Effects of Surface Microstructure and Chemical Compositions of Steels

on Formation of Fe-Zn Compounds during Continuous Galvanizing*

By Akihiko NISHIMOTO,** Jun-ichi INAGAKI*** and Kazuhide NAKAOKA***

Synopsis
The effects of surface microstructure and chemical compositions on char-
acteristics of Fe-Zn compounds which formed on continuously galvanized
steel sheets have been investigated by using ultra low carbon and low carbon
steels.
From SEM observation, morphology of Fe-Zn compounds formed at interface between steel and plating layer were classified into three types; outburst structure, fine granular structure, and pillar-like structure.
The amount of outburst structure increases with decreasing solute carbon content in steels. Phosphorus inhibited the formation of outburst structure when solute carbon was combined with a carbide forming element such as Nb or Ti.
A comparison between distribution of Fe-Zn compounds and correspond-ing steel surface indicated that the outburst structure formed preferentially at grain boundaries exposed on the steel surface, whereas fine granular structure formed mainly at the interior of surface grains.

1. Introduction

Recently, applications of continuous galvanizing sheets for the automotive parts have led to the demands for improvement of their mechanical properties. To improve the mechanical properties, alloying elements are added, and annealing conditions at CGL are modified. Therefore, the effects of surface micro-structure and chemical compositions of steels on forma-tion of Fe-Zn compounds have become substantially important.
The effects of steel chemistry on the interac-tion between iron and zinc have been studied by many researchers.)-13) In continuous galvanizing lines (CGL), it is considered that aluminum in molten zinc affects the interaction.4-13) Previous studies concerning the effects of steel chemistry in aluminum bearing zinc bath have shown that Ti accelerated the growth rate of Fe-Zn compounds, while Si and P retarded it.

In the present study, the effects of surface micro-structure (especially, grain boundaries exposed on steel surface) and chemical compositions of steels on the formation of Fe-Zn compounds in continuously

galvanized steel sheets were investigated.

II. Experimental Procedure

1. Chemical Compositions and Processing

The chemical compositions of steels utilized in the

present study are listed in Table 1. The steels were prepared with 50 kg vacuum melting furnace and hot-rolled at laboratory. In order to examine the effect of carbon content on the formation of Fe-Zn

compounds, ultra low carbon steel (Steel 1) were decarburized further in a wet 20%H2 N2 atmo-

sphere; the hot-rolled plates were normalized, decar-burized, and homogenized as shown in Fig. 1. These decarburized plates and the other as-hot-rolled plates

(Steels 2 to 7) were pickled, cold rolled from 3.2 to 0.6 mm, degreased by wiping with an organic solvent. They were spot welded to a cold strip coil, and sub-sequently galvanized at Keihin No. 2 CGL. Details of this procedure are described elsewhere.l3) The galvanizing conditions are shown in Table 2.

2. Observation of Fe-Zn Compounds

Morphology of Fe-Zn compounds which formed on each galvanized specimen was investigated using a scanning electron microscope (SEM). Cross sec-tions of the plating layers were observed by back-scattered electron imaging without etching. After removing vj-phase (Zn), the distribution of Fe-Zn compounds in the parallel-to-the-surface section was
observed in secondary electron image.

Table 1. Chemical compositions of steel investigated.

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Fukuyama Research Laboratories, Technical Research Center, Nippon Kokan K.K., Kokan-cho, Fukuyama 721.
Technical Research Center, Nippon Kokan K.K., Minamiwatarida-cho, Kawasaki-ku, Kawasaki 210.

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3. Identjication of Fe-Zn Compounds
Electron back-scattering Mossbauer spectroscopy was performed to identify the Fe-Zn compounds observed in this study. Mossbauer spectra were obtained with ELSCINT's AME-50 Type constant acceleration apparatus using a source of 50 mCi 57Co. These spectra were then computer fitted and decom-posed into several partial-spectra.

