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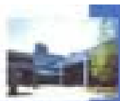

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Corrosion Protection of a Metal Spray Coating By Using An Inorganic Sealing Agent For Its Micropores

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An investigation has been carried out to determine the corrosion protection that an inorganic sealing agent provides for micropores of spray coating films. The sealing agent used is composed of silicate compounds and easily penetrates the micropores of spray coating films. Generally speaking, its stability under ultraviolet light is much higher than any organic sealing agents available. In this study, the sealing capability of the inorganic agent was tested using several kinds of spray-coated specimens. In addition, observations were made about the anti-corrosion characteristics of these sealed specimens. The samples used for this study were Zn/Al spray coated steel and pure aluminum spray coated steel. The inorganic silicate-sealing agent was applied to all of the specimens. However, some of them were ground until the sealing agent was completely removed from the surface of the specimens. For the latter case, the silicate-sealing agent remained only in the micropores of the spray-coated films. These specimens were observed by SEM-EDX to observe the sealing condition. Their corrosion characteristics were also observed by performing a CASS test. Using these results, we were able to evaluate the sealing agent's protective capability for spray coatings.

1 Introduction

Recently, the demand for high corrosion resistance of structural steels has been increasing each year. Various materials including weather resistant steel, hot galvanized steel etc. have been investigated. Corrosion resistant spray coating is one of the promising processes to improve the weather resistance of steels. Even though aluminium, zinc and aluminium-zinc spray coatings have high corrosion resistance, they often need other top coatings to prolong their life cycles for practical use in atmospheric environments. Many kinds of top coatings have been proposed so far. Sealers for pores of spray coatings seem to be a promising choice for this purpose. Spray coating films have many pores which may be filled with sealers to decrease corrosion characteristics.

In this paper we focused on the application of a silicon sealer to reduce corrosion characteristics. The sealer is basically an alkoxysilane compound that could penetrate into pores easily. This is due to their high fluidity before they are completely hardened by the reaction of the humidity of air. Today, the top coatings have some restrictions in regards to the environmental standards. However, this silicon sealer will be in compliance with the environmental regulations.

This paper provides information about the corrosion resistance of the sealed aluminium and zinc/ aluminium spray coatings. It also discusses the applicability of the sealer to the corrosion protection of spray-coated steels in atmospheric environments.

2 Experimental

2.1 Specimens and Sealer

The substrates for all coated specimens were plain carbon steels (JIS SS400). The dimension of each specimen was 150mm x 70mm and the thickness was 3mm. The two kinds of spray coatings, pure aluminium and zinc-aluminum coatings by arc spray coating (Daihen Co. AS400), were applied to the steels. The diameters of the wire for the spray coating were 1.3mm. Zinc was used as a negative electrode and aluminium as a positive one for the Zn/Al spray coating. On the other hand, aluminium wire was used as both positive and negative electrodes for the aluminium spray coating. All of these films were spray coated by arc spray coating with a certain voltage (21V), current (250A) and the wire was provided at a certain rate (20m/min). The air pressure was 0.58Mpa. The thickness of the spray coated films ranged from 130 micrometers to 250 micrometers. The schematic figure for the spray coating in this study is shown in Fig.1. These spray coated specimens without any post treatments served as a control for corrosion characteristics. They were called "non-sealed specimens" in this study.

