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Development and Quality Properties of Aluminized Stainless Steel Sheet

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Abstract:

Aluminized stainless sheet steel was developed by taking advantage of the cathodic protection afforded by aluminized coating to improve the pitting corrosion resistance of automobile exhaust system components. Aluminized stainless steel, which has the corrosion resistance of the aluminized coating itself improved by chromium diffusion from the steel base into the aluminized coating, has high corrosion resistance, and is expected to also have many applications as a high-grade building material. The material's development history and quality properties are also described.

1. Introduction

Stainless steel sheet excels in corrosion resistance and heat resistance, and is being increasingly used in automobiles, household appliances, and construction materials, among other things. It may develop local corrosion, called pitting corrosion, depending on the corrosive environment and may be susceptible to pinpoint rust in salty environments associated with coastal areas. Coated stainless steel sheet was developed to account for these shortcomings of bare stainless steel and to impart new properties to stainless steel.

The above-mentioned weaknesses of bare stainless steel can be overcome by coating it with a metal that provides a cathodic protection effect. Since its potential is more noble than that of carbon steel, stainless steel may be cathodically protected by not only zinc coatings, but also aluminum and tin coatings that cannot be expected to cathodically protect carbon steel. The stainless steel metal coating has been studied in this context, and a new type of aluminized stainless steel sheet with excellent corrosion and heat resistance was developed. The development history and quality properties of the aluminized stainless steel follow.

2. Concept of Development

Aluminized stainless steel sheet was originally developed for automotive exhaust system components in general and mufflers in particular. Cold-rolled carbon steel and aluminized carbon steel with higher corrosion resistance were long used as automotive exhaust system materials. The automobile exhaust emission regulations of 1978 required the installation of three-way catalytic converters for cleaning the exhaust gases. The resultant change in exhaust gas composition produced a more corrosive environment. In addition, the muffler service life warranty for three years or 60,000 km, whichever comes first, was introduced in 1989. These moves led to demand for the development of muffler materials with still higher corrosion resistance.

The authors first investigated the corrosive environments to which the interior and exterior muffler surfaces are exposed. The

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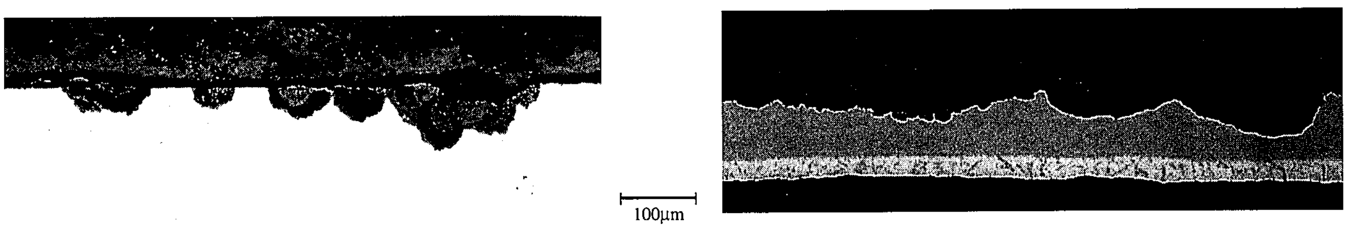
Table 1 Chemical analyses of exhaust gas condensates

Car	pH	Na	K	Cl^-	F^-	Br^-	SO_4^{2-}	NO_3^-	NO_2^-	NH_4^+	HCHO	Formic acid	Acetic acid	Butyric acid
A*[1]	3.9	0.1	0.1	0.2	0.9	1.6	ND(<1)	ND(<1)	3.6	24	12	1.1	60	5.3
B*[2]	6.4	0.1	0.1	0.3	0.6	26	7.3	3.3	2.2	92	1.7	3.9	ND(<2)	5.3

Regular gasoline was used, and samples were taken when cars were in idling condition.
A*[1]: 1977 model car without catalytic converter
B*[2]: 1987 model car with catalytic converter



(a) 11% Cr steel (bare)

