Reaction between Fe–C Binary Alloys
and Liquid Zinc

by

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Twenty binary Fe-C alloys with a full-annealed structure were immersed in a pure zinc bath at 733 K for 600 s to clarify the reactivity of pearlite structure with liquid zinc. The structure of an alloy layer formed was observed and its thickness and the quantities of iron reacted with zinc were measured. The results obtained are as follows:

(1) The alloy layer formed on a steel containing carbon up to a eutectoid level consists of a gamma layer next to the steel base, followed by a delta 1 layer and a zeta layer, and many ternary carbide particles are found in the alloy layer, increasing in number in propotion as a carbon concentration increases. Many cementite projections are found at an alloy layer／steel base interface, and the zeta layer grows irregularly in a hyper-eutectoid carbon level.

(2) The thickness of the alloy layer and the quantities of iron having reacted with zinc do not depend on the carbon concentration up to the eutectoid level.

(3) Cementite disrupts into the ternary carbide particles, and these particles are placed on the straight or curved line, or are distributed sparsely, depending on the cementite size and its relative position to the alloy layer／steel base interface.

(4) The reactivity of pearlite structure is comparable with that of ferrite structure in 733 K, 600 s immersion.

I. Introduction

A galvanizing is one of the popular methods for preventing the corrosion of steel. During the galvanizing of steel, iron reacts with zinc and forms a so-called alloy layer which consists of several intermetallic compound layers. Moreover iron dissolves into the zinc bath at the alloy layer. This reaction between iron and liquid zinc is affected by alloying elements as well as by such impurities in steel as carbon, silicon and so on. An effect of carbon on this reaction had already been studied with several results. The effect of carbon on the Fe-Zn reaction mainly depends on the form in which carbon in present. In other words, a coarse pearlite structure and a globular cementite structure are more reactive with zinc than a quenched and tempered structure[1]–[4]. The reason has not yet been accounted for why pearlite, a lamellar structure composed of ferrite and cementite, is more reactive than ferrite, although cementite is less reactive than ferrite[5].

Recently Uchiyama et al.[6] reported that a ferrite／cementite interface is more reactive than ferrite, and deduced this high reactivity of pearlite to the formation of more reactive ferrite／cementite interfaces. On the other hand, at 733 K the reactivity of pearlite is comparable with that of ferrite. These authors also

reported that a heat treatment of steel which meant a change of carbon form did not affect the reaction between iron and liquid zinc in a short immersion time at 733 K[7].

On the basis of above-mentioned results, the reactivity of pearlite with liquid zinc was studied by employing full-annealed Fe-C binary alloys.

II. Experimental procedure

Electrolytic iron and a given amount of carbon powder were melted with a high-frequency vacuum induction furnace and cast into rods with 30mm dia. to produce 20 Fe-C alloys with different carbon concentrations. The chemical composition of these alloys is shown in Table 1. Manganese, phosphorus and sulphur of alloys that correspond to a blank has not been analysed, but their levels are comparable with those of others, because all alloys are produced by using same materials and same methods.

Disks, 28 mm dia. x 2 mm thick., were cut from these rods, and a small hole was drilled near the edge of each disk to suspend it for the galvanizing. The cut surfaces were abraded with succesive grades of emery paper and finally polished with diamond paste. These disks were then annealed at 1173 K for 3.6 ks in vacuum below 10^{-5} mmHg, furnace cooled, repolished and degreased with trichloroethylene prior to the galvanizing.

The galvanizing is performed at 733 K for 600 s with a pure zinc bath. The zinc bath was prepared anew for every immersion. The thickness of the alloy layer and the quantities of iron having reacted with zinc were measured, and the structure of the alloy layer was observed.

