# Continuous Coating of Insulating Film on Stainless Steel Foil

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# Abstract

An insulating film of sol-gel silica glass has been fabricated on a stainless steel foil by a continuous roll to roll process using a micro gravure coater with a furnace. A film with a thickness of  $1 \ \mu$  m and resistivity of 1E + 09 cm<sup>2</sup> has been obtained on a ferritic stainless steel foil of 80  $\mu$  m. The stainless steel foil with an insulating film may be applied to flexible substrates for a solar cell and others.

#### 1. Introduction

Stainless steel foil is produced through high-precision rolling of high-purity stainless steel material to a thickness of approximately 100  $\mu$  m or less; it is lighter in weight and has excellent flexibility and corrosion-resistance properties. By virtue of its superior strength and corrosion resistance to those of aluminum or copper foil, stainless steel foil is used for applications such as the springs for hard disc drives and other electronic devices. It has also been applied as a catalyst carrier for exhaust gas purification systems in the automobile industry.

While glass is mainly used at present for the substrates of thinfilm solar cells, display devices and the like, new stainless steel foil products with various kinds of insulating coating films are being developed for such applications to replace glass. Use of the stainless steel foil with an insulating film makes it possible to manufacture these devices in the same structure as with glass substrates because of the insulating film, and in addition, brings about the original advantages of stainless steel foil. One of the advantages is that size increases are easier, while weight reduction of roof-mounted solar cells is also easier than glass substrates; the demand for these cells for residences and commercial buildings is expected to increase rapidly. Because of its flexibility, the stainless steel foil with an insulating film is attracting attention also as the material for the substrates of flexible display devices and electronic paper. Furthermore, use of the stainless steel foil for the substrates of these products allows a continuous roll-to-roll manufacturing process suitable for mass production, making it possible to reduce production costs.

As the material for flexible insulating substrates of these devices, good heat resistance is a significant advantage of the stainless steel foil with an insulating film over organic resin films, its competitor. In this respect, the insulating film to be applied to the stainless steel foil must have heat resistance to temperatures between 250 and 600

. Nippon Steel Corporation has studied various sol-gel materials for use as the insulating coating film, focusing mainly on organic/inorganic hybrid materials<sup>1-3)</sup>. As a result, the company has found that hybrid sol-gel materials that have a network structure of metal oxide (M-O) exhibit heat resistance superior to that of organic resin. Based on such findings, we developed a technology to coat a surface of stainless steel foil in coil with an insulating film by applying a silica-based, heat-resistant coating solution to the foil and drying, baking and coiling it on a continuous processing line. This paper reports the developed technology.

# 2. Development of Silica-based Insulating Coating Film

### 2.1 Synthesis of silica-based coating solution

A silica-based coating solution was synthesized using tetramethoxysilane and methyltriethoxysilan as the raw materials and hydrolyzing them in an organic solvent using titanium tetraethoxide and acetic acid as catalysts; titanium tetraethoxide is known to act as a catalyst to accelerate the hydrolysis and polycondensation reactions of alkoxysilane<sup>4</sup>). Through hydrolysis and polycondensation, tetramethoxysilane and methyltriethoxysilan form a network structure of siloxane bonds (Si-O-Si) modified with methyl groups as shown in **Fig. 1**. The properties of the coating solution thus synthesized are different depending on the mixing ratio of the raw materials and the kinds and addition amounts of the organic solvent and catalysts.

As an example, Fig. 2 shows the relationship between the addi-

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Fig. 1 Synthesis of coating solution



Fig. 2 Average molecular weight of coating solution and pencil hardness of film after drying versus acetic acid content

tion amount of acetic acid relative to the total Si, the average molecular weight of the coating solution and the pencil hardness of the film in the case where tetramethoxysilane and methyltriethoxysilan were mixed in a ratio of 1 to 1. The molecular weight of the coating solution tended to increase with the addition of acetic acid up to a molar ratio of 0.2 relative to Si, and then saturate in the range of molar ratio higher than 0.2. The hardness of the coating film after drying at 160 for 1 min also changed with the molecular weight of the coating solution: the higher the molecular weight of the solution, the higher the pencil hardness of the film tended to be. The composition of the coating solution was finally selected in overall consideration of factors such as the film hardness after drying, the change in the molecular weight over time, the thickness, resistivity and heat resistance of the coating film obtained.

