Effect of Nickel Addition in Hot Dip Galvanizing of Mini-mill Steels Containing Silicon

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실리콘을 함유한 미니밀 소재의 용융아연도금성에 미치는 니켈첨가의 영향

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Abstract

In this study the effect of nickel addition on the coating weight of mini-mill steels containing silicon has been studied. It is shown that the pure zinc accelerated growth of the alloy layers occurred by a rapid growth of the zeta phase at 0.06%Si. The addition of 0.06%Ni to a pure zinc bath was found to be very effective in reducing the coating weight and promoting preferential development of the delta phase. The coating obtained by immersion in the Zn-Ni bath shows the presence of a nickel-rich region between the zeta phase and the eta phase. It is suggested that nickel prevents the rapid growth of the zeta phase due to the formation of the Zn-Ni-Fe ternary compound, which may act as a barrier to inward diffusion of zinc or iron at the zeta-eta boundary.

1. INTRODUCTION

For the past decade, the galvanizing of steels containing silicon has been perhaps the most active area in galvanizing research. Understanding the coating development on these steels is becoming more and more important. The trend to a greater use of silicon in steels arises primarily from (a) the introduction of mini-mill steels containing inevitable silicon and (b) the increasing demand by architects for weldable high strength structural steels. Steels containing certain levels of silicon are "reactive" towards zinc in that there is a rapid growth of the zinc-iron alloy lay-

ers on the steel substrate, producing a coating of excessive thickness. Such coatings are brittle, adhere poorly to the steels base and hence can be easily damaged during handling. Consequently, the galvanizing industry is faced with the need to seek solutions that overcome difficulties associated with the batch hot dip galvanizing of these steels. Although an understanding of the mechanism by which silicon affects the galvanizing process is not yet available, it is generally known that the rapid growth of the alloy layer between the steel substrate and outer zinc coating occurs at two concentrations of silicon. The concentrations are $\sim 0.06\%$ (known as Sandelin range[1]-[3]) and above $\sim 0.3\%$ [4]. In order to overcome the detrimental effects of silicon on the growth of Zn-Fe intermetallic compounds, a number of approaches have been explored experimentally. These are known variously as Technigalva[5]-[6], Polygalva[7] and high-temperature galvanizing process.[8] Of these approaches, only the Zn-Ni Technigalva system fulfilled initial commercial promise in batch galvanizing. In this process the addition of a nominal 0.1%Ni to the zinc by means of a Zn-2%Ni master alloy was found to partially offset the detrimental effect of silicon during the galvanizing process.

However, the role of nickel addition on the growth rate of alloys formed in this process, particularly in relation to mini-mill steels containing silicon, still has not been fully elucidated. Therefore, it seems appropriate in the present study to investigate the effect of the addition of nickel on the coating weight for mini-mill steels containing silicon in the batch galvanizing as a function of nickel content in zinc bath, and to clarify the role of nickel on Fe-Zn alloying reaction.

2. EXPERIMENTAL PROCEDURE

Four mini-mill steels, with silicon contents of 0.02, 0.06, 0.15 and 0.24%, were used in the study. Chemical compositions of the steels are shown in Table 1. Specimens 50mm(w) × 100mm(l) ×2mm(t) were pickled in 15% hydrochloric acid at 20℃ for 15 min, then washed and fluxed in a 10% aqueous solution of zinc ammonium chloride at 45℃.

The batch galvanizing of the specimens was carried out in 40Kg of liquid zinc contained in carbon crucibles. After immersion times of 1, 3, 5 and 10 minutes, the samples were slowly brought out of the bath through a clean zinc surface and tapped and shaken to help remove excess zinc. Five dipping tests were carried out at bath nickel levels of, 0%, 0.03%, 0.06% and 0.10%. The bath temperature during the test ranged from 440℃ to 480℃.

Galvanized samples were dissolved into a 10% HCl solution containing 0.3% corrosion inhibitor

Table 1. Chemical compositions of mini-mill steel sheet (in wt.%)

Specimen	Si	C	Mn	P	Cu	Ni	Cr
A	0.02	0.04	0.34	0.01	0.10	0.04	0.02
B	0.06	0.06	0.32	0.01	0.14	0.06	0.04
C	0.15	0.05	0.35	0.02	0.12	0.06	0.06
D	0.24	0.05	0.38	0.02	0.11	0.05	0.05

$((CH_2)_6N_4)$, subject to chemical analysis of zinc coating and to measure coating weight. The cross sections of the specimens were examined using a Scanning Electron Microscopy (SEM). The distribution of the alloy elements in the depth directions of the coating layer was analyzed with a Glow Discharge Spectrometer (GDS).