A matrix structure after a annealing is ferrite + pearlite for steel No. 1 − No. 15 (a hypo-eutectoid steel), pearlite for steel No. 16 (an eutectoid steel), and pearlite + cementite for steel No. 17 − No. 20 (a hyper-eutectoid steel). Representative matrix structures after the galvanizing are shown in Photo. 1. During the galvanizing the sample was tempered and a coarsening of cementite occured.

III. Experimental results

1. Metallographic observation

The representative structures of the alloy layer formed on Fe-C binary alloys are shown in Photo. 2. For hyper-eutectoid steels and the eutectoid steel, the alloy layer consists of a gamma layer next to the steel base, followed by a delta 1 layer, which is divided into two regions, a delta 1k and a delta 1p, and a zeta layer as shown in Photo. 2(b). This alloy layer morphology is similar to that formed on pure iron. In the alloy layer are found many ternary carbide particles increase in number in propotion as a carbon concentration of steel increases. For hyper-eutectoid steels, the alloy layer also consists of the gamma layer, the delta 1 layer and the zeta layer. Besides, many cementite projections are found at an alloy layer／steel base interface and the zeta layer partially has an outburst structure, as shown in Photo. 2(b).

Ternary carbide particles found in the alloy layer have an appearance changing from place to place. Sometimes they are small and are placed on a straight or slightly curved line, and sometimes they

Table 1　Chemical composition of Fe-C alloys (mass %).