#### 2.2 Factors influencing resistivity of coating film

#### (1)Film thickness

A synthesized coating solution was applied to a surface of foil of a ferritic stainless steel YUS 190 (equivalent to JIS SUS 444) using a bar coater; here, bars having different surface roughness were used to change the thickness of the coating film. The thickness of the foils was 80  $\mu$  m, and their surface finish was super-bright (SB), i.e. Ra < 0.03  $\mu$  m. After the application of the coating solution, the foils were dried at 160 for 1 min to remove volatile matter such as the organic solvent, and then heat treated at 400 for 30 min in a nitrogen atmosphere to harden the coating film. To evaluate the resistivity of the film, voltages were applied between a Pt upper electrode 1 mm in diameter and the foil (lower electrode), and the resistivity of the coating film was calculated from the minute electric current between the two.

**Fig. 3** shows the relationship between the thickness and resistivity of the coating film; here, the resistivity is the resistance under application of 60 V. A resistivity of  $1 \times 10^9$  cm<sup>2</sup> or higher was obtained with a film thickness of approximately 1  $\mu$  m or more. However, with a film thickness of 1.5  $\mu$  m, there was a problem in that the film cracked and short circuiting occurred between the upper and lower electrodes. It was presumed that when the film thickness is less than 1  $\mu$ m, the coating film has defects owing to uneven surface condition of the foil such as microscopic protrusions leading to a decrease in resistivity. Therefore, to secure a sufficient resistivity, it is necessary to control the coating film thickness to approximately 1  $\mu$  m.

(2)Temperature and time of heat treatment

To examine the influences of the temperature and time of heat treatment on the resistivity of the coating film, the coating solution was applied to the coils of the foil, which were then dried and heat treated in a nitrogen atmosphere at 300 and 400 for different time



Fig. 3 Relationship between film thickness and resistivity

periods. Measurements were then taken for the resistivity of the coating films at 60 V. Fig. 4 shows the results. The resistivity was higher when the heat-treatment temperature was 400 than when it was 300 . In the case of the heat treatment at 400 , the resistivity of the coating film after a heat-treatment time of as short as 1 min was substantially the same as that of 30 min.

(3)Atmosphere of heat treatment

The air inevitably comes into a continuous heat-treatment furnace together with the processed material even when nitrogen gas is blown into it. In such an event, humidity in the air may interfere with the polycondensation reactions of silanol groups, and oxygen in the air pyrolytically decompose methyl groups. In consideration of the above, the foils at were heat treated at 350 for 5 min using a tubular furnace under the following three conditions: blowing nitrogen gas into the furnace at a flow rate of 1000 l/min; blowing compressed



Fig. 4 Resistivity versus heat-treatment temperature and time

1.0E+11

1.0E+10

1.0E+08

1.0E+06

1.0E+05

1 0E+04

1.0E+11

1.0E+10

1.0E+09

1.0E+08

1.0E+07

1.0E+06

1.0E+05

1.0E+04

0

20

Resistivity ( Q • cm<sup>2</sup>)

(c)

٥

20

40

Voltage (V)

40

Voltage (V)

(Ω • cm<sup>2</sup>) 1.0E+09

Resistivity 1.0E+07

(a)

air having a dew point of -27 at the same flow rate; and leaving the furnace open to the air. As seen in Fig. 5, the resistivity behavior of the specimens heat treated in the compressed-air atmosphere was very similar to that of the specimens heat treated in the normal-air atmosphere: the resistivity of these specimens was lower than that of the specimens heat treated in the nitrogen atmosphere by two to three decimal places. The fact that the resistivity of the former specimens was lower irrespective of the humidity in the furnace atmosphere seems to indicate that the deterioration of the resistivity resulted from oxygen in the air.

To study the influence of the oxygen concentration in the furnace atmosphere on the resistivity, the foils were heat treated in a tubular furnace at different temperatures for 2 min blowing nitrogen gases of different oxygen concentrations into the furnace, and measured the resistivity of the coating film. Fig. 6 shows the results. When



Fig. 6 Effect of heat-treatment temperature and atmosphere on resistivity (a) N, 100%, (b) 0.01%O,/N, (c) 0.1%O,/N, (d) 0.5%O,/N,

the oxygen concentration of the gas blown into the furnace was 0.01% or less, the coating film showed a good resistivity of approximately  $1 \times 10^{9}$  cm<sup>2</sup> or higher irrespective of the voltage applied. With an oxygen concentration of 0.1%, on the other hand, the resistivity was good when the heat-treatment temperature was 450 , but when the heat-treatment temperature was 400 , the resistivity fell by one decimal place as the applied voltage increased. The resistivity was markedly low when the heat-treatment temperature was 500 . With an oxygen concentration of 0.5%, the resistivity decreased as the heat-treatment temperature increased.