3. RESULTS

The effect of the addition of nickel on the coating weight is shown in Fig. 1 as a function of silicon content for an immersion time of 1 min. The increase of coating weight during hot-dip galvanizing of steel is not linear with silicon content: a high rate occurred on steel containing 0.06% Si. It is shown that pure zinc accelerated growth of the alloy layers occurred by rapid growth of the zeta phase at 0.06%Si. This result is quite consistent with previous observations[1]-[3]. Th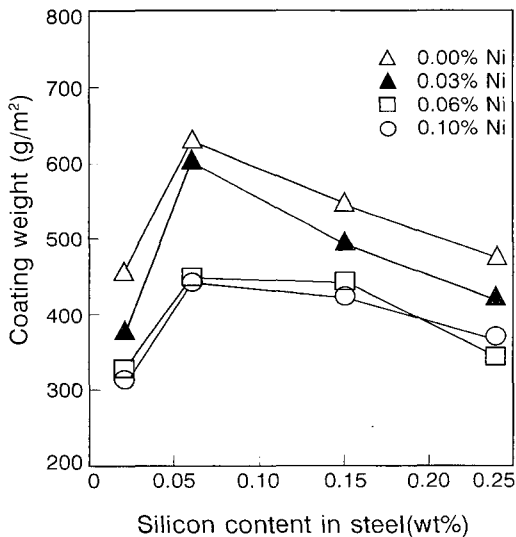e presence the 0.06%Ni resulted in considerable reductions to the coating weight. The addition of more than 0.06% to a pure Zn bath, however, was found to be ineffective in reducing the coating weight.

The increase in coating weight occurred by increases in thickness of both the zeta and delta phase layers except the anomalous behavior of the 0.06%Si steel. This can easily be seen in the cross section of an alloy layer of 0.06%Si steel. Fig. 2(a) shows the cross section of an alloy layer obtained from the pure Zn bath. Rapid development of the alloy layer on the 0.06%Si steel was due entirely to the growth of the zeta phase. In the presence of 0.06%Ni(Fig. 2(b)), the nickel evidently promoted the preferential development

Fig. 1. Effect of nickel content in Zn bath on coating weight as a function of silicon content in steel (460℃, 1min)
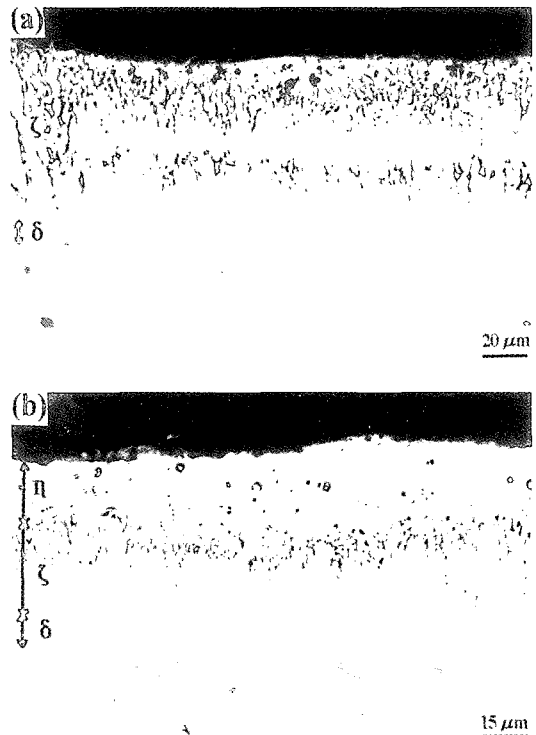

Fig. 2. Cross section of zinc coating for 0.06%Si steel obtained from different Zn baths : (a) pure Zn and (b) Zn-0.06%Ni

of the delta phase and suppressed the development of the zeta phase. As the delta phase grows faster than the zeta phase layer during the galvanizing process, a reduction in coating weight would be expected.

