

Influence of Ni and Cu Addition on Galvanizing Properties of Steel Containing Si and Mn

– Development of High-strength Steel Sheet for Galvanizing –

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Abstract

High-strength steels have been developed and applied to automobiles to reduce vehicle weight, improve fuel economy and enhance collision safety, all at the same time. However, conventional high-strength steels (Si-Mn steels) have a drawback of poor galvanizability (the wettability with molten zinc and the rate of Fe-Zn alloying reactions) owing to the formation of complex Si-Mn oxides in sub-surface layers. As a result of studies, addition of Ni and Cu to Si-Mn steels was found effective in improving the galvanizability of the steels. The improvement is presumably due to a change in the morphology of sub-micron-size oxides in sub-surface layers during the annealing before the hot-dip galvanizing.

1. Introduction

One of the most important issues in the automobile industry in the last several years is how to reduce vehicle weight to decrease CO₂ gas emission by improving fuel economy while enhancing collision safety. Use of high-strength steel sheets has expanded as an effective measure to satisfy these requirements, which are fundamentally, mutually incompatible. In addition, for securing good corrosion resistance, use of hot-dip galvanized (GI) and galvanized (GA) steel sheets for car bodies has become a common practice, and high-strength GI and GA steel sheets of a 590-MPa class or higher have been developed especially for applications to structural members of a car body¹⁾.

High-strength steel sheets are produced, generally, through combination of the addition of solid-solution hardening elements such as C, Si, Mn and P and/or precipitation-forming elements such as Ti and Nb by respective adequate amounts and the control of microstructures in production processes. However, alloying elements sig-

nificantly affect the galvanizing properties (the wettability with molten zinc and the rate of the Fe-Zn alloying reactions, hereinafter referred to as galvanizability) of a steel²⁾. For example, when elements having a strong affinity for oxygen, such as Si and Mn, are added, their oxides form in the sub-surface layers of a steel sheet during the annealing before the molten zinc bath, and as a result, the wettability of the sheet surfaces with molten zinc becomes poor, leading to quality defects such as non-coating. The oxides also retard the Fe-Zn alloying reactions in the production of GA steel sheets³⁾, resulting in the deterioration of the corrosion resistance, weldability and other properties of the products. The countermeasures against these problems include the control of Si and Mn amounts not to exceed respectively prescribed upper limits, and electrolytic plating with Ni, or the like, as a pre-treatment for hot-dip galvanizing.

However, these countermeasures entail problems such as difficulty in realizing required material properties and construction of an additional facility. In pursuit of measures to avoid such problems, the authors studied modifications of steel chemistry to change the

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morphology of oxides as measures to improve the wettability of the steel sheets and accelerate the alloying reactions. As a result, they found that addition of Ni and Cu was the most effective in avoiding the problems since the addition of the elements made it possible to control the shape of the sub-micron-size oxides that formed in sub-surface layers of steel sheets containing high amounts of Si and Mn during annealing and thus to improve the galvanizability of the steel sheets without having to resort to the measures such as the pre-treatment by electrolytic plating.

This paper reports the results of the studies on the galvanizability improvement effects of the addition of Ni and Cu to Si-Mn steels and the relationship of the wettability and rate of the alloying reactions with the morphology of the oxides^{4,5}.

2. Development Concept

When a steel sheet containing Si and/or Mn undergoes annealing before hot-dip galvanizing, oxides of these elements in thin films of a sub-micron thickness form to cover the steel substrate as shown in Fig. 1(a). The oxide films deteriorate the wettability of the steel sheet with molten zinc leading to quality problems such as non-coating and the retardation of the Fe-Zn alloying reactions. The oxide films form because the atmosphere of the annealing section of a hot-dip galvanizing line is an oxidizing atmosphere for Si and Mn. If it is possible to fragment the oxide films as shown in Fig. 1(b) or form the oxides inside the steel substrate (internal oxidation) as shown in Fig. 1(c), the steel sheet surfaces will be partially or entirely free of the Si/Mn oxide films, and its galvanizability is expected to improve significantly.

