The Surface-Treated Steel Sheets*

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I. Introduction

Statistics tells us that, in the year of 1983, the Japanese production of crude steel had been 97.2 million t, and that 76.0 million t were the rolled products of ordinary steels. If we look more closely into the figure with regard to the group of plates and sheets, further, we see that hot rolled sheets occupied 11.1 %, cold rolled sheets 15.4 %, electric sheets 1.6 %, and surface-treated sheets 13.1 %. The hot rolled sheets include, as is the custom, the coils that exceed 3 mm in thickness estimatably to the tune of some 40 %. Therefore, the actual proportion of sheet steels in the whole rolled ordinary steels must have been 37 % by weight. Here, I submit that welded pipes and tubes should be included in the sheet steel industry. Then, the percentage of welded pipes and tubes having the wall thickness of less than 3 mm against the total rolled ordinary steels becomes about 6 %.

This means that, of the ordinary steels, the portion that is used after once rolled into the sheet form is as much as 43 % of the total, and if we took the American or European practice of separating sheets from plates at about 6 mm, this figure would be 50 %. Inasmuch as the functions of sheets are to cover, to wrap, and to contain, further, the functional presentation for them should be by the surface area, and you would allow me to say that at the present state of Japanese cultural development, some 50 % by weight of ordinary steels is being used for their surface functions. Some may say that "the tonnage days are over", but I will say that steels are being used today overwhelmingly for their lightness, arising from the thinness.

Today, all of us are being told that our future lies with "light, thin, short, and small". Scientifically, however, this ought to read "light, thin, *fine*, and small", and this famous slogan can be taken to mean that human being is observed to fall for things that are light, on one hand, and that our stakes are on those things like sheets and foils, fine wires and fine tubes, and super-fine powders, namely, on the things that rely more on the surface than the volume, on the other hand.

Beside the mechanical aspect, the materialistic aspect, that in what way a material should be put to service, is important in the usage of materials. Since almost all the sheet steels are to be used in our living environments, and since the earth is the planet of

water, I wish to start my Memorial Lecture off with quantitative examination of chemical action of water on the earth and discussion of behaviors of sheet steels in that circumstance.

II. Corrosion of Sheet Steels

In the first place, as for the chemical interaction of water with metallic materials, the pH of the aqueous solution in question, *i.e.*, if it is acidic or alkaline, and its redox-potential, *i.e.*, if it is oxidizing or reducing, are of the primary importance.¹⁾ Thus, we are able to describe any aqueous environment solely by its E_h (the redox-potential with regard to the standard hydrogen electrode) and its pH, as in Fig. 1. This means that, when the total pressure is 1 atm and the temperature is 25 °C, liquid water is stable only in such oxidation-reduction conditions as defined by the domain bounded by the two lines of ㉑ and ㉒. Here, the higher the redox-potential, the more oxidizing the solution.

Figure 1 pertains to the characteristics of natural water, and we owe L.G.M. Baas Becking and his associates for this.²⁾ The congregations around the points pH ~4, E_h ~600 mV, and pH ~5, E_h ~500 mV are rain water; that at pH ~7, E_h ~450 mV is fresh water; that pH ~8, E_h ~400 mV is sea water; and that along pH ~8 with low E_h 's is the environment that bacteria can prosper. In this figure the

Fig. 1. Distribution of redox-potential-pH measurements of natural aqueous environments.

* Based on the Special Lecture delivered by Prof. Hisamatsu on the commemoration of his receiving Nishiyama Medal in the 109th ISIJ Meeting on March 31, 1985, at Tokyo Institute of Technology in Tokyo and published in *Tetsu-to-Hagane*, **71** (1985), 1719, in Japanese. English version received on August 30, 1985. © 1986 ISIJ

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sheet steels are being used mostly in the oxidizing region with $\text{pH}=4\sim7$ and $E_h=600\sim400$ mV.

I have shown the effects of pH on corrosion rates of iron and zinc in an aerated water at room temperature in Fig. 2. Thanks to the protective film of itself a corrosion product that zinc³⁾ develops in a neutral environment, its corrosion rate can be quite low. Iron,⁴⁾ on the other hand, is characterized by a constant and appreciable corrosion rate over pH's of 4 to 10. This is due to the two facts that, even though a

corrosion product film of hydrated oxide does form on the surface, its power of environment insulation or oxygen diffusion inhibition is small, and that the film containing Fe(III) has an effect of promoting dissolution of the base iron.

