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Manufacturing Methods and Properties of Hot-Dipped One-Side Galvannealed Steel Sheets by the Stop-Off Coating Technique*[1]

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(2) Titanium oxide in needle-like crystals, recrystallized on the coating surface, prevents zinc sticking between 800 and 900°C.

(3) Slightly absorbed zinc and magnesia on the bare side after removing the coating improve phosphate nucleation and corrosion resistance after painting.

(4) The one-side galvannealed steel sheet using extra low carbon steel containing niobium shows extra deep drawability, having an elongation of 49% and a $\bar{r}$ value of 2.0.

1 Introduction

It is well known that the most conspicuous corrosion of car bodies occurs from the inner surface. In the lapped portions (hemmed portions and spot-welded portions) such as doors and hoods, where neither phosphate coating or electrodeposition coating has been effected, a severe corrosion of bare steel sheets proceeds with the passage of time, due to the invasion of moisture, etc. Therefore, precoated steel sheets which have undergone corrosion-preventing treatment are necessary for the inner surfaces of the outer panels of vehicles. On the other hand, the outer surfaces of car outer panels require cold rolled steel sheets with good phosphatability and electrodeposition coating properties in order to obtain a satisfactory coating adhesion and the stability of external appearance. Usually, therefore, one-side precoated steel sheets are used as vehicle steel sheets, especially for outer panels of export specifications.

Among the various types of pre-coated steel sheets, hot-dipped galvannealed steel sheets possess superior perforation corrosion resistance[1] as well as good spot weldability and coating adhesion characteristics, and thus are optimal for corrosion preventing treatment of inner surfaces.

Conventional methods for manufacturing hot-dipped one-side galvannealed steel sheets include the grinding method, in which one side is mechanically ground after double plating. However, this method has certain disadvantages, such as a tendency for part of the plating to remain as well as the formation of electrodeposition coating defects called craters, and high cost; therefore, nongrinding type manufacturing methods now prevail.

As non-grinding methods for hot-dipped one-side galvannealing techniques, the meniscus method[2], the electromagnetic pumping method[3,4], the roll coating

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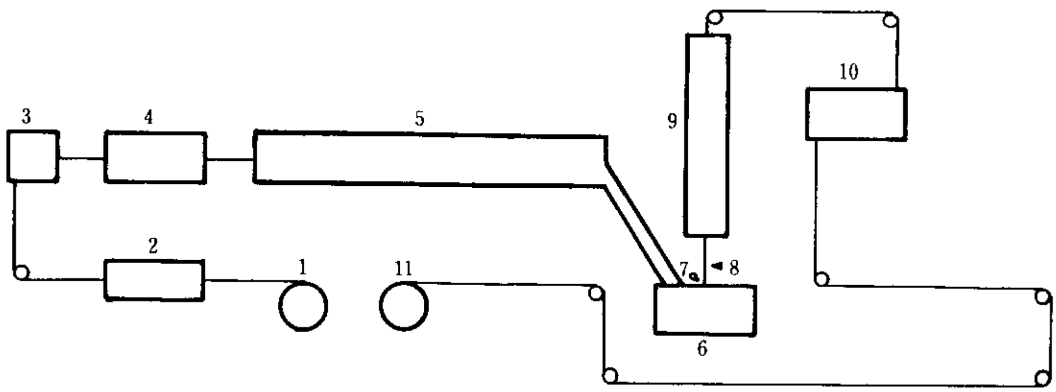


1 Uncoiler
2 Electrodegreasing tank
3 Roll coater
4 Preliminary drying furnace
5 Annealing furnace
6 Galvanizing pot
7 Flame wiper
8 Gas wiper
9 Galvannealing furnace
10 Roll bender
11 Recoiler

Fig. 1 Profile of continuous galvanizing line for producing one side galvannealed steel strip

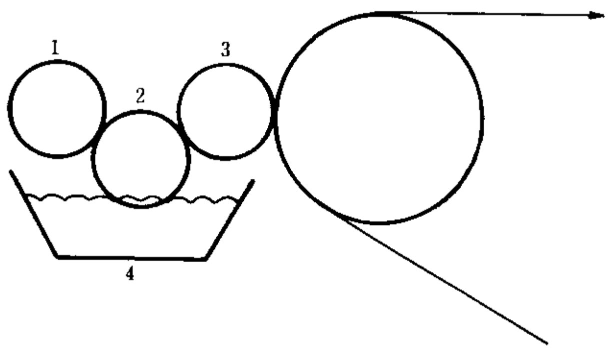
method[5], the mechanical pumping method[6] and the stop-off coating method[7-12] have been proposed and applied to practical use. The stop-off coating method, in which one side is covered prior to plating, has an advantage that the non-plated surface is not exposed to dirt and blueing caused by zinc or dross during the plating process. In particular, in the manufacture of hot-dipped galvannealed steel sheets, pickling and post-treatment are not required, since the cold rolled surface is not oxidized by air during heat treatment, and stable quality is easily ensured.

The present report describes a process for manufacturing hot-dipped one-side galvannealed steel sheets by the stop-off coating method as well as the characteristics of stop-off agents, the properties of ungalvannealed surfaces and the mechanical properties of the galvannealed steel sheets obtained by the process described herein.