(4)Mechanism of decrease in resistivity

To study the relationship between the conditions of heat treatment and the resistivity of the coating film, the foils were treated at 450 for 2 min in different furnace atmospheres, namely 100% nitrogen, 0.5% oxygen + nitrogen and normal air, and the films were examined by the Fourier transform infrared spectrometry (FTIR) by the reflection method. **Fig. 7** shows the results. The broad peak at 1,000 to 1,150 cm<sup>-1</sup> results from Si-O bonds. As the oxygen concentration in the furnace atmosphere increased, the peak resulting from Si-CH<sub>3</sub> bonds near 1,250 cm<sup>-1</sup> decreased, if only slightly, and the peak resulting from silanol (SiOH) groups in the coating film near 900 cm<sup>-1</sup> increased. We presume that under the heat treatment in an atmosphere containing oxygen, silanol groups formed after the pyrolysis of methyl groups.

The broad peak of the stretching vibration of O-H at 3,000 to  $3,600 \text{ cm}^{-1}$  tended to increase as the amount of silanol groups increased. This is because the existence of highly polarized silanol groups caused the coating film to absorb humidity in the air more easily. Thus, it was presumed that heat treatment in an oxygen-rich atmosphere increased the amount of silanol groups in the film and the humidity it absorbed, leading to a decrease in the resistivity of the film.

The influence of the temperature of the heat treatment on the resistivity can also be explained in terms of the amount of silanol groups in the coating film. Since the coating solution is prepared through the hydrolysis of alkoxysilane as shown in Fig. 1, the coating film that is formed after the drying of the solution contains silanol groups in a quantity. The rate of the polycondensation reactions of silanol groups during the heat treatment increases as the heat-treatment temperature becomes higher, and the amount of silanol groups remaining in the film decreases; for this reason the resistivity increases as the heat-treatment temperature becomes higher as shown



Fig. 7 FT-IR spectra of films heat-treated in (a)  $\rm N_2,$  (b) 0.5%O\_2/N\_2, and (c) Air

in parts (a) and (b) of Fig. 6. With respect to part (c) of Fig. 6, on the other hand, while the resistivity of the film heat treated at 450 is higher than that of the film heat treated at 400 because of the decrease in the amount of silanol groups resulting from the polycondensation reactions, the resistivity of the film heat treated at 500 is lower presumably because of the increase in the amount of silanol groups that form after the pyrolysis of methyl groups as a result of 0.1% oxygen. In the case of part (d) of Fig. 6 where the furnace atmosphere contains 0.5% oxygen, the pyrolysis of methyl groups are significant, and for this reason, the resistivity decreases as the temperature of the heat treatment becomes higher.

(5)Condition of heat treatment in continuous processing line

The above tests made it clear that the resistivity of the coating film began to decrease as the concentration of oxygen in a nitrogen atmosphere increased to 0.1% or more. With a small-scale continuous processing line, it is difficult to control the amount of air mixing with the furnace atmosphere, or the oxidizing or reducing capacity of the furnace atmosphere. In addition, the bluing of the foil surface without the coating film due to an oxidizing atmosphere is another concern. In consideration of the above, it was decided to use a reducing atmosphere of nitrogen gas containing 1% hydrogen as a realistic countermeasure against the oxidation of the film. However, yet another concern with a small-scale line was that, since the emissivity of the coating material was unknown, the foil could be discharged from the furnace before being heated to the furnace temperature when the line speed was high. In consideration of all of the above, tests were conduct on heat treatment at 550 and 600 for a holding time of 0 min in the nitrogen atmosphere containing 1% hydrogen. As a result, high resistivity of 1E + 09 cm<sup>2</sup> or more was obtained up to 60 V under any of the test conditions.

#### **3.** Tests of Continuous Film Application 3.1 Specification of test equipment

Tests were conducted on continuous roll-to-roll film application to stainless steel foils using a multi-test coater OS-300 made by Ohmura Research Laboratories Co., Ltd. (Nagasaki, Japan). The coater was originally designed for applying a solution to plastic films using a micro gravure roll or the like and then drying the solution in the air. A micro gravure roll is capable of non-contact application of a coating solution evenly to a thin substrate, and is suitable especially for forming a thin film. Additionally, as is clear from the results of the tests described earlier, it is necessary for realizing a good resistivity of a sol-gel film to bake the film at high temperatures and in a low-oxygen atmosphere, and for this reason, a muffle-type baking furnace into which nitrogen and hydrogen could be blown was newly installed at the exit from the final drying oven.