Steel No.	C	Si	Mn	P	S
1	0.019	<0.01	<0.01	0.003	0.005
2	0.210	<0.01			
3	0.218	<0.01	<0.01	0.004	0.005
4	0.264	<0.01			
5	0.307	<0.01			
6	0.354	<0.01			
7	0.412	<0.01			
8	0.440	<0.01			
9	0.484	<0.01			
10	0.534	<0.01			
11	0.537	<0.01	<0.01	0.003	0.005
12	0.611	<0.01			
13	0.648	<0.01			
14	0.722	<0.01	<0.01	0.003	0.004
15	0.730	<0.01			
16	0.851	<0.01			
17	1.024	<0.01	<0.01	0.006	0.005
18	1.034	<0.01	<0.01	0.004	0.005
19	1.235	<0.01	<0.01	0.005	0.005
20	1.341	<0.01	<0.01	0.006	0.004
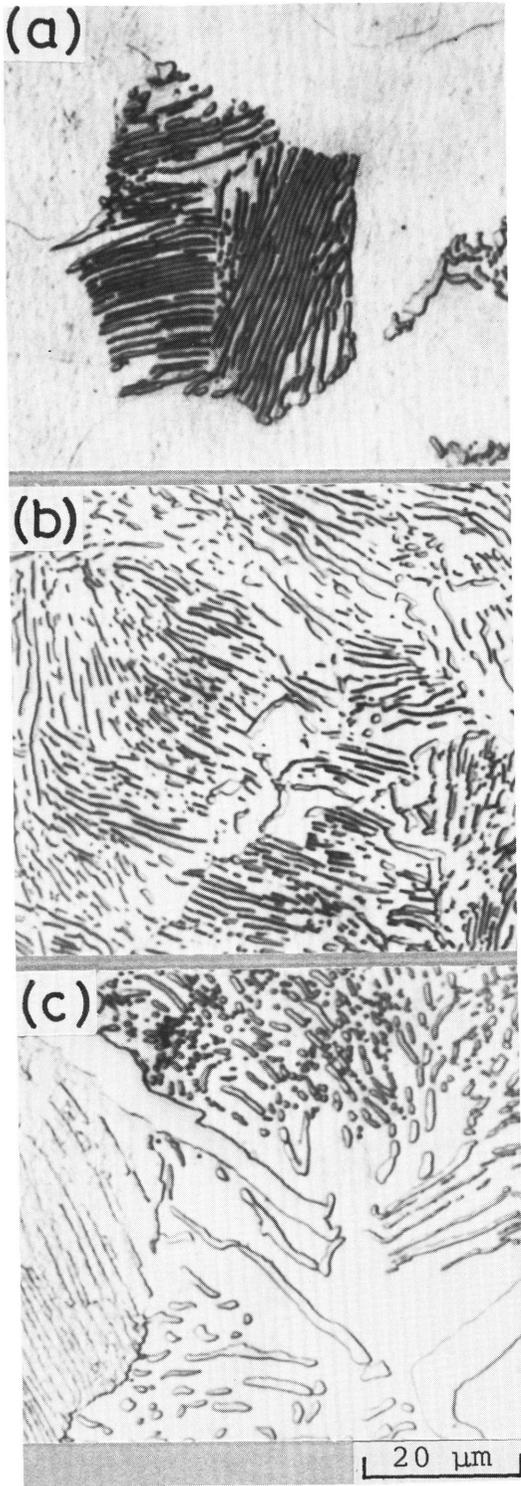
Photo. 1 Matrix structures of (a) Fe-0.218 %C, (b) Fe-0.851%C and (c) Fe-1.341%C alloys galvanized at 733 K for 600 s. (Nital etch)
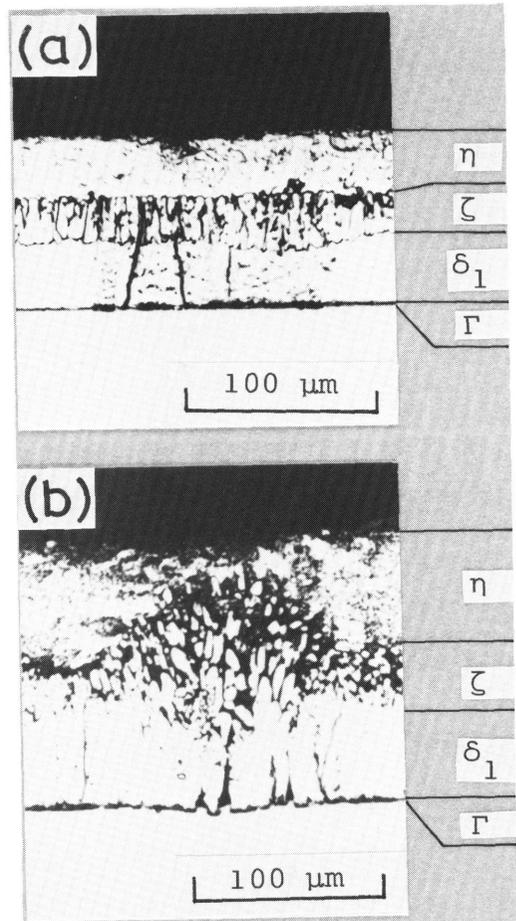
Photo. 2 Structures of the alloy layer formed on (a) Fe-0.440%C alloy and (b) Fe-1.341%C alloy. Galvanizing is performed at 733 K for 600 s. (Nital etch)

are great and are distributed sparsely. These appearances are shown in Photo. 3.