A point of notice here is that the corrosion rate of zinc tends to lie right on the abscissa axis for a pH 7 to 12 range, demarking the domain where galvanizing is of a practical proposition as the corrosion rate of galvanized products is sufficiently low to warrant economy. In contrast, iron may be said to "corrode" over the whole range of pH. Further, aside from the surface topographical differences, ordinary steels are no different from pure iron in the service conditions for sheets.

In Fig. 3, I have compared the corrosion domains, *i.e.*, those regions that are unsuited for practical uses because of corrosion, for eight common metals by their empirically determined potential-pH diagrams. Of those universal purpose structural metals, you will observe that only iron, the most useful, shows peculiarity: iron alone has its corrosion domain extended over the entire pH range including that of around the neutral point. Experiences tell us that, except for iron, we may use these metals in our living environ-

Fig. 2. Effects of pH on corrosion rates of iron and zinc in aerated water at room temperature.

Fig. 3. Experimental potential-pH diagrams showing corrosion domains for common 8 metals, Al, Ti, Cr, Zn, Fe, Ni, Pb, and Cu.

Fig. 4. Assessment of corrosion behavior of stainless steels by synthesizing the corrosion domain diagrams of iron and chromium.

ment without being bothered by corrosion, but that for iron we have to take a certain precaution, such as to give a margin for corrosion to the thickness or to provide an anti-corrosion surface-treatment. In the Fig. 3 lead is presented with the effects of dissolved anions. This is to conform the behavior of lead to our experiences gained in the natural environment, but in distilled water lead is a metal of little corrosion resistance, showing a behavior like that of iron.

Thus, some form of surface-treatment is a must to counteract the corrosion for steel sheets. Otherwise, we will have to resort to alloy steels with high chromium contents. This can be assessed in Fig. 4, which has been synthesized by overlapping the empirical potential-pH diagram of iron in Fig. 3 with that of chromium: there is a wide non-corrosion domain for stainless steels. And this is precisely where the famous word the “Ferritic Explosion” has been given birth to, meaning progressive replacement of mild steels with stainless steels. The demand of the time is for irons of better durability.

III. Surface-treated Steel Sheets

The most of the surface-treated steel sheets may be classified into three categories of the electroplated, the hot-dip coated, and organic coated by the manufacturing methods as summarized in Table 1. Here, it is to be remembered that nowadays mainly because of changes that had occurred in the service environments the normal practice is to apply organic coating on the surface of metallic coated sheets. So the metallic coatings on sheets are often required to satisfy the conditions to be good substrates for organic coatings.

1. Hot-dip Coating with Zinc, Aluminum, or Zinc-Aluminum Alloy

To open my discussion of surface-treated steel sheets, I would choose the hot-dip coated steels. Here, I note that practically all the continuous hot-dipping lines, including aluminizing, of the world have been developed on the basis of the Sendzimir Process, as schematically illustrated in Fig. 5. This

Table 1. Classification of surface-treated steel sheets.

Surface-treated steel sheet	Electroplated steel sheet	Electro-tinplate Tin-free steel Electrogalvanized sheet Composite zinc plated sheet Electrolytic copper-plated sheet
	Hot-dip coated steel sheet	Galvanized sheet Galvannealed sheet Zinc-aluminum alloy coated sheet Aluminized sheet Terne sheet
	Organic-coated or laminated steel sheet	Paint-coated sheet Film-laminated sheet

process features the reduction cleaning as well as annealing by means of a hydrogen and nitrogen mixed gas atmosphere, the cooling and transportation of the steel in a non-oxidizing manner into the molten bath, and the special hot-dipping process that makes use of the hydrogen as flux as it is adsorbed on the steel surface.