**Fig. 8** is a schematic illustration of the test equipment. The length of the muffle furnace was 1.5 m, and the length of each of the drying ovens 1, 2 and 3 was also 1.5 m. Coils of stainless steel foil of YUS 190, 150 mm in width and 80  $\mu$  m in thickness, were used as the specimens, and the coating solution was supplied to the coater after passing through a filter having a filtering accuracy of 1  $\mu$  m. **Table 1** shows an outline of the specification of the test equipment. Since the equipment was originally designed for processing plastic films, some modifications were introduced to it for processing stainless steel foils.

### 3.2 Film forming

(1)Film thickness control

The application amount of the coating solution was controlled



Fig. 8 Schematic illustration of coating equipment

Table 1 Specification of coating equipment

Coating width		300mm
Line speed		1-20m/min
Drying oven	Temperature	Max. 190
Furnace	Temperature	Max. 600
(newly-installed)	Atmosphere	$H_2(0-1\%) + N_2$
	Dew point	< -20

by changing the surface condition of the micro gravure roll and the line speed: rolls having three levels of surface condition, namely #150, 100 and 80 in terms of the pitch of grooves, were prepared, and the line speed was set at two levels, 1 and 2 m/min. Fig. 9 shows the relationship between the coating conditions and the X-ray fluorescence intensity of Si in the film; the X-ray fluorescence intensity of Si increases with increasing film thickness. When the line speed was 2 m/min, the pick-up amount of the coating solution increased as the groove pitch number of the micro gravure roll became smaller, and the film thickness increased as a consequence. However, in a film thickness range where the X-ray fluorescence intensity of Si was more than 800 kcps, the film developed cracks and flaked off. When the line speed was 1 m/min, on the other hand, it was confirmed that the coating solution dripped off the foil surface before the drying and the film thickness was not always proportionate to the pick-up amount. The film thickness decreased as the setting of the furnace temperature became higher at either of the line speeds. This is presumably because the low-molecular-weight components of the coating solution formed 3-member rings or the like and escaped from the system before they were incorporated into the network structure of the film, and the effects of these processes became more conspicuous as the furnace temperature became higher. (2)Resistivity

**Fig. 10** shows the relationship between the temperature setting of the muffle furnace, the X-ray fluorescence intensity of Si (film thickness) and the ratio of insulated points. Here, the ratio of insulated points.



Fig. 10 Ratio of insulated points versus XRF intensity of Si



Fig. 9 Effect of coating conditions on XRF intensity of Si Line speed (a) 2m/min, (b) 1m/min

lated points was measured by providing 16 upper Pt electrodes each 1 mm in diameter, applying voltages up to 60 V between the upper electrodes and the foil and counting the number of the points where short circuiting did not occur. As is clear from the graph, the ratio of insulated points was 100% with films thicker than a certain value. It became also clear that the ratio of insulated points was higher with higher temperature setting of the furnace. This is because the amount of silanol groups in the film decreases as the furnace temperature becomes higher as far as the oxygen concentration in the furnace atmosphere is low.

(3)Trial Production of Coils of Stainless Steel Foil with Insulating Film

Based on the above results, the insulating films was applied to coils of the stainless steel foil under conditions selected to realize



Photo 1 Photograph of a stainless steel foil with an insulating film

good resistivity of the film and to prevent its flaking off due to excessive thickness. **Photo 1** shows a stainless steel foil with an insulating film thus obtained. Evaluations were made of the resistivity of the coating film using three enlarged upper electrodes, each 1 cm square. It was found that the resistivity was as high as 1.0E + 09 cm<sup>2</sup> or higher up to an applied voltage of 110 V. The result evidences the formation of uniform insulating films having very few defects.

#### 4. Closing

A coating solution was synthesized for forming a silica-based insulating film, continuously applied it to a surface of stainless steel foil and the foil was dried and heat treated. The resistivity of the insulating film thus formed was as high as 1.0E + 09 cm<sup>2</sup> or more. The developed silica-based insulating coating film is a silica film containing methyl groups as its only organic components, and excellent in heat resistance. While this paper has focused on the formation of an insulating film approximately 1  $\mu$  m in thickness, Nippon Steel is also developing other insulating films approximately 10  $\mu$  m in thickness that exhibit higher withstanding voltages.

Besides the stainless steel foils with an insulating film, the company has also proposed other metal foil products with different kinds of functional coating films having good adhesion or oxidation resistance, and is endeavoring to develop new metal foil products taking advantage of such functional films.

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