SHORT COMMUNICATION

MECHANISM OF THE REACTION BETWEEN LIQUID ZINC AND STEEL*

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THE REACTION between liquid zinc and steel, such as occurs during hot-dip galvanizing, shows some unusual kinetic features which as yet have not found a completely satisfactory explanation. The purpose of this note is to present a mechanism based upon recent results from the literature and some preliminary experiments obtained in our laboratory.

The main kinetic features of the reaction under consideration are:

- (a) For silicon-free steels the reaction follows approximately parabolic kinetics up to 490°C and above 530°C, but is much faster and shows linear kinetics between these temperatures. Also the rate found above 530°C when extrapolated to lower temperatures coincides with the rate experimentally found at these temperatures.^{1,2}
- (b) Several alloying elements, most notably silicon, increase the attack, both in the parabolic and linear regions, and shift the onset to linear kinetics to a lower temperature.^{1,3}

During the reaction, a multiple Fe-Zn alloy layer is formed consisting of Γ , δ_1 , ζ and η -layers, using the designations of the phase diagram established by Schramm.^{4,5} The δ_1 layer always shows two sublayers of different morphology: an inner, compact layer consisting of small equiaxial crystallites (δ_{1k}) and an outer layer consisting of large columnar crystallites (palisade layer, δ_{1p}). According to Schramm the homogeneity range of δ_1 at 450°C is from 8.2 to 13.1 at. % Fe.

Upon the basis of this phase diagram several authors have tried to explain the kinetic features. Allen and Mackowiak⁶ and Harvey⁷ both suppose that, in the parabolic region up to 490°C, volume diffusion in the ζ -layer is rate-determining leading to parabolic kinetics. Destabilization of ζ above that temperature is then responsible for the change-over to linear kinetics, for which different explanations are given. These authors are not able to explain the reversion to parabolic kinetics above 530°C. Horstmann⁸ proposed a mechanism in which volume diffusion in the Γ -layer is rate-determining below 490°C and above 530°C. Between these temperatures Γ is supposed to be absent due to porosity of the δ -layer, Harvey,⁷ however, has shown that Γ is also present between 490° and 530°C, which contradicts Horstmann's assumption.

Sedzimir and Szymanke⁹ and Bablik *et al.*¹⁰ in proposing a mechanism for the influence of silicon also use the assumption that volume-diffusion in ζ is the rate-

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determining step. Both assume that the morphology of the ζ -layer is influenced by uptake of Si or SiO_2 in the alloy layers leading to a non-adhering and porous coating. In this case also the reversion to parabolic kinetics at higher temperatures remains unexplained.

Recently Ghoniem and Löhberg^{11,12} proposed a modification of a part of the original phase diagram. According to these authors δ_{1p} and δ_{1k} are distinct phases, separated in the phase diagram by a two-phase $\delta_{1p} + \delta_{1k}$ region. The homogeneity ranges at 450°C are estimated to be δ_{1p} : 8.7–10.0 at. % Fe, δ_{1k} : 12.9–13.4 at. % Fe. The maximum temperature at which ζ is stable according to Ghoniem and Löhberg is 495°C instead of 530°C as stated by Schramm. This was already tentatively proposed by Allen and Mackowiak⁶ and Horstmann.⁸ The maximum temperature of existence of δ_{1p} is 530°C, so that above this temperature only δ_{1k} and Γ remain as stable phases.

Electron microprobe analyses of galvanized specimens of a silicon-free steel show that there is a jump in Fe concentration on crossing the $\delta_{1p} - \delta_{1k}$ boundary from 10 at. % to 12 at. % Fe. Similar measurements performed by Onishi *et al.*¹³ in an investigation of solid state diffusion in the Fe–Zn system shows a similar jump from 9.5 at. % to 13 at. % Fe. These measurements are in reasonable agreement with the phase diagram proposed by Ghoniem and Löhberg, but not with that of Schramm which predicts a gradual change in concentration over the whole δ_1 layer.