2 Manufacturing Facilities

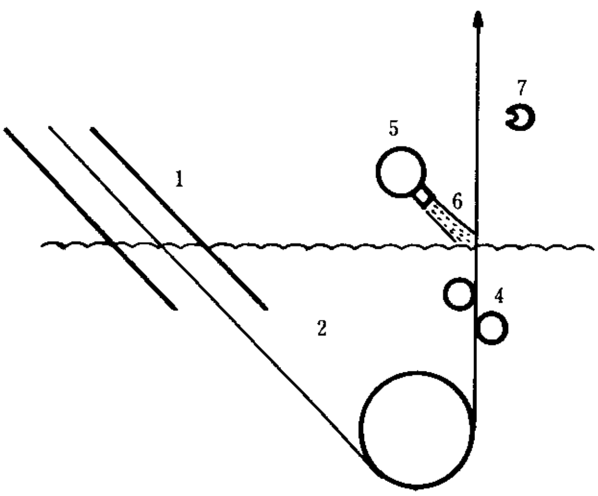
A schematic diagram of the manufacturing line is shown in **Fig. 1**. Characteristic of the Kawasaki Steel manufacturing process employing the stop-off coating method is the provision of the following apparatus at appropriate points in a continuous galvanizing line with non-oxidizing furnaces:

(1) A unit for electrodegreasing of the oils (rolling oil and rust preventive oil) on the sheet surfaces, which makes the application of the stop-off agent possible
(2) A three roll reverse coater (**Fig. 2**) which coats the stop-off agent onto one side of the strip
(3) A preliminary drying furnace which removes the free water in the stop-off agent slurry
(4) A flame wiper (**Fig. 3**) which prevents the sputtering of molten zinc onto the surface coated with the stop-off agent when raised above the zinc pot



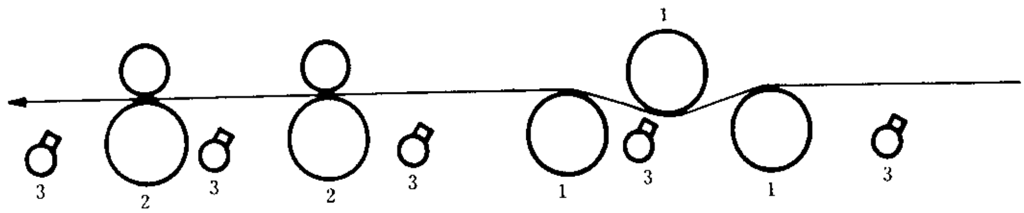
1 Doctor roll
2 Pick-up roll
3 Applicater roll
4 Slurry pan

Fig. 2 Roll coater



1 Snout
2 Molten zinc
3 Sink roll
4 Supporting roll
5 Flame gun
6 Flame wiper
7 Gas wiper

Fig. 3 Flame wiper above zinc pot



1 Roll bender
2 Brush roll
3 Water spray

Fig. 4 Roll bender and brush roll

(5) A roll bending and brush wiping unit (**Fig. 4**) for removing the stop-off agent

The explanation of the process in the order of sequential arrangement of the appratus is as follows. First of all, the stop-off agent slurry is coated onto one side of the electrodegreased strip by the roll coater. After dehydration in the air at 300°C for 20 seconds in the preliminary drying furnace, a non-oxidizing furnace heating at an air ratio of 1 or less and then a radiation heating annealing in AX gas containing 10% or more hydrogen are performed. As a result of this annealing, the stop-off agent becomes a vitreous film densely covering one side of the strip. This vitreous film serves to separate the zinc from the steel sheet in the zinc pot and also possesses the property by which zinc does not adhere to the vitreous film itself. However, above the zinc pot, the violently churning molten zinc splashes onto and adheres to the vitreous film, and therefore the flame wiper removes this zinc from the surface of the film with high temperature and high velocity gas flow. When the steel is passed through the galvannealing furnace after one-side galvanizing, iron diffuses from the base metal on the galvanized side, and a Zn-Fe alloy coating is formed. The vitreous film is not changed even by this galvannealing heat treatment, and can thus completely prevent the blueing of the ungalvannealed surace. Next, the strip reaches the roll bending unit via the air jet cooling zone and the water quench. The roll bending unit repeatedly bends the strip with small rollers and thus mechanically removes the vitreous film. Finally, the exfoliated film is removed by brush wiping. The present continuous galvannealing line also includes a temper roll and can be employed for in-line production. By virtue of the processes described above, the external appearance of the ungalvannealed surface after hot-dipped one-side galvannealing becomes entirely similar to that of oridnary cold rolled surfaces, and likewise the external appearance of the galvannealed surface is entirely similar to that of ordinary galvannealed surfaces.

3 Characteristics of Stop-Off Coatings

3.1 Functions

The functions and characteristics required of stop-off agents are as follows:

(1) Separation of steel sheets from zinc during the galvanizing process and prevention of oxidation of steel sheets during galvannealing heat treatments
(2) Prevention of zinc adhesion on the coating itself
(3) Easy removed from steel sheets by roll bending

3.2 Composition and Structure

The first function of stop-off agents is to form a fine, dense coating and shield the steel sheet from zinc and air. For this purpose, the steel sheet is coated with a water slurry containing a mixture of sodium silicate, sodium borate and magnesium oxide and then baked. **Photo 1** shows the surface configurations of coatings which were annealed for one second at various temperatures after coating, observed with a SEM. In the case of annealing at 700°C, the melting and covering of the coating are inadequate; cracks of length ranging from ten-odd micrometers to several tens of micrometers are present, and spherically-shaped zinc is locally galvanized onto the steel sheet. In the case of annealing at 800°C, these cracks disappear, and a fine dense coating is formed. **Figure 5** shows the X-ray diffraction pattern of the coating annealed at 800°C. Diffraction signals of sodium silicate and magnesium oxide were obtained; however, a borate type diffraction peak was not observed. The borates are present in an amorphous state. In **Fig. 6**, the X-ray diffraction intensities for the (203) plane of sodium silicated in a coating 20 μm thick are plotted against each temperature. The diffraction intensity increases with temperature up to 800°C, but decreases beyond it. The reason for this phenomenon is that the crystallization of sodium silicate progresses for temperature up to 800°C, whereas sodium silicate becomes amorphous due to fusion when the temperature exceeds 800°C. Therefore, the firm, dense coating in Photo 1 is mainly atributed to the fusion of borate