The influence of the immersion time on the coating weights of three different silicon steels galvanized in pure Zn and in Zn-0.06%Ni is shown in Figs. 3 and 4, respectively. It is evident from Fig. 3 that, during galvanizing in pure Zn, the increase in coating weight was much higher for 0.06%Si steel than for 0.02%Si and 0.24%Si. In the pure Zn bath, the coating growth of 0.06% Si steel is linear with the immersion time, indicating a reaction controlled mechanism. In the Zn-0.06%Ni bath, however, growth rates were considerably reduced and parabolic with the immersion time (Fig. 4). The total thickness of the reaction layers grew parabolically with time, indicating a diffusion controlled mechanism. Therefore, the growth kinetics of 0.06%Si steel was
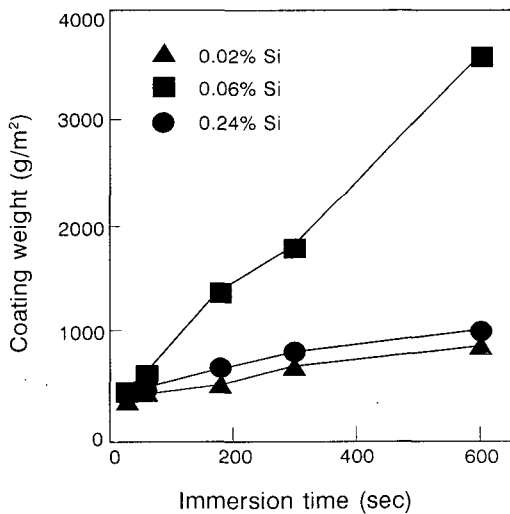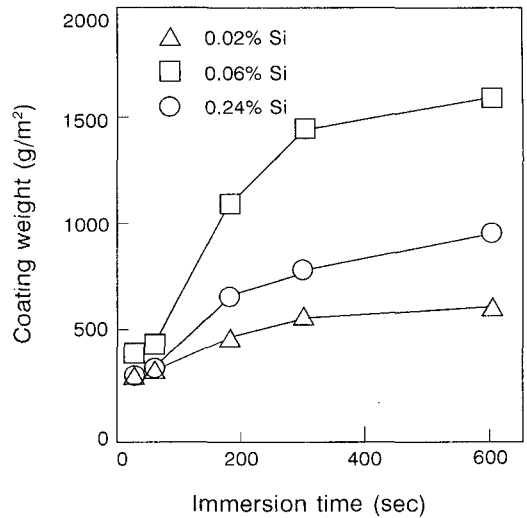

Fig. 4. Relationship between immersion time and coating weight for galvanizing on three different silicon steels from Zn-0.06%Ni bath

changed from a linear controlled to a diffusion controlled mechanism by the addition of nickel.

Fig. 5 shows the coating weight of 0.06%Si steel obtained from a Zn-0.06%Ni bath as a

Fig. 3. Relationship between immersion time and coating weight for galvanizing on three different silicon steels from pure Zn bath
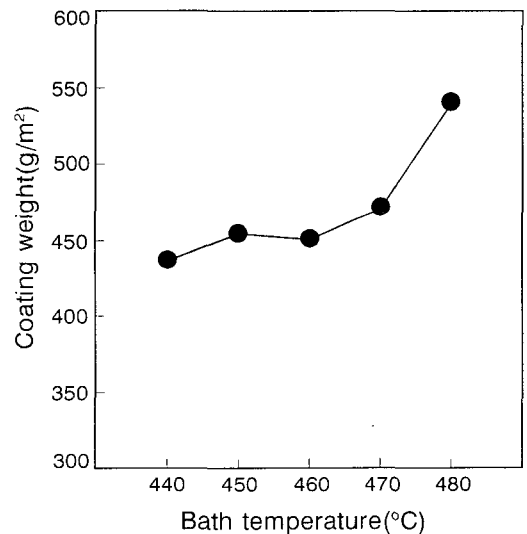

Fig. 5. Effect of bath temperature on coating weight of 0.06%Si steel (Zn-0.06%Ni bath, 1min)

function of bath temperature. The coating weight increased gradually with the bath temperature up to 470 ℃ and then increased rapidly. The reaction kinetics are following a parabolic law in temperature regions from 440 to 470 ℃ and above 530 ℃ (because of a diffusion controlled growth of the intermetallic layers) and a linear law from 480 to 530 ℃.