III. Experimental Results
1. Effect of Carbon

Photograph 1 shows the plating layers of galvanized steels with different carbon content obtained by the above mentioned decarburization treatment of Steel

1, and that of Steel 2 for comparison, Total carbon content obtained by chemical analyses and solute car-bon content measured by internal friction method after galvanizing are listed in Table 3.
Fe-Zn compounds shown in Photo. 1 can be classi-fied into two types based on their morphology. One is an outburst structure (Type-1), and the other is a fine granular structure formed near the interface (Type-2).
Fe-Zn compounds formed on the low carbon steel (a) mainly consists of Type-2. Those formed on the ultra low carbon and the further decarburized steels

(b) (e), on the other hand, are composed of both Type-1 and -2. Increasing carbon content in steel causes a decrease in the fraction of Type-1. These observations indicate that carbon in steel inhibits the formation of outburst structure.

Effect of carbon on the galvannealing behavior has also been investigated. The galvanized speci-mens were reheated at 450 °C for 10 to 120 sec in an infrared furnace. After this alloying treatment, Vickers hardness was measured on the cross sections

of alloy layers by using a micro-micro Vickers hard-ness tester with 2.9 g loading.
The relationships between alloying period and average hardness of alloy layers are shown in Fig. 2. It is obvious that the hardness of alloy layers increases with an increase in alloying period; in other words, alloy layers harden with the progress of alloying treat-ment. In addition, as the carbon content of steels decreases, the rate of hardening increases. Thus carbon in steel also affects the growth characteristics of Fe-Zn compounds.

2. Effects of Other Alloying Elements
Galvanized specimens of Steels 3 to 7 were dipped into a dilute hydrochloric acid solution with an in-hibitor to remove v -phase, and distribution and morphology of Fe-Zn compounds that remained at interface were observed by SEM.
Photograph 2 shows the scanning electron micro-graphs of interface layer of each sample. Photograph

Fig. 1. Sc hematic diagram of experimental procedure.

Table 2. Galvanizing conditions.

Photo. 1.

Table

Scanning electron micrographs showing the effects
of carbon content on the formation of Fe-Zn com-pounds.
(Carbon content of each specimen is shown in Table
3. Typical morphology of Fe-Zn compounds will be shown in Photo. 4.)

3. Total- and solute-carbon contents of galva-nized steels (Steels 1 and 2).

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2 (a) indicates that Fe-Zn compounds formed on Nb-B-containing ultra low carbon steel (Steel 3) mainly consists of Type-1 (outburst structure) with a small fraction of Type-2 (fine granular structure). This suggests that the addition of Nb reduces the inhibi-tion effect of solute carbon, through precipitation of niobium carbides. The same tendency is shown in a Ti-containing low carbon steel whose carbon content is 110 ppm (Steel 7, Photo. 2(b)). In this case, carbon is considered to be combined with Ti in the steel. On the other hand, in the case of Nb-B-P-containing ultra low carbon steel (Steel 4, Photo. 2(c)), the Fe-Zn compound only consists of Type-2.

This suggests that phosphorus in steel inhibits the formation of outburst structure in the similar way to carbon (Steel 6; Photo. 2(d)). Photograph 2(e) indicates that the addition of Si leads to formation of

the pillar-like structure in which pillar-like crystals are coarsely distributed in fine granular structure. This type of structure (Type-3) was also observed in Si-containing low carbon steel, as has been reported by the present authors.l3~

3. Effects of Surface Microstructure

After observing Fe-Zn compounds, the specimens are dipped into a dilute hydrochloric acid solution without inhibitor to reveal the steel surface, and nital etching was performed for microstructural examination.

Relationships between the morphology of Fe-Zn compounds and the microstructure of Steels 3 and 4 below the interface are shown in Photo. 3. In these

photographs, good correspondences are observed. It is obvious, from Photos. 3(a) and (b), that the outburst structure forms preferentially at grain boundaries exposed on the surface and, on the other hand, a fine granular structure is observed only on the interior of surface grains. The same tendency was observed in Steels 1 and 7.