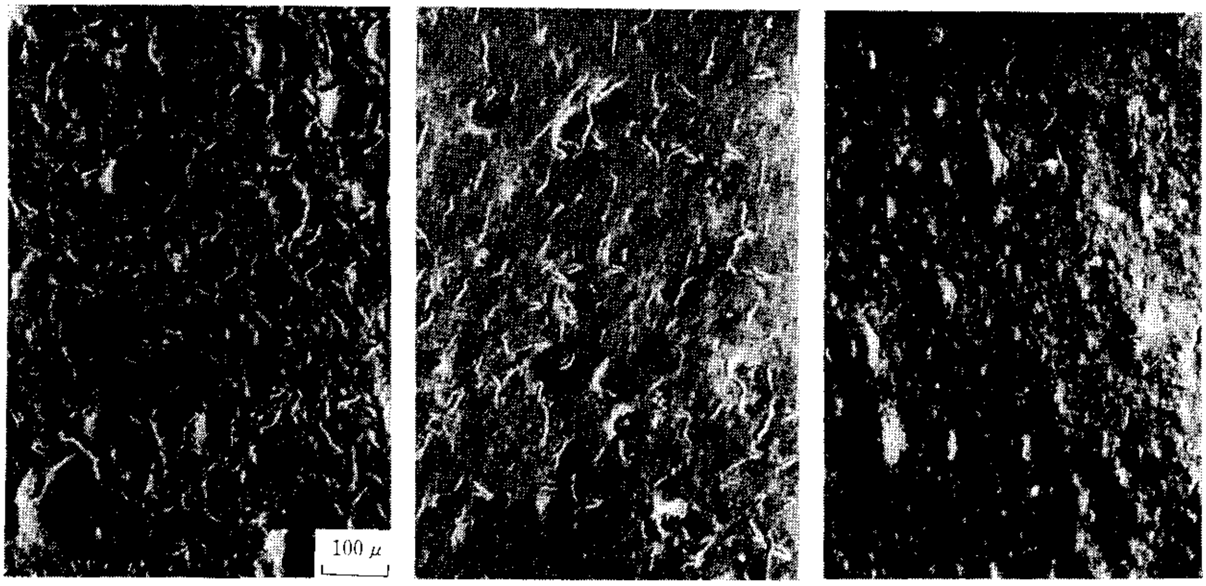


Photo 1 Scanning electron micrographs of the stop-off-coating consisting of sodium silicate, sodium borate and magnesium oxide at various annealing temperatures

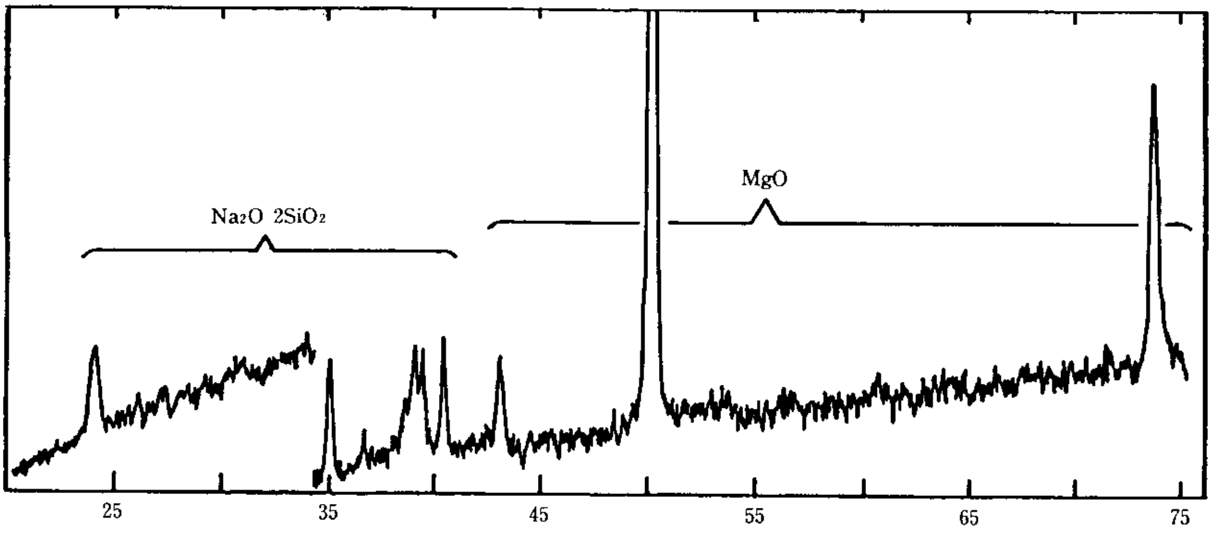


Fig. 5 X-ray diffraction patten of the stop-off-coating formed at 800°C (Co Kα, 50 kV, 60 mA)

type glass. At 800°C or higher, the coating becomes even more dense, due to the added contribution of silicate glass, and consequently the steel sheet can also be shielded from the atmosphere which constitutes the cause of blueing.