Now, it has been my long-standing wonder why and how Dr. Sendzimir (1894~) of the Sendzimir Rolling Mill fame, an indubitably ingenious man, but mechanical engineer nevertheless, had come to think up of a flux that was not a chloride as was conventional for galvanizing. Very fortunately, I have been able to communicate with him, still very much up and about at over 91 years of age, through good offices of one of our major trading companies. He wrote me back,⁵⁾ telling me that he happened to develop an intense dislike toward the pickling-fluxing type galvanizing lines for their unsanitariness and the fume-laden atmosphere, and that this led him to a resolution that one day he would invent a fluxless, clean process—it was over 50 years ago.

He knew that a good surface for galvanizing could be obtained by reduction with hydrogen gas while annealing, but he soon ran into difficulties, when he

Fig. 5.
An improved Sendzimir continuous galvanizing line.

Fig. 6. An automated gas wiping system.

became aware of the thermodynamical calculations and experiments on iron/iron oxides equilibrium by Dr. Langmuir of General Electric, and he was able to establish a process comprising oxidation at 400 °C, reduction at 750 °C, cooling down to 500 °C non-oxidizingly, and dipping immediately into the zinc bath. He then proceeded to build an industrial continuous galvanizing line of 10 m/min, for which he himself designed the ammonia cracking tower on a catalyst of his own choice. The plant was constructed in Kostuchna, Poland, and duly started operation in 1933. The Poles celebrated the 50th anniversary of the line in 1983 in a big way.

I can see in his letter how rewarded he was by the remark of the then President of Poland, himself a noted physico-chemist, made in 1935 on his state visit of the plant that this is a sanatorium rather than a galvanizing plant. That Dr. Sendzimir had positively and squarely challenged what he condemned and disliked as unsanitary, the kind of thing that he could have avoided or escaped from if he so chose, to an invention that constituted even 50 years later the backbone of all the world's continuous lines, from this we should learn a good morale for ourselves and to transmit it to young people.

There was a disadvantage in the Sendzimir's 1933 continuous line. It was the lack of wiping mechanism, owing to which the line speed remained no more than 10 m/min. Today this has been rectified by the gas-jet wiper, Fig. 6, with which zinc gets squeezed right at the entry of the uptake from the bath. The coil is rapidly cooled immediately thereafter so as to finish in a smooth surface that prohibits spangling. This is important because spangled surface is not fit to serve as the substrate for in-line organic coating. Such a surface will consume a large quantity of paint.

The bath composition is now with aluminum 0.15 % or more to inhibit the growth of Fe-Zn alloy

Fig. 7. Variation of phases appearing as alloy layers with aluminum content in galvanizing bath and with immersion time of steel sheet in the bath held at 465 °C.

layer. Further, a surface that is particularly good as the substrate for organic coating is obtained by developing the δ phase layer, for which a bath composition of $\text{Al} < 0.15\%$ and the galvannealing, in which the coil is heat-treated following the wiping, are both effective as may be understood in Fig. 7.⁶⁾

Now, our environment is becoming acidic. Here in Japan we are exempt from the so-called acid-rain, thanks to our peculiar geographical position. But everywhere the world over, the life of zinc coating is getting shorter these years.⁷⁾ To counter to this, many a research has been conducted to prolong the

life of zinc coating: for example, based on a long-term exposure test results,^{8,9)} the Bethlehem Steel Corp. has developed a 55%Al-Zn alloy coating. This alloy utilizes the observation, shown in Fig. 3, that aluminum is more resistant to acidic environments than zinc. The Zn-Al system has no intermediate phases, being always composed of an Al-rich phase and a Zn-rich phase. The Zn-Al type coatings practically used are two systems consisting of 55%Al-Zn alloy and also of 5%Al-Zn alloy.

With regard to the aluminum hot-dip coating, a pure aluminum coating for atmospheric exposure service purposes and the Al-Si alloy coating for high temperature anti-oxidation purposes (ARMCO's Type 2 and Type 1, respectively) have been developed. In this country the thick coating of Al-Si alloy coating has been used for atmospheric exposure uses. Photograph 1 compares the state of film of (a) an Al-Si coating and (b) a 55%Al-Zn alloy coating, both as exposed to ambient air long time in a same industrial locality.