In fact, a paper reported that the wettability at hot-dip galvanizing improved as a result of changing the atmosphere of the annealing furnace before the plating bath so as to cause internal oxidation⁶. Another paper proposed a method of improving galvanizability by forming internal oxides through a heat treatment of a hot-rolled steel sheet and then applying cold rolling and annealing⁷. The proposed measures aimed at improving galvanizability by changing the shape of the oxide films in sub-surface layers as shown in Fig. 1(c). However, these papers dealt with steels containing Si and Mn by comparatively small amounts, and there have been no reports dealing with steels containing these elements by 1% or more each. Past experiences of the authors suggest that it is difficult to apply those proposed measures to steels that contain Si and Mn by 1% or more each.

The object of the present study was to develop such a new chemistry of a high-Si, high-Mn steel as to form oxides having a shape as shown in either part (b) or (c) of Fig. 1, and thus to improve the galvanizability of the steel with an ordinary hot-dip galvanizing line without any additional provisions. As a result, the authors found that even with a steel containing Si and Mn by 1% or more each, the addition of Ni and Cu caused Si-Mn oxides to form in a morphology

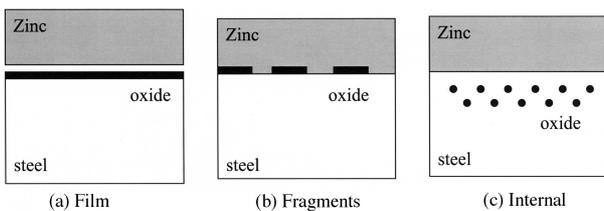


Fig. 1 Schematic illustration of morphology of Si-Mn oxides

where the shapes shown in parts (b) and (c) of Fig. 1 are combined, improving the galvanizability of the steel.

3. Test Method

Table 1 shows the chemical compositions of the steels used for the test. A base steel containing Si and Mn by more than 1% each and a developed steel containing Ni and Cu on the basis of the chemistry of the base steel were prepared by vacuum melting, and rolled into sheets by hot rolling (initial temperature 1,230°C, finishing temperature 900°C, coiling temperature 720°C) and cold rolling (from 4 to 0.8 mm in thickness) on laboratory mills. Galvanizing tests of test pieces cut out from the steel sheets thus produced were carried out on a laboratory hot-dip galvanizing line shown in Fig. 2 having a non-oxidizing furnace (NOF) and a radiant-tube type reducing furnace (RF). Fig. 3 shows the heat cycles in the furnaces and Table 2 the atmospheres therein. The atmosphere gas of the NOF was produced through combustion of coke oven gas at an air-fuel ratio of 0.9, and the exit temperature was controlled to 650 to 700°C. A steel sheet oxidizes slightly in a NOF and iron oxide (FeO) forms in sub-surface layers. The temperature of the RF, which had an atmosphere of 20% hydrogen + nitrogen and a dew point at -30°C, was controlled to 800 to 850°C. Although the above atmosphere is reductive for iron, it is oxidizing for Si and Mn, and as a consequence, while the iron oxide (FeO) having formed in the NOF is reduced into pure

Table 1 Chemical compositions of the examined steel

	C	Si	Mn	P	S	Ni, Cu
Base steel	0.081	1.32	1.32	0.014	0.006	-
Developed steel	0.087	1.33	1.32	0.015	0.006	Addition