The second property required of stop-off agents is that molten zinc does not adhere to the coating surface itself. This is because, if zinc adheres to the coating surface itself, the shape of the strip is damaged before the coating is removed. The composition of the stop-off agent described above is inferior in this respect. This was considered to be due to the presence of silicate glass and borate glass on the coating surface. Hence, we attempted to impart the property of repelling molten zinc by adding aluminum oxide and titanium oxide, which are of poor wettability with respect to molten metals. By mixing titanium oxide and aluminum oxide into the three-component coating material mentioned above, and by annealing at temperatures in the range from 800 to 900°C, the adhesion of zinc was completely prevented. **Photo 2** shows an SEM-observed surface configuration of coatings containing admixed titanium oxide

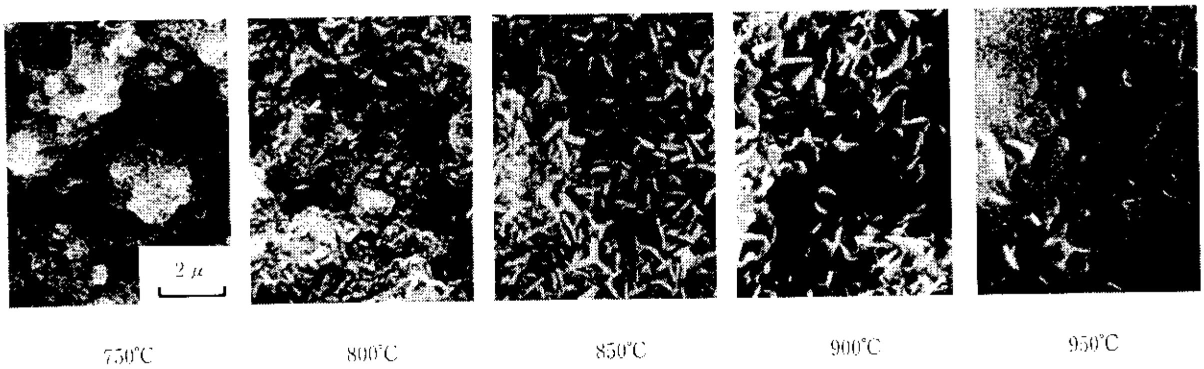


Photo 2 Scanning electron micrographs of the titanium oxide and aluminium oxide added stop-off-coating (sodium silicate, sodium borate and magnesium oxide) annealed at various temperatures

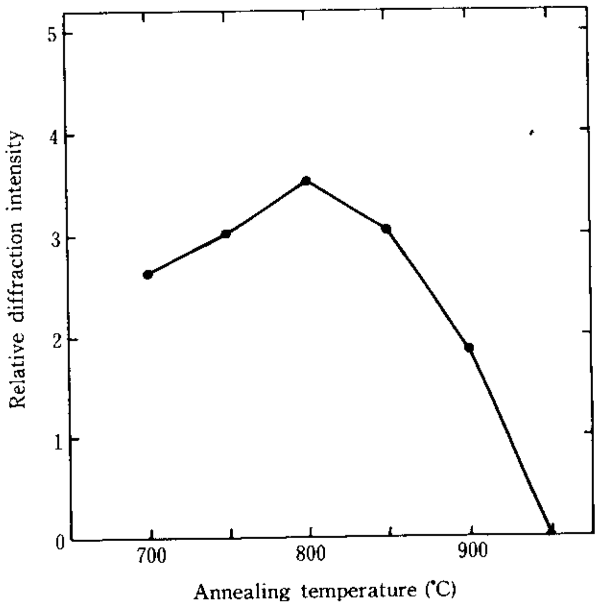


Fig. 6 X-ray diffraction intensity of $Na_2O{\cdot}2SiO_2$ (203) in the stop-off-coating at various annealing temperatures (coating thickness; 20 μm)

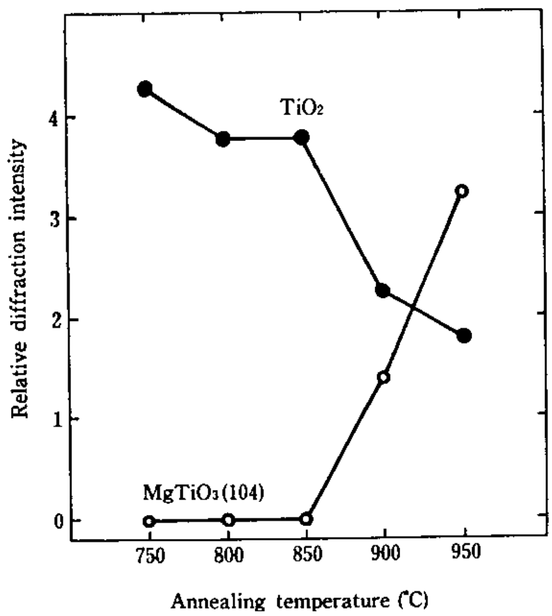


Fig. 7 X-ray diffraction intensity of TiO_2 and $MgTiO_3$ in the stop-off-coating at various annealing temperatures (coating thickness; 20 μm)

and aluminum oxide which were annealed for one second at various temperatures. Photo 2 shows that in the temperature range from 800 to 900°C; needle-like crystals ranging from 1 to 2 μm in size are precipitated on the coating surface and that, at temperatures above 900°C, these needl-like crystals vanished into the coating. Therefore, it follows that it is these needle-like crystals which serve to repel the zinc. In **Fig. 7**, the X-ray diffraction intensities of TiO_2 and $MgTiO_3$ in a coating 20 μm thick are plotted against various annealing temperatures. These variations in diffraction intensity demonstrate that the formation and disappearance of needle-like crystals on the coatings are caused by the particle growth of TiO_2 and formation of $MgTiO_3$, and that the property of repelling zinc is provided by the needle-like crystals of TiO_2. Aluminum oxide plays the role of maintaining the needle-like crystals of TiO_2 intact up to a high temperature, and in fact these needle-like crystals disappear at 850°C if aluminum oxide is not added.