2. Alloy layer thickness
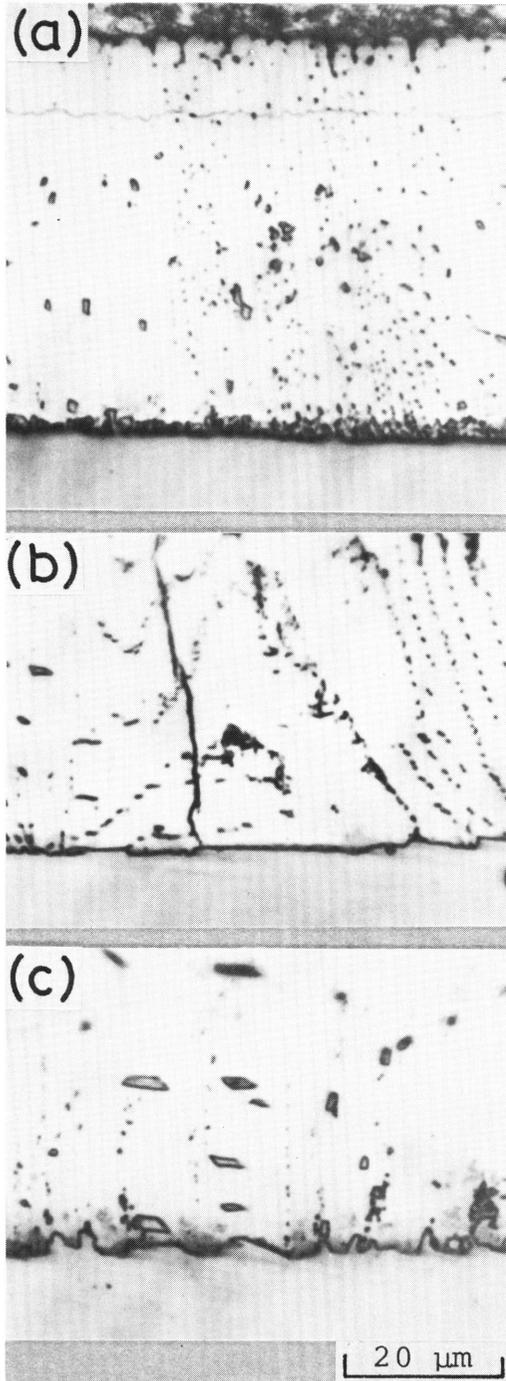
Photo. 3 Several appearances of cementite disruption.
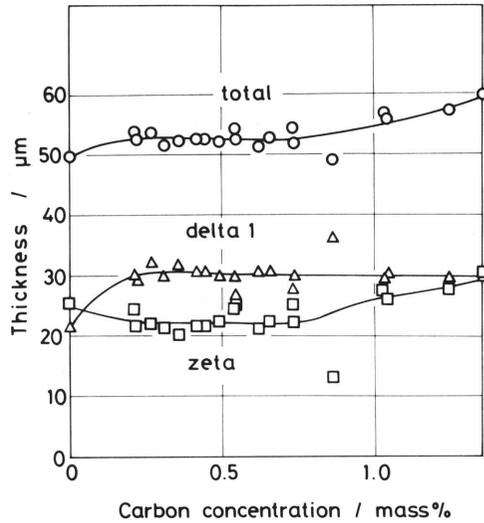
Fig. 1 Relation between the thickness of the alloy layer formed on Fe-C binary alloys immersed in the pure zinc bath at 733 K for 600 s (μm) and the carbon concentration (mass %).
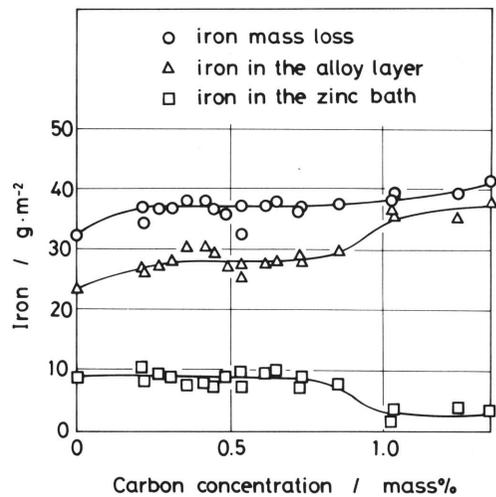
Fig. 2 Relation between the quantities of iron having reacted with zinc of Fe-C binary alloys immersed in the pure zinc bath at 733 K for 600 s (g $\cdot$ m^{-2}) and the carbon concentration (mass%).