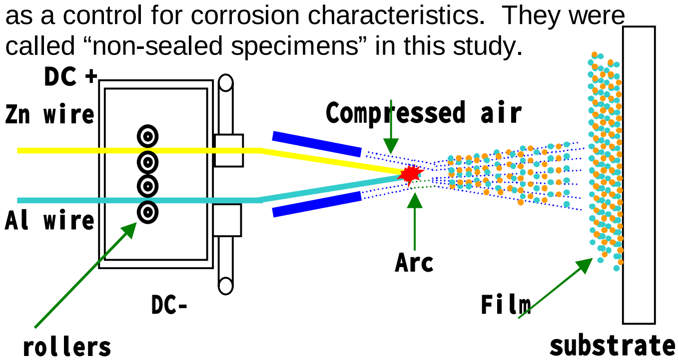

Fig.1 Schematic diagram for spray coating

A silicon sealer was applied to these spray coated specimens. The silicon sealer was one of alkoxysilane compounds (Rhombic Co., 1-69 Shiohama, Yokkaichi, Mie 510-0851, Japan) and it penetrated into the pores of coatings very easily due to its low viscosity (61.5mPa･s). After it inter-penetrates into pores and coats the spray coating, it reacts with the moisture of the ambient atmosphere and hardens due to the formation of inorganic polymer. It is usually very stable under ultraviolet light. Each spray-coated specimen was ground and

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then the silicon sealer was applied to it with brushes. For some specimens, the sealed surfaces were ground once again so that no sealer remained on their surfaces. In these cases, sealers existed only in the pores of the surface layers. We call this kind of specimen "sealed specimen" in our study. On the other hand, we made another kind of specimen in which the sealer mixed with CoO based paints was applied to the sealed specimens. We call them "coated specimens" in our study. For the latter, the spread was 130g/m^2. The coating process by the silicon sealer is shown in the Fig.2 schematic.

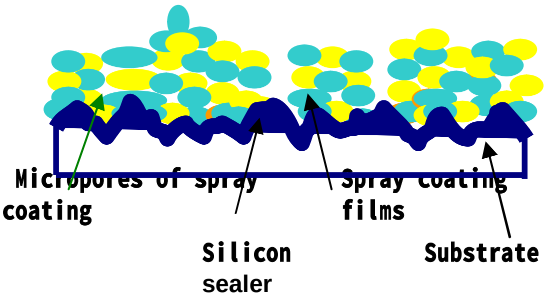


Fig.2-1 Sealed spray coated specimens

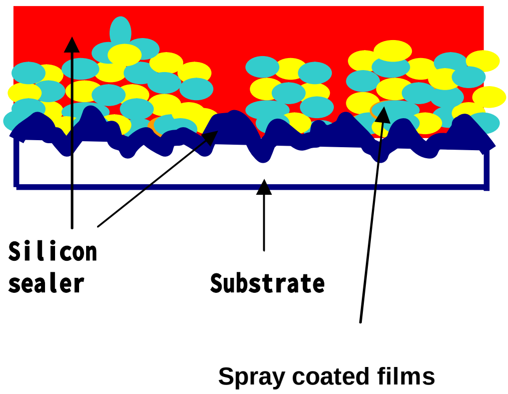


Fig.2-2 Coated spray-coated specimens

2.2 Experimental Procedure

2.2.1 Cass Test

Corrosion characteristics were evaluated mainly by CASS tests. The solution used for the CASS test was composed of NaCl (50g/L), $CuCl_2 \cdot 2H_2O$(0.26g/L) and acetic acid (1ml/L). The pH was adjusted to 3.0-3.2. The CASS Test was carried out according to the Japanese Industrial Standard (JIS H8502: 1999). The temperature in the chamber was 50 degrees C, using the commercially produced apparatus (Suga, CAP-90). The amount of spray was 1.5/80cm^2/h and the compressed air pressure was 0.1MPa.

2.2.2 Surface Observation

Surface Observation was done by both the naked eye and by SEM-EDX. For the former, each specimen before and after CASS tests was checked by the naked eye and a digital camera took the pictures. On the other hand, the cross sections of specimens' surfaces were observed by a scanning electron microscope (SEM: Hitachi S-4300)-EDX (Horiba EMAX-7000). The acceleration voltage was 20kV and element mapping was carried out for cross sectional surface areas of the specimens.

3 Experimental Results

3.1 Cass Test Results

Seven kinds of specimens were examined by CASS tests and their corrosion characteristics were evaluated by gravimetry. The specimens are shown in Table 1.