The third property required of stop-off agents is that the coating can be completely removed by roll bending after the galvanizing and galvannealing heat treatment. The following characteristics are necessary in order to ensure this property: the coating should not react chemically with the steel sheet and must form a continuum in order to effectively propagate bending stress. The components of the stop-off agents described above do not react with the steel in the temperature range from 800 to 900°C, and the coatings form a continuum, as was explained in connection with Photo 1, which provides excellent propagation of bending strain at temperatures of 800°C or higher. Since these coatings are easily separated by compressive strain, an apparatus which applies repeated inward bending is employed, as shown in Fig. 4.

4 Characteristics of Ungalvannealed Surfaces

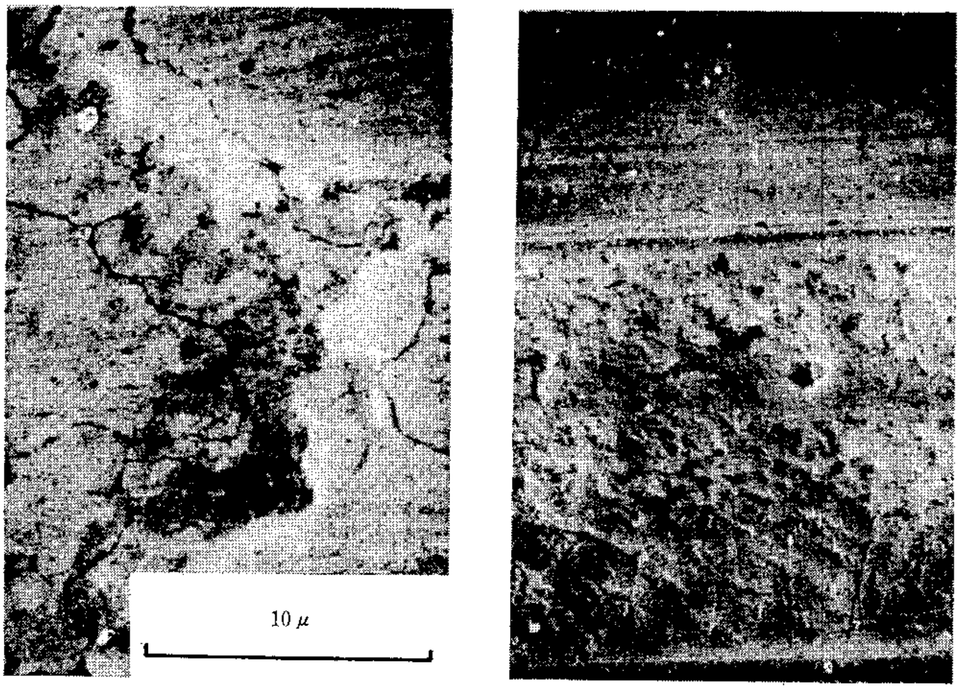
4.1 Surface Configuration

Photo 3 shows an SEM-observed configuration of an ungalvannealed surface after removal of the stop-off agent, in comparison with a cold rolled sheet surface manufactured in a continuous annealing furnace. Both sheets are composed of extra low carbon steel containing niobium.[13] In the continuously annealed cold rolled steel, clear grain boundaries were formed by thermal etching, whereas the surface of the material which had been covered by the stop-off agent exhibited scarcely any thermal etching and no residual stop-off agent was present in the depressed grain boundaries.

4.2 Phosphatability

since the ungalvannealed side becomes the outer surface of the automobile body, the quality of the phosphate pretreatment is extremely important as regards coating adhesion characteristics and corrosion resistance subsequent to coating. In the case of the conventional one-side galvanizing-by-grinding technique, zinc amounting to several tens of milligrams per square meter remains on the ground surface, the phosphate crystals became coarse, and uncovered portions were created, which was disadvantageous with respect to corrosion resistance. Also, in the case of electroplating, similar phenomena occur if several tens of milligrams of the plating material per square meter are unavoidably thrown-around onto the non-plated surface. On the other hand, it has been reported that, if manganese in the form of manganese oxide or manganese sulfide is deposited on the steel sheet surface, the formation of phosphate crystal nuclei is facilitated, and fine, dense crystals precipitate.[14] Such deposition of manganese compounds occurs easily in the case of conventional box annealed cold rolled steel sheets because of the comparatively long time duration of the annealing process, but in the case of continuous annealing which is becoming predominant, this deposition is difficult to take place because of the comparatively short annealing time. Therefore, continuously annealed materials require some substance to form nuclei for phosphate crystals.