The relation between the thickness of the alloy layer formed on Fe-C binary alloys and the carbon concentration is shown in Fig. 1. The total thickness of the alloy layer shows a constant thickness of ca. 50 μm in the carbon concentration range up to ca. 0.7 mass%, and increases in the carbon concestration range of above 1.0 mass%. The thickness of the zeta layer has a similar dependence on the carbon concentration. On the other hand, the thickness of the delta 1 layer increases as the carbon concentration increases to 0.2 mass%, then has a constant thickness of ca. 30μm up to 1.341 mass%C.

　3. Iron having reacted with zinc

　　The relation between the quantities of iron having reacted with zinc of Fe-C binary alloys and the carbon concentration is shown in Fig. 2. Iron mass loss and the quantity of iron remaining in the alloy layer increase slightly as the carbon concentration increases to 0.2 mass%, then have a constant values of ca. 37 and ca. 27 g·m^{-2} respectively in the carbon concentration of 0.2 − 0.7 mass%, and increase above 1.0 mass% C. While the quantity of iron dissolved into the zinc bath has a constant value of ca. 9 g·m^{-2} up to a eutectoid carbon level, and decreases above 1.0 mass% C.

IV. Discussion

　　The results obtained in this study, Photo. 2, Fig. 1 and Fig. 2 show that carbon less than the eutectoid level does not affect the Fe-Zn reaction under the galvanizing condition employed in this study. This means in turn that pearlite has a comparable reactivity with ferrite. This result is consistent with the result obtained in the early paper[6].

　　Horstmann[4] has studied the Fe-Zn reaction in the range of 3.6 ks − 18 ks and 703 K − 723 K using a steel bearing 0.88 mass%C. According to his report, a coarse pearlite structure and a grobular cementite structure were more reactive than a quenched and tempered structure. Bablik[1] reported a similar result on a steel bearing 0.78 mass% C. These results do not coincide with our results. Considering a steel composition, the steel used by Bablik contained 0.14 mass% Si, 0.39 mass% Mn, 0.017 mass% P, and 0.024 mass% S in addition to 0.78 mass% C. This level of silicon affects the Fe-Zn reaction strongly; this effect of silicon is called "Sandelin effect"[11]. Besides, carbon and silicon in steel play a complementary role to the Fe-Zn reaction[12]−[14]. So the result obtained by Bablik does not show the carbon effect only. The steel used by Horstmann contained 0.01 mass% Si, 0.16 mass% Mn, 0.015 mass% P and 0.007 mass% S in addition to 0.88 mass% C. Phosphorus and silicon have a complementary effect on the Fe-Zn reaction[15], but the level of phosphorus and silicon of the steel used by Horstmann seems to have been too low to affect on the Fe-Zn reaction. According to Sebisty et al.[16], 0.16 mass% Mn has also no influence on this reaction. So the steel used by Horstmann seems to be essentially a binary alloy as like as steels employed in this study. In other words, the steel composition does not account for the difference between Horstmann's result and ours. As mentioned in section II. Experimental procedure, steel is tempered during the galvanizing and the matrix structure changes. Because of a long immersion time used by Horstmann, a tempering effect may be sufficient to account for the difference.

　　According to Price's report[5], the alloy layer structure formed on the pearlite structure was different from that formed on the ferrite structure using a steel of unknown composition. They further reported that the effect of heat treatment on the Fe-Zn reaction was neglisible at 723 K, 3.6 ks, namely iron mass loss for a quenched structure and a quenched and tempered structure is comparable with that for the pearlite structure. This result coincides with that of our former experiments[6], but is inconsistent with that obtained by Horstmann[4]. The iron mass loss value for the pearlite structure in 723 K, 3.6 ks immersion is comparable with our corresponding value computed in accordance with a parabolic time law. Horstmann's value is 4 times greater than Price's and ours.

　　The cementite projection at the alloy layer／steel base interface as shown in Photo. 2(b) shows that

cementite is less reactive than ferrite. The cementite projection reacts with zinc at the top and disrupts into ternary carbide particles in the alloy layer. The reason of this cementite disruption seems to be the displacement and shearing caused by a growth of the alloy layer and the difference in adhesion of cementite between the alloy layer and the steel base.