Photographs 3(c) and (d) show that, when phos-

phorus is added to steel, formation of the outburst structure at grain boundaries is entirely inhibited. This tendency was also observed in Steels 2 and 6.

4. Identification of Observed Fe-Zn Compounds

As mentioned above, morphology of Fe-Zn com-

pounds which formed on the interfaces were classified into three types (see Photo. 4).

Fig. 2. Relationships between alloying period and average hardness (Hv) of alloy layers. Symbols a to d correspond to those in Photo. 1 and Table 3.

Photo. 2.
Scanning electron micrographs showing
the effects of alloying elements on for-mation of Fe-Zn compounds, observed on the Zn-removed surface of specimen.

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Electron back-scattering Mossbauer spectroscopy was performed to identify these Fe-Zn compounds. Scanning electron micrographs of specimens are shown in Fig. 3 ((a) for a fine granular structure (Type-2) and (b) for a fine pillar-like structure seen at the surface of outburst structure (Type-1)) with the corresponding Mossbauer spectra. The spectra were

computer fitted and then decomposed into partial spectra. The result for Type-3 is not shown here, because there is not considerable difference between

the Mossbauer spectra of Type-1 and -3.
In each spectrum, a singlet and a doublet are observed. The relevant parameteres are listed in Table 4 with those reported by Graham et a1.14 and by Dunlop et a1.15~ According to Graham et al., the spectrum of a-phase was a singlet and that of o1-phase was a broadened asymmetric doublet. Dunlop et al., on the other hand, reported that the spectrum of c-phase was compatible with a close quadropole split doublet whose isomer shift was 0.43±0.01 mm/ sec. The isomer shift of the singlet obtained in the present study is in good agreement with Dunlop's result. There are some deviations in the isomer shifts from that reported by Graham. By considering the relative location of peaks, however, it can be speculated that the singlet and the doublet represent c-phase and o1-phase, respectively. A com-parison of each peak heights shows that the Fe-Zn compounds, shown in Fig. 3(a), are mainly composed of o1-phase, while those in Fig. 3(b) are mainly com-posed of c-phase.
It should be noted that the detectable depth in this method is limited to only a few thousand Ang-stromes below the surface. However, taking into account a previous study,16~ the outburst structure and the pillar-like structure which were observed in the Si-containing steel are assumed to be composed of aluminum bearing c-phase with an occluded alumi-num bearing o1-phase at the Fe-Zn interface. The
fine granular structure may be aluminum bearing C1-phase.

Photo. 3. Scanning electron micrographs showing (left) and surface microstructure (right).

the relationships between
Each of arrow and symbol

distribution of Fe-Zn compounds
indicates corresponding locations.

Photo. 4. Scanning electron micrographs
phology of Fe-Zn compounds.

showing typical mor-

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1 V. Discussion

1. Formation and Growth o f Outburst Structure

The reaction mechanisms in Fe-Zn-AI system were discussed by several investigators. Urednicek and Kirkaldy16~ proposed a concept of diffusion path on an isothermal section of the ternary diagram. In the above paper, diffusion paths were mapped in the iso-

therm, and the corresponding diffusion profiles were explained on the empirical basis that the initial phase nucleated at the solid-liquid interface was Fe2A15 phase. Yamaguchi and Hisamatsu17~ classified the structures of Fe-Zn compounds observed in galvanized sheets into twelve types, and discussed their formation and growth mechanisms by the above mentioned concept. In both studies, the nucleation of Fe-Zn compound was related to the drop of aluminum concentration near the liquid-solid interface.
In the present study, it was revealed that the forma-tion of outburst structure took place at grain bounda-ries on the steel surface. This suggests that the drop of aluminum concentration that leads to the nuclea-

tion of Fe-Zn compound occurs initially at the grain boundaries. Therefore, the mechanism for the for-mation of the outburst structure can be described as follows.