However, in the case of continuously galvannealed steel sheet onto which a stop-off agent has been applied, trace adhesion of zinc and residual magnesium are observed on the ungalvannealed surface after the removal of the stop-off agent. This zinc penetrates



(a) Cold rolled steel surface continuous annealing (b) Bare side surface of the stop-off-coating process

Photo 3 Scanning electron micrographs of steel surface upon the removal of the stop-off-coating as compared with the surface of cold rolled steel as produced with a continuous annealing line

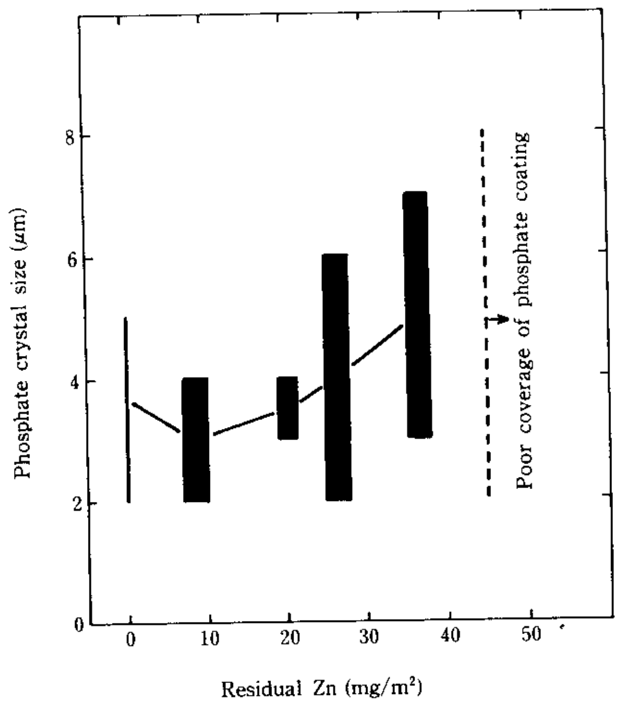


Fig. 8 Effect of residual zinc on phosphate crystal size (dip type phosphate treatment; Bonderite 3004)

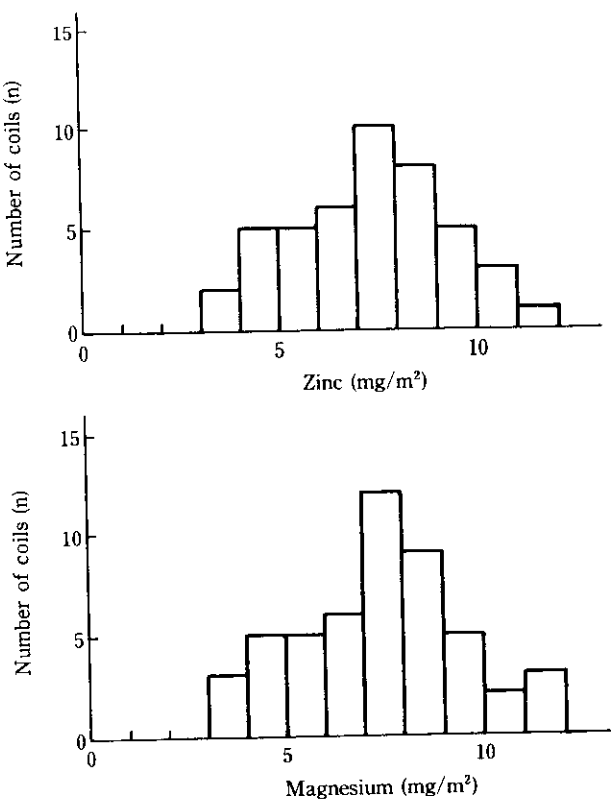


Fig. 9 Variations of residual zinc and magnesium among tested coils

through the stop-off coating when the steel sheet passes through the plating bath, and the magnesium is a residue left by the constituents of the stop-off agent. Since the quantities of adhered zinc and residual magnesium actually turn out to be of the same order of magnitude, **Fig. 8** simply shows the relation between these adhering substances, as represented by the quantity of zinc, and the size of the phosphate crystals. Also, **Photo 4** shows SEM photographs of the crystal configurations. As had hitherto been known, when zinc adheres to the amount of several tens of milligrams per square meter (or about 40 mg/m² or more in the present experiments), the crystals become coarse, and non-coated portions occur. On the other hand, it is known that, when the quantity of adhered zinc is in the range from several mg/m² up to 10 mg/m², the phosphate crystals

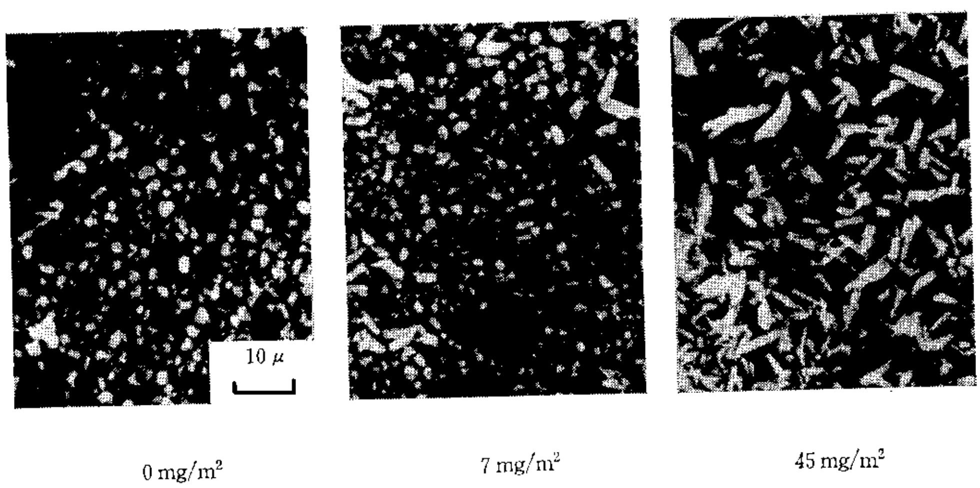


Photo 4 Appearances of phosphate films formed on steel surfaces with various amounts of residual zinc (phosphate; Bonderite 3004)