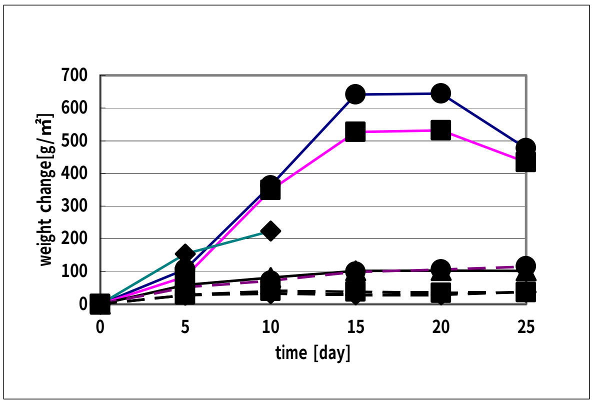
Table 1 Specimens used in this study

Specimens	Contents
Spec.1	Zn-Al spray coating without silicon sealer
Spec.2	Zn-Al spray coating whose pores were filled with silicon sealer
Spec.3	Zn-Al spray coating whose surface was coated by silicon sealer.
Spec.4	Aluminum spray coating without silicon sealer
Spec.5	Aluminum spray coating whose pores were filled with silicon sealer
Spec.6	Aluminum spray coating whose surface was coated by silicon sealer.
Spec.7	Hot Dip Galvanized Steel specimen

Spec.7, which is hot dip galvanized steel (JIS HDZ55) without any top coatings, was used as the reference in this study. All of the other specimens were spray-coated specimens. Spec.1 was the non-sealed Zn-Al alloy spray coated specimen. Spec.2 was the sealed Zn-Al alloy spray coated specimen. Spec.3 was the coated Zn-Al alloy spray coated specimen. Spec.4 was the non-sealed aluminium spray coated specimen. Spec.5 was the sealed aluminium spray coated specimen. Spec.6 was coated aluminum spray-coated specimen.

The weight change during CASS tests for all of these specimens is shown in Fig.3. The original weights were measured before CASS tests and then again measured with time successively. Before the weights for the specimens were determined, the specimens were washed with tap water. This was done in a way so that it didn't hit the specimens' surfaces and dried in 24 hours at 25 degrees C. In this case, the surface corrosion products were not removed by hydrochloric acid.

For spec.7, the CASS test was stopped at the end of 10 days. When the general tendencies were compared between Zn-Al spray-coated specimens and Al spray coated ones, the latter showed high corrosion resistance. It suggests that the aluminium spray coated specimen generally has higher anti-corrosive characteristics than Zinc-aluminum spray coated specimens. Spec.1 (non-sealed Zn-Al spray coated specimen) was the most corrosive and much more corrosive than both of the hot dip galvanized specimen (spec.7) and non-sealed aluminum spray coated specimen (spec.4). Generally speaking, spray coated surfaces are more porous than hot dip galvanized ones. Therefore, the corrosion characteristic for the former is higher than that for the latter. When the silicon sealer was applied to the spray coated specimens, the corrosion resistance improved. For the sealed Zn-Al spray coated specimen (spec.2), the corrosion resistance was better than the non sealed specimen (spec.1), although it was still more corrosive than that of the hot dip galvanized steel (spec.7). This suggests that the sealing of pores by silicon sealer improved the corrosion prevention characteristics to some extent. However, the corrosion resistance was improved



— ● — spec.1 — ■ — spec.2
------■---- spec.3 ----▲--- spec.4 ----●--- spec.5
----◆------ spec.6 — ◆ — spec.7

Fig. 3 Weight change during CASS tests without acid treatment.

drastically for the coated Zn-Al spray coated specimen (spec.3). It suggests that top coating of spray-coated specimens by the silicon sealer could improve the anti-corrosiveness. In this case, the anti-corrosiveness for spray coating was higher than that of hot dip galvanized specimens.

On the other hand, the corrosion prevention characteristic for the aluminum spray coated specimen without silicon sealer was inherently very high, according to Fig.3. The sealed specimen for it improved anti-corrosiveness slightly. However, the coated specimen for aluminum spray coating improved the anti-corrosiveness drastically. When the coated specimens for aluminum spray coating was compared with that for Zn-Al spray coating, both anti-corrosiveness were almost the same. It indicates that the coating by silicon sealer was highly effective for the corrosion prevention.

