two microstructures are basically what we see at the two peaks in the galvanizing reactivity. At the first peak there is liquid penetration between ζ grains but the δ_1–ζ interface is mainly intact. At the second peak the ζ crystals are detached. They grow larger with time because of the pumping of iron from δ_1 through the liquid to ζ. There is no thermodynamic driving force for new nucleation of ζ on the δ_1 phase.

4. CONCLUDING REMARKS

The mechanism described above accounts for many of the observed anomalies in intermetallic growth during galvanizing. However, numerous other factors can influence galvanizing behavior. Current research is aimed at testing the validity of the proposed model and demonstrating its general applicability.

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