The appearance of ternary carbide particles is varied as shown in Photo. 3. This change in appearance may be due to a size of cementite and its relative position to the alloy layer/steel base interface. These are illustrated in Fig. 3. A fine cementite disrupts more easily than a large one (Fig. 3(a)). A cementite perpendicular to the alloy layer/steel base interface disrupts into the ternary carbide particles placed on a straight line (Fig. 3(a)) and that made an angle $\leqq 90°$ to this interface disrupts into the ternary carbide particles placed on a curved line (Fig. 3(b)). A cementite parallel to the interface offers a slightly strong resistance against the disrupture (Fig. 3(c)).
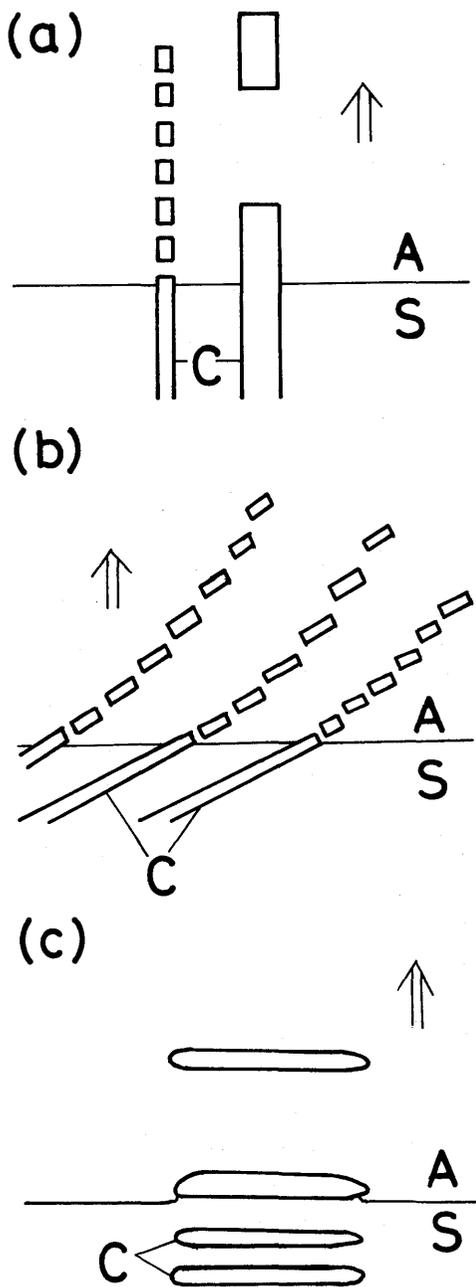
V. Conclusion

The effect of pearlite on the Fe-Zn reaction was studied at 733 K and 600 s employing 20 full-annealed Fe-C binary alloys.

The structure of the alloy layer and the quantities of iron reacted having with zinc were discussed. The results obtained are as follows:

(1) The alloy layer formed on the steel containing carbon up to the eutectoid level consists of the gamma layer next to the steel base, followed by the delta 1 layer and the zeta layer, and many ternary carbide particles are found in the alloy layer, increasing in number in propotion as the carbon concentration increases. Many cementite projections are found at the alloy layer/steel base interface, and the zeta layer grows irregularly in a hyper-eutectoid carbon level.

(2) The thickness of the alloy layer and the quantities of iron reacted with zinc do not depend on the carbon concentration up to the eutectoid level.

(3) Cementite disrupts into the ternary carbide particles, and these particles are placed on the straight or curved line, or are distributed sparsely, depending on the cementite size and its relative position to the alloy layer/steel base interface.

(4) The reactivity of pearlite structure is comparable with that of ferrite structure in 733 K, 600 s immersion.

Fig. 3   Scheme of the cementite disruption.
A : alloy layer, S : steel base , C : cementite

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