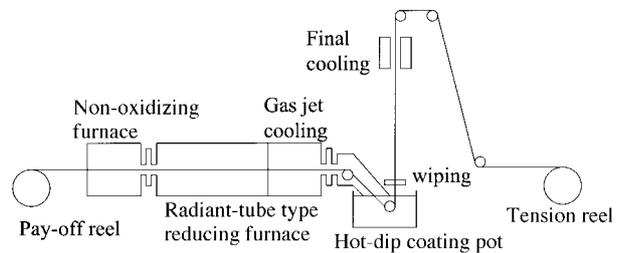


Fig. 2 Configuration of laboratory hot-dip galvanizing line

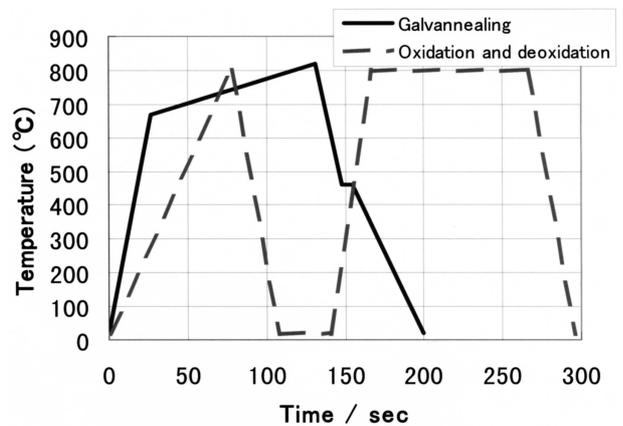


Fig. 3 Thermal cycles of experiments

Table 2 Atmosphere of the examination

	Galvannealing	Oxidation and deoxidation
Non-oxidizing furnace (NOF)	COG gas combustion atmosphere Air ratio: 0.9	O ₂ : 0.5%+CO ₂ : 10%+H ₂ Dew point: 50°C
Reducing furnace (RF)	H ₂ : 20%+N ₂ Dew point : -30°C	H ₂ : 15%+N ₂ Dew point: -30°C

iron, Si and Mn are oxidized there.

After the RF, the test pieces underwent cooling with nitrogen gas to 420°C, and then galvanizing in a bath of Zn-0.10Al (effective Al) kept at 460°C. The immersion time in the bath was 5 s, and the zinc coating weight was controlled by gas wiping to 70 to 100 g/m² per surface. The wettability with molten zinc was evaluated in terms of the occurrence of non-coating by visual inspection of the test piece surfaces after the processing. The rate of the Fe-Zn alloying reactions was investigated by measuring the alloy layer thickness at section surfaces after holding the galvanized test pieces at 500°C for 15 s in an infrared heating furnace and then cooling them.

Besides the above galvanizing test, some of the cold-rolled test pieces were subjected to heat treatment simulating the heat cycles of the NOF and RF for the purpose of reproducing the surface condition of the steel sheets just before entering the plating bath. The heat cycle simulating that of the NOF was applied by heating the test pieces from room temperature to 800°C at a rate of 10°C/s in an atmosphere of 0.5% oxygen + 10% carbon dioxide + nitrogen having a dew point at +50°C, and then cooling back to room temperature. The heat cycle simulating that of the RF was applied by heating the test pieces from room temperature to 800°C at a rate of 30°C/s in an atmosphere of 15% hydrogen + nitrogen having a dew point at -30°C, holding at the temperature for 100 s, and then cooling back to room temperature.

Fig. 3 and Table 2 also show the conditions of the above reproduction tests (oxidation and deoxidation). The differences between the tests on the galvanizing line and those to reproduce the surface condition were the following: (1) the heating and cooling were applied twice each in the latter; and (2) the effects of the Ni and Cu addition were made to show distinctly in the latter by raising the heating temperature of the heat treatment simulating the NOF to higher than that of the NOF in the former. After the above heat treatment simulating the NOF-RF annealing, the morphology of the sub-micron-size oxides forming in sub-surface layers was investigated by sectional observation using a scanning electron microscope (SEM) and a transmission electron microscope (TEM) and the element analysis of the sheet surfaces using an electron probe micro analyzer (EPMA).