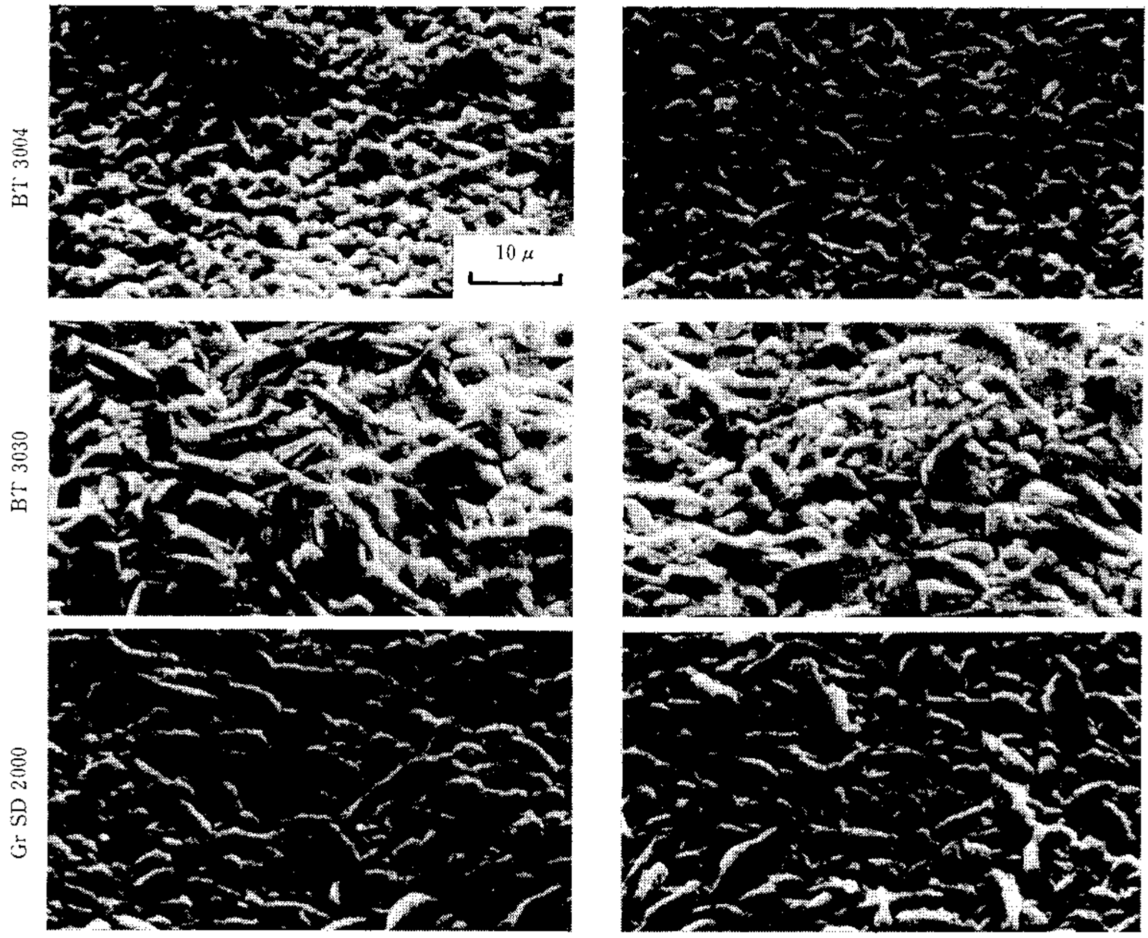
become even more fine and dense than those formed on continuously annealed cold rolled materials and thus excellent phosphatability is obtained. Therefore, it follows that adhesion and residues of zinc and magnesium to the extent of several mg/m^2 on the ungalvannealed surface subsequent to the removal of the stop-off agent contribute to the formation of phosphate crystal nuclei. Industrially, the adhesion and residues of zinc and magnesium are regulated by appropriately controlling the physical properties of the magnesium oxide in the stop-off agent. **Figure 9** shows the distributions of residual zinc and magnesium obtained in actual industrial results, expressed in numbers of coils. The figure shows that the peak distribution lies in the range from 7 to 8 mg/m^2 for both zinc and magnesium.

4.3 Reactivity to Various Phosphate Solutions

Reactivity of the steel sheets to various commercially available phosphate solutions was studied. The dipping type solutions used for treatment were BT3004 and BT3030, manufactured by the Nihon Parkerizing Co., Ltd., and Gr-SD2000, manufactured by the Nippon Paint Co., Ltd. **Photo 5** shows SEM photographs taken after 120-sec treatment in accordance with the treatment specifications for the respective solutions. The results are compared with the corresponding results for continuously annealed cold rolled steel manufactured from the same material. The shapes and sizes of the phopsphate crystals differ in accordance with the type of solution; however, for all the solutions, the crystals obtained after stop-off-coating are finer than those obtained after continuous annealing.