Upon the basis of this new phase diagram, the following explanation of the kinetics of the iron–zinc reaction can be proposed. At temperature below 495°C, a closed ζ layer is formed on silicon free steel. The ζ layer has a reasonable plasticity at these temperatures, as follows from the fact that its hardness is only 150 kp.mm⁻² compared with 220 kp.mm⁻² for δ_{1p} and 290 kp.mm⁻² for δ_{1k} according to Ghoniem.¹¹ This means that it is able to keep the underlying δ_{1p} and δ_{1k} layers intact. If it is then assumed that diffusion in the δ_{1k} layer is the rate-determining process, this explains the parabolic kinetics under these circumstances.

At temperatures above 495°C the ζ phase is not formed according to Ghoniem and Löhberg's phase diagram. Upon the direct contact of δ_{1p} with liquid zinc, this layer then shows cracking due to either: (a) intergranular penetration of Zn along the columnar grain boundaries; (b) a Kirkendall effect as Zn diffuses much faster than Fe as shown by Allen and Mackowiak;⁶ (c) volume differences between the δ_{1p} and δ_{1k} layers as suggested by Ghoniem.¹¹ Because of the good adhesion between the δ_{1p} and δ_{1k} layers and the low ductility of the δ_{1k} layer, these cracks will propagate through δ_{1k} . This then causes a direct contact of liquid Zn with either Γ or Fe itself, leading to linear kinetics. This cracking can of course also be a periodic phenomenon, as suggested by Ghoniem,¹¹ leading to a pseudo-linear attack. This is in accordance with the experimental fact that in the layers formed between 495°C and 530°C cracks which are perpendicular to and penetrating to the steel surface have nearly always been found in our experiments.

Above 530°C the δ_{1p} -layer can no longer be formed and because the reason for cracking is then removed, a closed δ_{1k} -layer will again be formed. This means a reversion to parabolic kinetics with a rate which, extrapolated to temperature below 495°C, is indeed expected to coincide with the rate experimentally found at these temperatures, in agreement with the results of Horstmann.^{1,2}

That diffusion in the δ_{1k} -phase is rate-determining in the parabolic region, is

supported by the following experimental observation. In the coatings on a silicon-containing steel no δ_{1k} -layer, or at least a much thinner one, is formed, depending upon the temperature at which the reaction is taking place. This is in agreement with the microstructures obtained, e.g. by Guttman and Niessen.¹⁴ In the layers obtained on a silicon-containing steel we find, in agreement with Guttman and Niessen, large amounts of ζ , which refutes Sedzimir and Szymanke's⁹ assumption that silicon hinders the nucleation of the ζ -phase. Also microprobe analysis shows that within the limits of detectability no silicon is taken up in the coating, thus refuting Bablik's explanation.¹⁰

According to the mechanism proposed here, a hindering of the nucleation of the δ_{1k} -phase, leading to preferred formation of the other much less protective phases, can explain the accelerated attack in the presence of silicon. Another possible explanation is destabilization of δ_{1k} in the presence of silicon. Unfortunately the ternary phase diagram for the system Fe-Zn-Si, as established by Köster,¹⁵ is based upon the Schramm phase diagram, so that no definite conclusion can be reached. The same difficulty applies to the explanation proposed by Guttman and Niessen¹⁴ that the silicon is rejected from the solid Fe-Zn compounds, giving a silicon-rich solution of liquid zinc between the δ - and ζ -layers. On the other hand, our explanation agrees with Guttman and Niessen's that diffusion in a δ -phase is the rate-determining step.

At the present time, further experimental work is in progress in our laboratory. It is intended to establish more definitely the Fe-Zn phase diagram in the concentration range of interest. Also kinetic experiments are being performed both on the reaction of steel with liquid zinc and on solid state diffusion couples in order to determine with greater certainty the nature of the rate-determining process.

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