After the CASS test, all of these specimens were immersed in hydrochloric acid and the corrosion products were removed. Then the weight was measured and the corrosion rates were calculated in the unit of $g/m^{2/}$year. The results are shown in Fig.4. The non-sealed Zn-Al spray coated specimen (spec.1) has the highest corrosion rate among the specimens

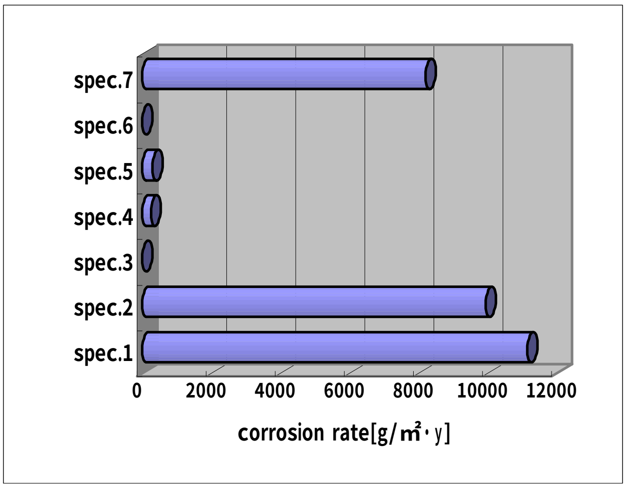


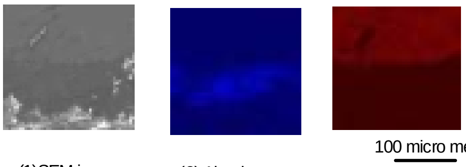
Fig. 4 Corrosion rates for different specimens calculated on the results of gravimetry (with acid treatment).

investigated in this study. When the silicon sealer was applied to the specimen and the pores were filled with it (spec.2), the corrosion rate was decreased to some extent. However, it was still slightly higher than that of the hot dip galvanized steel. However, for the coated specimen for Zn-Al spray coating (spec.3), the corrosion rate was decreased drastically. It was much lower than that of the hot dip galvanized specimen (spec.7). The aluminum spray coated specimen (spec.4) had a pretty low corrosion rate. It was much lower than that of the hot dip galvanized specimen (spec.7). From this perspective, we can conclude that the anti-corrosiveness for the aluminum spray coated specimen was inherently pretty high. When the pores were filled with silicon sealer (spec.5), the corrosion rate decreased slightly than that of the non-sealed specimen (spec.4). Since the non-sealed specimen had high corrosion resistance inherently, the sealing effect in this case was not so significant. However, the coated specimen for the aluminum spray coating showed the very low corrosion rate. The extremely low corrosion rate for the coated Zn-Al spray coated specimen (spec.3) was almost the same with that of the coated aluminum spray coated specimen (spec.6). All of these results suggest that the application of silicon sealer to the top coating was very effective to prevent the corrosion for spray-coated specimens.

3.2 Surface Observation

From visual checks for all of these specimens, the following characteristics were observed.

For non-sealed specimens, Zn-Al spray coated specimens showed much more corrosive and rugged surfaces than aluminum spray coated specimens. The tendency coincided with the result for gravimetry described in the previous section. For sealed specimens, the appearance was not so different between Zn-Al and Al spray coated specimens. For coated specimens, both types of spray coated specimens didn't show any significant difference and both surfaces were not so corroded. However, the Zn-Al spray coated specimen produced white rust at the deficient coating site on the surface.


100 micro meter

(1)SEM image (2) Aluminum distribution (3) iron distribution

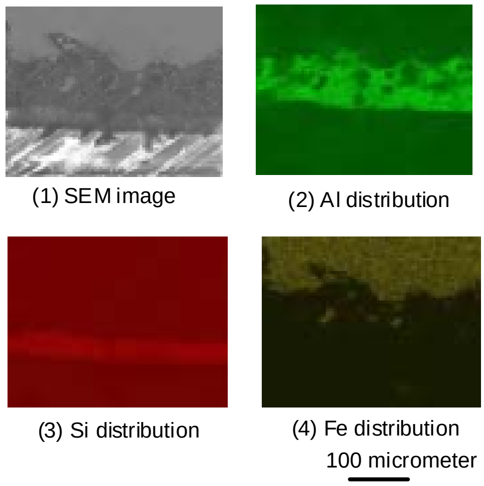
Fig5 SEM-EDX analysis of non-sealde alumnum spray coated specimen after CASS test