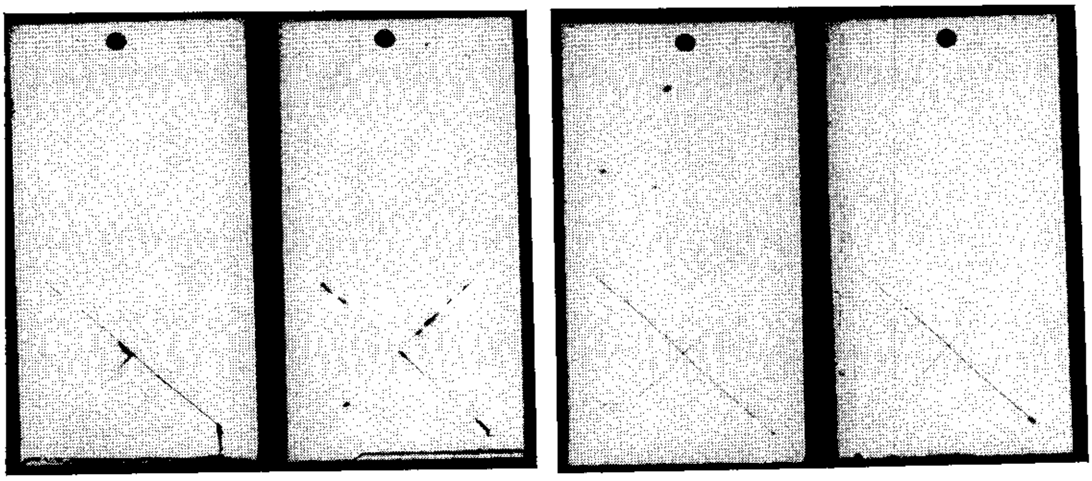
4.4 Corrosion Resistance after Painting

Corrosion resistance after painting (cationic electrodeposition coating, middle coating and top coating) was investigated. After this 3-coat painting process, followed by cross-scribing, 5% salt spray testing was performed, and the results obtained from steel sheet after stop-off-coating were compared with those from continuously



(a) Cold rolled steel after continuous annealing (b) Bare side after stop-off-coating process

Photo 5 Appearances of phosphate films on cold rolled steel after continuous annealing and bare side after the stop-off-coating process with various phosphate treatments



(a) Cold rolled steel after continuous annealing (b) Bare side after stop-off-coating process

Photo 6 Corrosion behaviors at cross scribed portions of 3-coat painted cold rolled steel as continuously annealed and bare side surface of the stop-off-coating process, SST (440 h)

Table 1 Chemical composition of KTUX and mechanical properties of one side galvannealed KTUX

	Chemical composition (wt %)							Mechanical properties						Thickness (mm)
	C	Sn	Mn	P	S	Al	Nb	*YS* (kgf/mm²)	*TS* (kgf/mm²)	*El* (%)	*YEl**2 (%)	$\bar{r}$	*AI**3 (kgf/mm²)	
KTUX*1	0.002	0.020	0.15	0.013	0.008	0.04	0.015	19	31	49	0	2.0	0.1	0.8

*1 Niobium added extra deep drawable steel sheet with extra low carbon
*2 Yield point elongation
*3 Aging index (100°C × 30 min. after 7.5% prestrain)

annealed cold rolled steel sheet composed of the same material. **Photo 6** shows the state of formation of red rust after 440 h. Clearly, from the results shown in Fig. 8, the fact that the degree of red rust formation on the ungalvannealed surface is less than that on the continuously annealed cold rolled steel sheet surface reflects a difference in phosphatability.

5 Mechanical Properties of Galvannealed Steel Sheets

Using recently developed extra low carbon niobium-contained steel materials, Kawasaki Steel manufactures hot-dipped one-side galvannealed steel strip possessing non-aging ultra-deep drawability characteristics, not requiring pre-annealing or post-annealing. **Table 1** shows the chemical composition and representative values of mechanical properties after galvannealing heat treatment. **Photo 7** is an example showing the press formability of the galvannealed steel sheet so obtained.

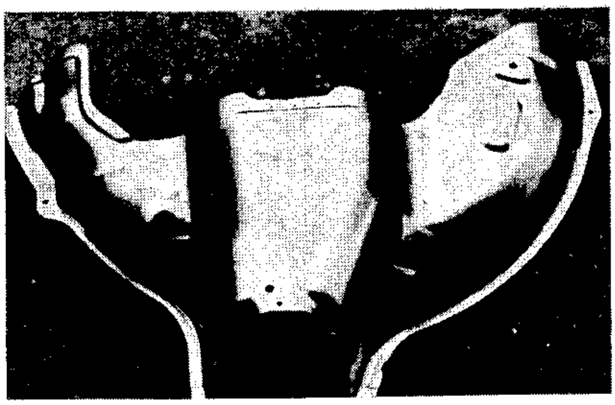


Photo 7 Press formed one side galvannealed steel sheet, showing bare side surface

6 Summary

Methods for manufacturing roll bending type hot-dipped one-side galvannealed steel sheets by the stop-off coating technique, the characteristics of the stop-off agents and the ungalvannealed surfaces, and the mechanical properties of the galvannealed steel sheets so obtained have been described above. The results obtained can be summarized as follows:

(1) The manufacturing facilities consist mainly of ordinary continuous hot-dipped galvanizing equipment, with accessory apparatus for processes such as electrodegreasing, roll coating, flame wiping and roll

bending.

(2) The stop-off agent consists of a water slurry containing sodium silicate, sodium borate, magnesium oxide, titanium oxide and aluminum oxide, and possesses characteristics such as the capability of shielding steel sheets from zinc and the atmosphere, poor zinc wettability of the coating itself, and the amenability to exfoliation of the coating by roll bending.

(3) The ungalvannealed surfaces possess superior corrosion resistance after coating, since fine phosphate crystals precipitate due to the adhesion of several milligrams of zinc and magnesium per square meter of surface.

(4) The present galvannealed steel sheets manufactured from extra low carbon steel containing niobium, maintain nonaging and deep drawability characteristics even after galvannealing, with hot-dipped galvannealed surfaces with excellent anti-perforation characteristics on one side and ungalvannealed surfaces with superior corrosion resistance after painting on the other.

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