When steel strip is immersed into aluminum bearing zinc bath, Fe-Al compound will immediately be formed at a liquid-solid interface because iron has greater affinity to aluminum than zinc.16) In this stage, the reaction rate seems to be greater at grain boundary where activity is higher than grain interior. Consequently, aluminum concentration in the liquid will drop more rapidly in the neighborhood of grain boundaries than on the surface grain interior (Fig. 4(a)). As mentioned above, this drop of aluminum concentration leads to the nucleation of Fe-Zn

compound (o1-phase), and the nucleus will rapidly penetrate through the thin Fe-Al compound16) (Fig.

Fig. 3. Mossbauer spectrum obtained from Fe-Zn compounds.

Table 4. Mossbauer parameters.

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4(b)).
In the cooling stage of strip, the reaction,

o1+,

is suggested to occur,18 and c-phase will grow rapidly in the thickness at grain boundaries. Since the reaction rate at grain interior is low, a transition of alloy phases from Fe-Al compounds to Fe-Zn com-pounds is considered to take place at a later stage of reaction (Fig. 4(c)). Consequently, the formation of outburst structure does not occur at the center of

surface grain interior, and only sidewise growth of C-phase (outburst structure) is observed at the latest stage (Fig. 4(d)).

2. Effects of Chemical Compositions of Steel
1. Effect of Carbon
The results shown in Photo. 1 clearly indicate that carbon in steel inhibites the formation of outburst structure. On the other hand, Photo. 2 shows that
addition of carbide forming elements such as Nb and
Ti reduces the inhibition effect. These results suggest that solute carbon in steel inhibits the formation of
outburst structure. Generally, solute carbon in steel
tends to segregate at grain boundaries in cooling after a heat treatment.19) The inhibition effect of carbon appears to be attributable to the segregation of solute carbon at grain boundaries, which reduces the total free energy at grain boundaries and con-sequently inhibits the formation of outburst structure

(Fig. 5).
2. Effects of Carbide Forming Elements Such as Nb and Ti

The experimental results and the above discussion lead to the assumption that the effects of carbide forming elements are associated with the reduction of solute carbon content. Abe and Kanbara,12~ however, reported that solute Ti in steel enhanced the reactivity between Fe and Zn. In the present study, effect of solute Ti was not investigated. Differ-ent mechanisms are required to account for the influence of solute Ti.

Fig. 4. Schematic illustration showing a formation model of Fe-Zn compounds.

Fig. 5. Schematic illustration showing an inhibition mech-anism of outburst structure by carbon.

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3. Effect of Phosphorus

The Fe-Zn compound observed in Steel 4 (Nb-B-P-containing ultra low carbon steel) had only fine granular structure (C1-phase) and the formation of outburst structure at surface grain boundaries, as observed in Steel 3 (Nb-B-containing ultra low carbon steel), was completely inhibited (Photo. 2(c)). This inhibition effect can be explained by the fact that phosphorus has a tendency to segregate to grain boundaries, similarly to carbon.
Abiko et al.2U-22) reported that the amount of segregated phosphorus at grain boundaries decreases with increasing carbon content in steel. Because of a very low solute carbon content, phosphorus in Steel 4 is considered to occupy a large number of grain boundary site and inhibit the formation of outburst structure by lowering the activity at grain boundaries.
4. Effect of Silicon

Photograph 2 (e) shows that a pillar-like structure (Type-3) was formed on Si-containing ultra low carbon steel. The same tendency was observed in a previous study of Si-containing low carbon steel.13> As has been discussed in the previous paper, it can be concluded that these pillar-like crystals are nucleated on unreduced Si-bearing oxides which were formed during CGL heat cycle and distributed randomly on the strip surface just before galvanizing,23>