4. Test Results

4.1 Addition of Ni and Cu and Change in wettability at hot-dip galvanizing

Fig. 4 shows surface appearance photographs of the galvanized sheets of the base steel (Si-Mn steel without Ni or Cu) and the developed steel (Si-Mn steel with Ni and Cu). Non-coating spots approximately 1 mm in size were found scattered over substantially all the surface areas of the specimens of the base steel. This result agrees with conventional knowledge. In contrast, in the specimens of the developed steel, the punctiform non-coating found in the base steel specimens was not found, evidencing good wettability. The above indicates that the addition of Ni and Cu to a Si-Mn steel improves

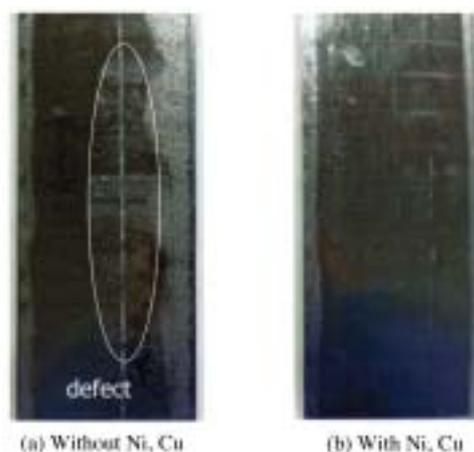


Fig. 4 The effect of Ni and Cu addition on surface appearance after galvanizing

the wettability with molten zinc bath and prevents the occurrence of non-coating.

4.2 Addition of Ni and Cu and Change in alloying reaction rate

Fig. 5 shows the thickness of the Fe-Zn alloy layers that formed in the galvanized sheets of the base and developed steels as a result of the holding at 500°C for 15 s. The alloy layers consisted of a δ phase. It is clear from the graph that the alloy layer thickness of the developed steel is greater than that of the base steel. This indicates that the addition of Ni and Cu to an Si-Mn steel accelerates the Fe-Zn alloying reactions.

4.3 Addition of Ni and Cu and Change in morphology of oxides forming during annealing

The above results indicate that the addition of Ni and Cu to a Si-Mn steel improves the wettability of the steel sheets with molten zinc bath and accelerates the Fe-Zn alloying reactions. In view of these results, the authors examined the morphology of the oxides that formed in sub-surface layers of the steel sheets during the annealing process before the plating bath in detail with specimens of the base steel (Si-Mn steel without Ni or Cu) and the developed steel

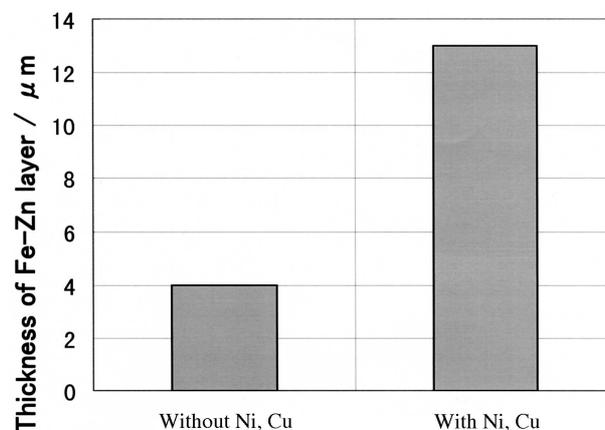


Fig. 5 The effect of Ni and Cu addition on thickness of Fe-Zn layer after alloying treatment

(Si-Mn steel with Ni and Cu), since the morphology of the oxides was suspected to be the cause of the effects.

Fig. 6 shows sectional SEM micrographs of the specimens of the base and developed steels. In the base steel specimens, oxides of Si and Mn were found to form a sub-micron-thickness film between the steel substrate and a pure iron layer that formed through the oxidizing and reducing processes, covering the steel substrate. In the developed steel specimens, on the other hand, the Si/Mn oxides between the steel substrate and the pure iron layer did not form a continuous film but film fragments. The authors also noted that the amount of sub-micron-size spherical oxide particles inside the steel substrate (internal oxides) tended to be larger in the developed steel specimens than in the base steel specimens. They noted further that the thickness of the pure iron layer, which formed in sub-surface layers through the oxidizing and reducing processes, tended to be larger in the developed steel specimens, although both the base and developed steel specimens had undergone the same heat treatment.