In the Al-Si coating of (a), corrosion of iron had started where the 3 μ m thick alloy phase (Fe-Al-Si ternary intermetallic compound) was cracked, but you will observe that the corrosion product formed there did not flow away, remaining in the place to work as a sort of protective substance to slow up the corrosion rate of the base steel. In the case of 55%Al-Zn alloy of (b), on the other hand, the Zn-rich phase corroded preferentially, due to which the base steel was, over the distance shown in this example at least,

clearly under the galvanic protection in a marked contrast to the case (a). However, there is a disadvantage to this, in that the large quantity of corrosion product of zinc tends to push up the remaining Al-rich phase layer. This means that the cathodic protection with zinc can cover a distance of roughly 300 μ m in the case of atmospheric exposure, but conversely that, as zinc is corroded excessively by the galvanic action, this feature can become a deficiency, too.

That the aluminized sheets have such a wide application is one of the things that amazed me so much when I joined the Nisshin Steel. Take the Al-Si alloy coating, for example. This is used for its good resistance to high temperature oxidation arising from the fact that any one of the three phases of aluminum phase, Al-Fe alloy phases, and iron phase that contains aluminum in solid solution is capable of withstanding high temperature oxidation. One usage born out of such property is found in the thermal reflector plate, which must keep the luster of the aluminum phase to as high a temperature as possible.

In the case of aluminized sheet made from continuously cast steel, however, complaints have been heard that the glossy silvery luster is more easily lost turning into dark gray than conventional sheets. This is summarized in Table 2.¹¹⁾ Here you will notice that the conversion of aluminum coating into dark gray on exposure to a high temperature corresponds to changing of both the Al-Si eutectic layer and the Al-Si-Fe ternary compound layer to the Fe-

Photo. 1. Cross-sectional views of (a) Al-Si alloy coating and (b) 55%Al-Zn alloy coating, exposed at the same industrial location.

Table 2. Relation between surface appearance and kind of intermetallic compound grown in Al-Si coating after heating.

Base steel Heating condition	Low-carbon rimmed		Al-killed	
	Surface appearance	Intermetallic compounds	Surface appearance	Intermetallic compounds
As hot-dipped	Glossy silver	(Al, Fe, Si) <u>H</u>	Glossy silver	(Al, Fe, Si) <u>H</u>
400 °C×1 000 h	Glossy silver	(Al, Fe, Si) <u>M</u>	Dark-gray	Al ₃ Fe, Al ₃ Fe ₂ , AlFe
500 °C×1 000 h	Dark-gray	Al ₅ Fe ₂ , AlFe	Dark-gray	Al ₃ Fe ₂ , AlFe

Fig. 8. Growth of Fe-Al alloy layer in Al-Si coating during heating at 400 °C, depending on the steel base.

Al compounds, as shown in Fig. 8. It was also observed that the darkening starts at 480 °C for the low carbon rimmed steel, but it is lower for the aluminum killed steel, only 380 °C. When heated to below their respective critical temperatures, either can form on its surface a dense Al_2O_3 film which provides a good oxidation resistance to preserve the glossy silvery luster.

Even in the temperature range where aluminum in the coating and iron in the base mutually diffuse at a high rate, the good protective function against high temperature oxidation does not deteriorate, even if the surface is darkened, because the Fe-Al intermetallic compounds formed have a good high temperature oxidation resistance. Yet, for a thermal reflector it is more desirable for its duty that the critical temperature should be higher. The height of this darkening temperature depends on the concentration of interstitial nitrogen atoms in the steel, so that for a very low carbon (50 ppm), high nitrogen (100 ppm) steel, the critical temperature is as high as 560 °C, which is the highest known.¹¹⁾

Here, formation of a barrier of AlN at the interface between coating and steel with aluminum in the Al-Fe-Si ternary compound and the interstitial nitrogen on low temperature heating is the cause of this phenomenon.¹²⁾ In a 50 ppm C, 100 ppm N steel of 0.8 mm thick and coated on both sides with Al-Si alloy, the amount of interstitial nitrogen required to form an AlN barrier that is capable of preventing the mutual diffusion of aluminum and iron up to 560 °C is what corresponds to a decrease in nitrogen of no more than 10 ppm¹¹⁾; the barrier then formed is exceedingly thin.