V. Conclusions

The effects of microstructure and chemical com-

positions of steel on the formation of Fe-Zn com-pounds were investigated in ultra low carbon and low carbon steels. The results are summarized as follows;

(1) Fe-Zn compounds formed on steels can be classified into three types based on their morphology; outburst structure (Type-1), fine granular structure (Type-2), and pillar-like structure (Type-3). By electron back-scattering Mossbauer spectroscopy, it was confirmed that they were mainly composed of c-phase (Type-1 and -3), and o1-phase (Type-2).
(2) Solute carbon in steel inhibited the formation and growth of outburst structure.

(3) Carbide forming element such as Nb and Ti reduced the above inhibition effect.

(4) Phosphorus in steel also inhibited the forma-tion of outburst structure when solute carbon was

combined with a carbide forming element such as Nb or Ti.

(5) Pillar-like structure (Type-3) was observed

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on Si-containing ultra low carbon steel.
(6) Good correspondence was observed between distribution of Fe-Zn compounds and surface micro-structure. Outburst structure forms preferentially at grain boundaries exposed on the steel surface.

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REFERENCES

J. Machowiak and N. R. Short: Int'l. Metals Rev., 24 (1979), 1.
D. Horstman: Proc. 4th Intern. Conf. on Hot Dip Gal-vanizing, Zinc Development Assoc., London, (1956), 29.
T. Gladman, B. Holmes and F. B. Pickering : JISI, 211 (1973), 765.
W. Koster and T. Godecke: INTERGALVA '70, Zinc Development Assoc., London, (1970), 128.
N. Dreulle, P. Dreulle and J. C. Vacher : Metall, 34 (1980), 834.
T. Ito, Y. Hirose, F. Kumon and M. Hasegawa : .Nisshin Steel Tech. Rep., 37 (1977), 13.
M. Nakayama, T. Kanemaru and K. Kishida : Tetsu-to-Hagane, 66 (1980), 51015.
M. Abe, T. Watanabe and T. Adaniya : Tetsu-to-Hagane, 67 (1981), 5322.
T. Fukuzuka, M. Urai and K. Wakayama : R & D Kobe Steel Engineering Reports, 30 (1980), No. 1, 77.
J. Inagaki, A. Nishimoto and K. Nakaoka : Tetsu-to-Hagane, 67 (1981), 5997; Trans. ISIJ, 22 (1982), B130.
M. Abe and S. Kanbara : Tetsu-to-Hagane, 68 (1982), 51109; Trans. ISIJ, 23 (1983), B60.
M. Abe and S. Kanbara : Tetsu-to-Hagane, 69 (1983), 51061.
A. Nishimoto, J. Inagaki and K. Nakaoka : Tetsu-to-Hagane, 68 (1982), 1404.
M.J. Graham, P. E. Beaubien and G. I. Sproule : J. Mat. Sci. ,15 (1980), 626.
J. B. Dunlop, J. M. Williams and G. Longworth: J. Phys, F, Metal Phys, 8 (1978), 2115.
M. Urednicek and J. S. Kirkaldy: Z. Metallic., 64 (1973), 899.
H. Yamaguchi and Y. Hisamatsu : Trans. ISIJ, 19 (1979), 649.
M. Ohbu, K. Asakawa and K. Tano : Tetsu-to-Hagane, 60 (1974), 705.
E. Sudou: Stretcher Strain, Japan Inst. of Metals, Sendai, (1970), 86.
K. Abiko and H. Kimura : Script. Met., 15 (1981), 1139. S. Suzuki, M. Obata, K. Abiko and H. Kimura: Script. Met., 17 (1983), 1325.
S. Suzuki, M. Obata, K. Abiko and H. Kimura : Trans. ISIJ, 25 (1985), 62.
Y. Tsuchiya and S. Terasaka: Tetsu-to-Hagane, 68 (1982), 5376.

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