Fig. 7 shows sectional TEM micrographs of specimens of the base and developed steels. As seen with the SEM micrographs in Fig. 6, the TEM micrographs show that the pure iron layer is thicker and the formation of internal oxide is more accelerated in the developed steel. A structural analysis revealed that the internal oxide was amorphous SiO₂. The authors also noted that the sub-surface Si-Mn oxide layer tended to be thinner in the developed steel.

Fig. 8 shows the results of EPMA element mapping of O, Si and Mn as measured from a surface of the specimens of the base and developed steels after the heat treatment simulating the NOF-RF annealing. The figure also shows element concentration distribution profiles obtained from the EMPA mapping. The measurement range

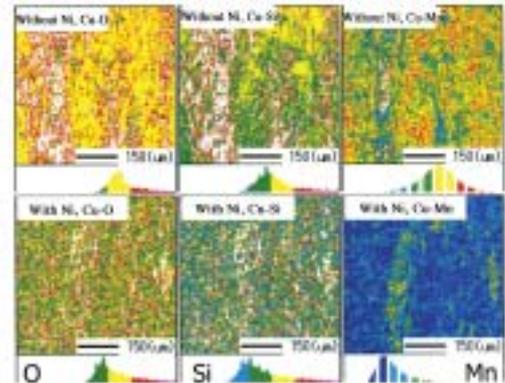


Fig. 8 Surface element analysis by EPMA

of the EPMA mapping in the depth direction is approximately 1.0 μm from the surface. The mapping shows that O, Si and Mn are distributed substantially at the same positions. This corresponds to the fact observed using the SEM that the Si/Mn oxides exist in the sub-surface layers of the steel sheets. It is also clear from the element distribution profiles that the concentrations of O, Si and Mn in the sub-surface layers are lower in the developed steel than in the base steel. The decrease especially of Mn concentration in the developed steel from that in the base steel is conspicuous. This is presumably because, judging from the TEM observation results, the thickness of the Si/Mn oxides forming in the sub-surface layers is smaller in the developed steel.

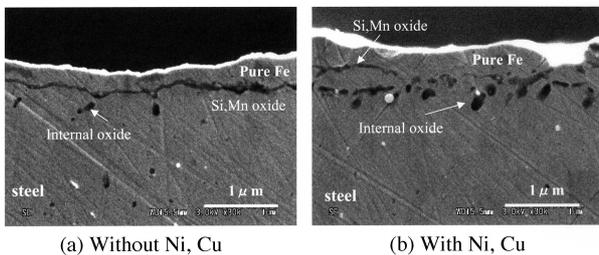


Fig. 6 SEM image of the section of annealed surface showing the effect of Ni and Cu addition on morphology of surface oxide after oxidation and deoxidation treatment

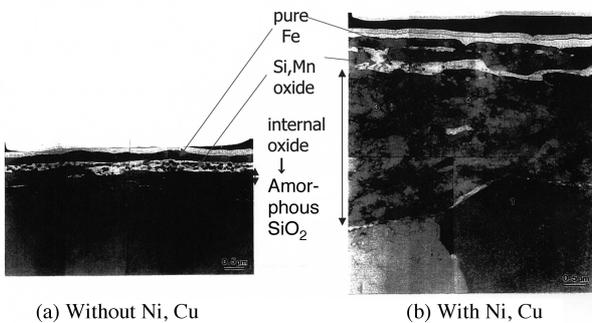


Fig. 7 TEM image of the section of annealed surface showing the effect of Ni and Cu addition on morphology of surface oxide after oxidation and deoxidation treatment

5. Discussion

The difference in the oxidizing/reducing behavior near a sheet surface resulting from the addition of Ni and Cu to a Si-Mn steel can be summarized as follows:

- 1) The addition of Ni and Cu fragments the film of Si/Mn oxides forming in the sub-surface layers and makes the film thickness smaller.
- 2) The addition of Ni and Cu accelerates the formation of internal oxide of Si.
- 3) The addition of Ni and Cu increases the thickness of the iron oxide (FeO) layer, which forms during the reduction process after the oxidation.