The major usage of Al-Si coated sheets is the component of automotive exhaust system. Here, if the

gas treatment converter is the type that employs reduction catalyst, the interior of the exhaust pipe may sometimes be subjected to a peculiar corrosion arising from repetition of condensation and re-evaporation of an ammonia-containing moisture in the exhaust. Though much depends on the driving program of the car, this does remind us that how it is the destination of materials to have to encounter new form of corrosion all the time. For this particular service the trends are to use a low alloy steel for the base.

Now, it is quite possible to apply aluminum porcelain enamel on the Al-Si coated sheet coils. From this the whiteboard, the writing board that is becoming popular in the classroom, is made and from this a new enameled steel sheet may be developed.

2. Electroplating

Here, I like to take up the surface-treated steel sheet for automotive outer panel as a representative use of the electroplated steel sheets. As is well known, the demand of surface-treated steel for automobile outer panel has originated from the increased liberal spray of snow-melting salts on the roads. However, I will limit my discussion on this type of sheets to a brief one, for there is an excellent review made by Mr. Ishihara, our president of ISIJ, available already.¹³⁾

Now, all the anti-corrosion technologies are an integral engineering that starts off with structural designing, and as such, various methods have been taken to counter the snow-melting salts.¹³⁾ As for the anti-corrosion measures for the inner surfaces of automotive panels, however, the truth is that practically nothing has been taken until comparatively recently, because the beauty of outlooks of an automobile has been attained by applying careful organic coatings to the cold rolled steel sheets. The electrodeposition primer coating method, which by its high throwing power has proved to be capable of providing a reliable primer coat for the inner surfaces of the outer panel. As this is yet insufficient, however, the fundamental practice is to have the steel mills supply body panels that are surface-treated one side only.

Then, it became apparent that even those outer surfaces that had been carefully coated had to fear the scab corrosion, which took place at cracks made by the flying pebbles. For this, the two-side surface-treated sheets have become called for. In the U.S.A., thick zinc coating will be demanded for the time being on the basis of past experiences, but soon enough the two-side surface-treated steels, of the kind of the two alloy electroplatings illustrated in Fig. 9, will become the mainstream. They will be the Zn-Fe alloy electroplated sheets and the Zn-Ni alloy electroplated sheets.

3. Organic Coated or Laminated Sheets

A substantial portion of steel sheets are used as coated with organic substances. They may be classified into the organic coated, the laminated, and the special coating, and most of them base themselves on the metallic coated sheets. For example, there is the

Fig. 9. Typical two-side surface-treated steel sheets for automotive body panels.

'Precoat' sheet, which is manufactured by coating the galvanized sheet so as to retain a good press formability as coated. One disadvantage common to those steel sheets is that the organic coating often interferes with welding. This difficulty will one day be solved by using inexpensive yet strong adhesives, but the present trend is to provide a high enough electric conductivity by resorting to a paint that contains metallic powder pigment to a high concentration. The one-side zinc-rich paint coating of Fig. 9 (2) has been developed to accommodate this purpose.

As the metallic coating to sheet steel became to be expected to work as the substrate for subsequent organic coating, properties of the metallic coating in relation to the chemical conversion treatment have become important. In this development, the progress achieved in the surface analysis has made a great contribution.¹⁴⁾

Viewing the trend thus, one would expect that the anti-corrosion metallic coating on a steel sheet, which has mostly been of a single metal such as zinc or aluminum, should become a thin plating of a high alloy or an intermetallic phase.* Here, the thinness of the plated metal film works favorably in resisting cracking on cold forming. However, the organic coating film made in a continuous coating line, which is of only several tens of μm and rather thin compared with ordinary structural paint coating films, appears not able to serve as a trustworthy barrier to penetrating oxygen and water-vapor. This means that much

more research work, first of all on the problems of corrosion of plated metals beneath the organic films, will be required for the line-coated surface-treated steel sheets so that they may develop their full potential as a composite material.

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* It is to be noted that thin alloy layer that is developed in the various currently popular metallic coating often contribute favorably to the corrosion resistance. The FeSn_2 in the tin plating and the $\text{Fe}(\text{Ni})\text{Sn}_2$ in the ternary plate are the examples. The γ phase utilized in the Zn-Ni alloy plating appears unique in its corrosion behavior.