Fig. 6 shows the nickel content of galvanized coatings, compared that of the Zn-Ni bath. The nickel content of the coating is about 2.5 times higher than that of the zinc bath. The implication is that if this process is to be used in practice, then nickel must be added continuously to the melt.

Fig. 7 shows the distribution of elements along

same result is obtained by electron probe micro-analysis of nickel along the coating layer. As a result of a higher Ni concentration in front of the zeta phase, the Fe-Zn alloy reaction is assumed to be retarded.
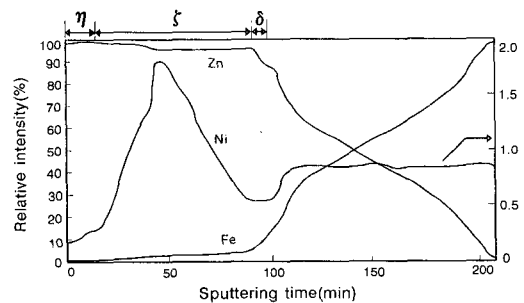
Fig. 7. GDS depth profile of coating layer obtained from Zn-0.06%Ni bath

4. DISCUSSION

4.1. The effect of nickel on the coating weight

The presence of silicon at approximately a 0.06% level in steel ("reactive" steels) can result in rapid alloy layer growth, producing a coating of excessive thickness. For the 0.06%Si steel, the coating is characterized by a thick and discontinuous zeta phase as shown in Fig. 2(a). The growth of intermetallic phases for this reactive steel is similar to that which occurs in silicon-free steel that has been hot-dipped at ~500 ℃ in the regime of rapid growth with zinc. This rapid growth also results in a dull coating appearance because the intermetallic phases reach the coating surface after withdrawal from the zinc melt. The mechanisms of the effects of silicon in steel on the structure and properties of galvanized coatings have been studied intensively and are
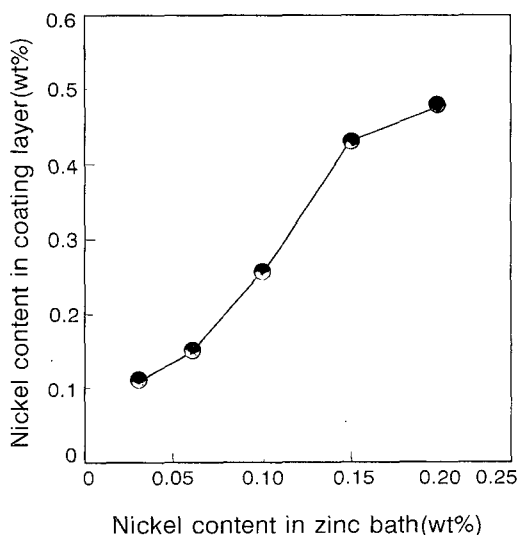

Fig. 6. Relationship of the nickel content between Zn-Ni bath and coating layer

the depth direction of the galvanized layer obtained from the Zn-0.06%Ni bath. Nickel is mainly distributed between the zeta and eta phases. The

still being investigated by a number of researche-rs[1~4].

In order to overcome the detrimental effects of silicon on the growth of Zn-Fe intermetallic com-pounds, a number of approaches have been ex-plored experimentally[5~8]. Of these approaches, only the Zn-Ni Technigalva system fulfilled the initial commercial promise in batch galvanizing. In the Technigalva process, up to 0.1% nickel is added to suppress the reactivity for steels contai-ning up to 0.25%Si. However, there has been some confusion in Technigalva practice about the efficiency of nickel usage and dross forma-tion.

Fig. 2(b) shows a photomicrograph of the coat-ing for a steel containing 0.06%Si that has been galvanized in Zn-0.06%Ni at 460℃. When this steel is dipped in the Zn-0.06%Ni bath, and com-pared to the normal galvanizing process(Fig. 2 (a)), abnormal growth of the zeta phase is elimi-nated. This characteristic intermetallic develop-ment results in a much lower rate of growth and a bright and even coating surface.