The SEM-EDX analyses for all of these specimens also show that the non-sealed specimen was highly corrosible and that the sealed specimens were still corrosible. However, this indicates that the coated specimens by silicon sealer had higher corrosion resistance. Fig.5 shows the results of a non-sealed specimen for aluminium sprayed coating. Fig.5-(1) was the SEM image for the cross section of the non-sealed specimen after a CASS test. Fig.5-(2) shows the aluminum distribution in the vicinity of the surface. For the top of the surface layer, we could observe the sites where the aluminium content was very low. It corresponds to the corroded sites. Fig.5-(3) shows the iron disbtribution which fixed the border between the substrate and the sprayed layer. Fig.6 shows results of a sealed specimen for aluminum spray coating. Fig.6-(1) was the SEM photo of the cross secion in the vicinity of the specimen's surface. Fig.6-(2) and (3) indicate aluminum and iron distribution, respectively. Fig.6-(2) shows that some sites of the aluminum sprayed layer were removed by corrosion. It suggests that the sealed specimen was also corrosible. On the other hand, Fig.7 shows the results of the coated specimen for aluminum spray coating. Fig.7-(1) was the SEM photo of the cross section for the specimen. Fig.7-(2), (3) and (4) correspond to the element distributions of aluminum, silicon and iron, respectively, in the same area. These photos show that the top coating composed of silicon sealer was very stable and had high corrosion resistance and that it completely protected the spray coating and substrate. The results indicate that the coating of a sprayed specimen had very high corrosion resistance.


200 micrometer

(1) SEM image (2) Al distribution **(3) Fe distribution**

Fig.7 SEM-EDX results of sealed Al sprayed specimen


(1) SEM image (2) Al distribution

(3) Si distribution (4) Fe distribution

100 micrometer

Fig.7 SEM-EDX results of coated Al sprayed specimens

3.3 Discussion

The silicon sealer used in this study significantly improved the corrosion resistance for spray coated specimens. The filling in of the surface pores for spray-coated specimens by the sealer increased the corrosion resistance to some extent. However, the top coating was more effective for corrosion prevention. In this study, the spread was about 130g/m2. However, the amount of the sealer can be decreased as much as possible. We have not clarified yet, how much we could decrease the thickness of the top coating for the effective coating. However, it can lead to the cost for the coating and therefore, it is a very important factor from the viewpoint of practical applications. Being compared with hot dip galvanized steels, the coated sprayed specimens by silicon sealer seem to have longer lives for their practical use. The sealer has a higher advantage for outdoor use than other organic conventional sealers, since the former is much more stable under ultraviolet light. Therefore, we can expect that the coated sprayed steels will be used for the steel structures much more often in the near future, when this type of inorganic sealer will be applied to aluiminum and zinc-aluminum spray-coated steel structures.

4. Conclusions

The application of an inorganic silicon sealer was applied to aluminum sprayed and zinc-aluminum sprayed specimens and the corrosion characteristics were investigated mainly by a CASS test. The following results were obtained in this study.

(1) Zinc-Aluminum spray coated specimens were more corrosible than that of hot dip galvanized steel.
(2) When the pores of the zinc-aluminum spray coated specimens were filled with the silicon sealer, the corrosion resistance was improved and the difference between hot dip galvanized specimens and the spray-coated specimen became slight.
(3) Aluminum spray coated specimens without silicon sealer showed corrosion resistant characteristics which were much higher than that of Zn-Al spray coated specimens.
(4) The filling in of pores for spray-coated specimens with the silicon sealer improved their corrosion prevention characteristics.
(5) The top coating, in addition to the filling of pores (of the spray coating with the silicon sealer) improved the corrosion prevention characteristics drastically.

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