Fig. 9 shows a schematic diagram of the mechanism of the improvement of galvanizability that results from the addition of Ni and Cu to an Si-Mn steel deduced from the above findings. With the base steel containing Si and Mn, Si/Mn oxides form in a membrane form in the sub-surface layers during the annealing process before the zinc plating bath. In contrast, with the developed steel containing Ni and Cu in addition to Si and Mn, the sub-surface Si/Mn oxides form intermittent film fragments and the internal oxide of amorphous SiO₂ forms inside the steel substrate. In addition, the pure iron layer forming in the sub-surface layers during the reducing process is thicker and the layer of the Si/Mn oxides is thinner in the developed steel. As a consequence, what occurs with the base steel is that the alloying reactions between the steel substrate and the molten zinc during the plating process is hindered at portions such as where the pure iron layer is thin and the thickness of the Si/Mn oxide film is thick, leading to the occurrence of the spots of non-coating. What is more, even in portions where the molten zinc contacts the steel substrate surface, the Si/Mn oxide film covering the steel substrate makes it

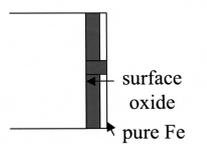
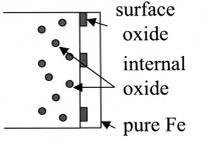
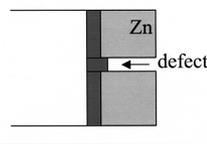
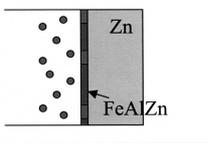
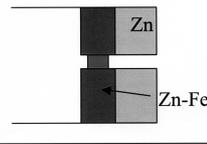
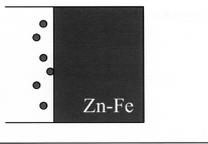
	C-Si-Mn steel external oxidation	C-Si-Mn-Ni-Cu steel internal oxidation
annealed (NOF+RF)		
galvanized		
galvannealed		

Fig. 9 Schematic diagram of mechanism of improvement of galvanizability by Ni,Cu addition

difficult for Fe in the steel substrate and Zn in the molten zinc to react each other to form an Fe-Zn alloy.

On the other hand, with the developed steel containing Ni and Cu in addition to Si and Mn, the pure iron layer is thicker and the Si/Mn oxide film is thinner and fragmented, and as a consequence, the alloying reactions during the immersion in the molten zinc bath and thereafter are expected to proceed easily. That is to say, the addition of Ni and Cu to a Si-Mn steel causes the shape of the oxides forming in the sub-surface layers during the annealing before the plating bath to change, and as a result, the galvanizability of the steel improves. Besides the above, the fact that the Mn concentration in the sub-

surface layers is significantly lower in the developed steel seems to indicate a possibility that the chemical composition of the Si/Mn oxides forming in the sub-surface layers is changed from what it is in the base steel. However, no distinct difference was confirmed within the scope of the present study.

6. Summary

The results of the investigation into the influences of the addition of Ni and Cu to steel containing Si and Mn on galvanizability and the morphology of the oxides forming during the annealing before the hot-dip zinc plating are summarized as follows:

- (1) The addition of Ni and Cu to a Si-Mn steel improves the wettability of steel sheets with molten zinc and suppresses the occurrence of non-coating.
- (2) The Ni/Cu addition accelerates the Fe-Zn alloying reactions during the immersion in the molten zinc bath and thereafter.
- (3) The Ni/Cu addition changes the morphology of the sub-micron-size Si/Mn oxides forming in the sub-surface layers during the annealing before the hot-dip zinc plating from continuous membranes to intermittent fragments, and at the same time, accelerates the formation of internal oxide of amorphous SiO_2 near a surface of the steel substrate. The change in the morphology of the oxides is presumed to cause the improvement in the galvanizability of the steel sheets in hot-dip zinc plating.

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