As little as 0.03%Ni in the zinc partially sup-pressed Sandelin-type growth and, at 0.06~0.1% Ni the Sandelin peak shown in Fig. 1, can be completely suppressed. Growth of the zeta layer on nonreactive steels is also slower and more even in a zinc bath containing 0.06%Ni relative to galvanizing in a pure zinc melt. The resultant coating is smoother, thinner, and brighter, and the incidence of dull coatings is reduced.

The main drawback when batch galvanizing in Zn-Ni baths containing typically 0.1%Ni is the dross formation whose stability is higher than that of a similar dross formed with Zn-Al baths. For baths with nickel contents of less

than 0.06%, the intermetallic zeta phase was identified. The zeta phase dross is isomorphous with $FeZn_{13}$ and contains less than 0.5% nickel. In baths with 0.07~0.09%Ni both the zeta and Γ_2 phases were identified and there was a signifi-cant increase in the nickel content of the dross. Therefore, the addition of 0.06%Ni to molten zinc in batch galvanizing is recommended be-cause of the reduced nickel content of the dross as well as significant reductions in coating weight.

4. 2. Role of Ni on Fe-Zn alloy reaction

To determine where the nickel is located in the zinc coating, a study was measured of a number of samples by the GDS. Fig. 7 shows the existe-nce of a nickel-rich region between the zeta phase and the eta phase after dipping in a 0.06% Ni-Zn melt at 460℃. Same result is obtained by the EMPA line scans of Ni along the coating layer. The innermost phases consist of the delta and zeta phases that normally occur in galvaniz-ing. The delta phase contains 7~12%Fe and the zeta phase contains 6~7%Fe. The nickel-rich region consists of a Zn-Ni-Fe compound. The outermost phase is the eta phase, and is practical-ly pure zinc.

Notowidjojo et al[9]. also found particles be-tween the tips of the columnar grains of the zeta phase and assumed them to be a Zn-Ni-Fe com-pound. A Zn-Ni-Fe phase to form a barrier layer must be thermodynamically stable in the liquid metal. It has been reported that when the nickel level in the liquid zinc is above 0.07% at 450℃, the composition of the intermetallic phase pres-ent in the dross is approximately 5%Fe, 4%Ni

and 91%Zn.[10]. It is likely that when the nickel content is higher than approximately 0.07%, it is thermodynamically possible that a phase other than zeta can form a barrier. The nickel content of the coating is about 2.5 times higher than that of the Zn-Ni bath (Fig. 6) and thus the Zn-Ni-Fe phase is stable.

Another possible explanation for the effect of nickel is the preferential formation of nonferrous silicide. The addition of nickel may lead to the formation of nickel silicide at the expense of iron silicide (FeSi), thus reducing the influence of silicon on the growth of the fragmented zeta phase[9] The formation of FeSi in the growing intermetallic layer creates the conditions for the fast growth of the fragmenting zeta phase during the galvanizing of the Sandelin type steel in nickel-free liquid zinc[11]. The formation of the nonferrous silicides seems a reasonable explanations for the effect of nickel, as it implies that the extent of the reduction of the reactivity of Sandelin type steel could be related to the nickel content. However, the formation of nonferrous silicides may not be the mechanism, or at least not the only mechanism, by which nickel is effective, since in low-silicon steels the growth of intermetallics is also reduced by the presence of nickel (Fig. 1).

From the above results it is suggested that nickel prevents the rapid growth of the zeta phase due to the formation of the Zn-Ni-Fe ternary compound, which may act as a barrier to inward diffusion of zinc or iron at the zeta-eta boundary.

5. CONCLUSIONS

1) The addition of 0.06%Ni to molten zinc significantly reduced the coating weight on steels containing silicon below 0.24%.

2) In the presence of nickel, abnormal growth of the zeta phase is eliminated and the coating becomes compact and adherent.

3) The growth kinetics of 0.06%Si steel was changed from a linear controlled to a diffusion controlled mechanism by the addition of nickel.

4) The nickel content of the coating is about 2.5 times higher than that of the Zn-Ni bath.

5) It is suggested that nickel prevents the rapid growth of the zeta phase due to the formation of the Zn-Ni-Fe ternary compound, which may act as a barrier to inward diffusion of zinc or iron at the zeta-eta boundary.

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