(b) Hot-dip aluminized low-carbon steel

Photo 1 Corrosion of mufflers in actual cars

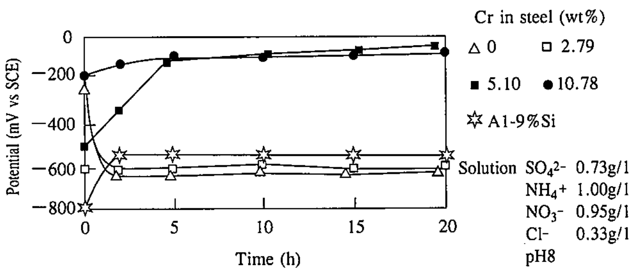


Fig. 1 Immersion potential in exhaust system interior surface environment

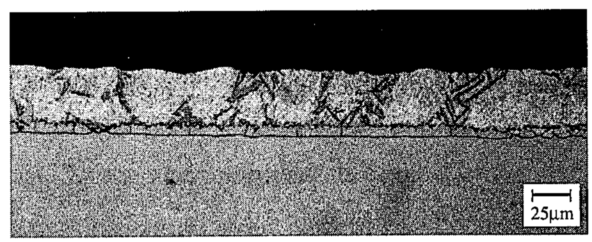


Photo 2 Cross-sectional microstructure of aluminized stainless steel

exhaust gas, whose composition is changed by the catalytic converter, is likely to condense in the muffler. The condensate greatly affects the life of the muffler. The corrosive environment outside the muffler is similar to that of the outer body panels. To prolong muffler life, greater attention needs to be focused on the internal environment. **Table 1** lists typical analyses of exhaust gas condensates formed on the interior surface of mufflers[1]. Among the main constituents that may affect the corrosion of the muffler are Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, and organic acid. Since the use of the catalytic converter increases the likelihood of NH_4^+ formation, the condensate is found to change from acidic to neutral. Driving the car raises the temperature inside the muffler. As the condensate is heated and dried in this process, NH_4^+ evaporates, reducing the pH of the condensate. The corrosion behavior of the muffler material also greatly depends on the driving condition of the car. When the car is driven at high speed, the condensate is less likely to collect in the muffler, resulting in less muffler corrosion. When the car is repeatedly started and stopped, the muffler is corroded at an accelerated rate[2].

Photo 1 shows the interior surface corrosion of commercial mufflers made of aluminized low-carbon steel and bare 11% chromium steel[3]. The corrosion of the bare low-grade stainless steel occurs as pitting corrosion. The aluminized low-carbon steel is generally severely corroded. The corrosion of aluminized low-carbon steel starts with the aluminized coating. When the corrosion permeates the alloy layer, corrosive factors pass through cracks in the alloy layer to reach the steel base. The steel base then corrodes. Thereafter, the corrosion of the steel base mainly proceeds inside of the alloy layer, finally resulting in general corrosion. This form of corrosion occurs because the potential of the aluminized coating and alloy layer is more noble than that of the steel substrate in the corrosive environment inside the muffler.

Fig. 1 shows the results of investigations to measure the immersion potential of various chromium levels in steel exposed to condensate inside an automotive exhaust system[4]. When the steel contains about 5% chromium or more, its potential is reversed with respect to that of the aluminized coating. In this region, the aluminized coating cathodically protects the steel base. The aluminized coating thus cathodically protects stainless steel.

3. Quality Properties

3.1 Properties as automotive exhaust system material

Hot-dip aluminized sheet steel is available in two types. Type I excels in heat resistance and formability and is covered by an aluminum alloy containing 10% silicon. Type II excels in corrosion resistance and has a commercially pure aluminum coating. Only type I is produced in Japan and it was studied in this work. **Photo 2** shows the cross-sectional microstructure of aluminized stainless steel containing 11% chromium. Silicon is distributed in a needlelike pattern in the aluminized coating.

The corrosion resistance of aluminized stainless steel within the muffler is described first. As noted before, condensate containing various corrosive factors collects in the muffler, and the muffler is alternately wetted, dried and heated in this condition. Automobile and steel manufacturers have studied corrosion test methods for this type of environment and proposed the heating-wetting cyclic corrosion test and semi-immersion corrosion test methods[5,6].

The present study applied the heating-wetting-drying cyclic corrosion test method shown in **Table 2**[1]. Specimens were not sealed at the edges and bottom surface. The composition of the corrosive solution was based on exhaust gas condensate constituents and determined in consideration of accelerated corrosion. Since the pH changes with drying, the specimens were immersed in two types of solutions, one with pH 3 and the other with pH 8. The test results are shown in **Fig. 2**. The aluminized low-carbon steel had red rust emanating from the exposed edges toward the inside. The bare 11% chromium steel had no or little general corrosion, but after some time, the section thickness was substantially reduced by pitting. When a steel containing more than 11% chromium was aluminized, it performed well without edge corrosion or pitting.

The results of a corrosion test simulating the external muffler surface environment are shown in **Fig. 3**, and the test method is shown in **Table 3**. The external muffler surface environment is considered to be basically the same as the outer body panel environment regarding salt damage, wetting, and drying. A cyclic corrosion test was conducted in consideration of these conditions. The bare 11% chromium steel developed red rust throughout immediately after the start of the test, while the aluminized 11% chromium steel exhibited good corrosion resistance.

The high corrosion resistance of aluminized stainless steel may be explained as follows. One reason is that the aluminized coating affords cathodic protection as initially expected. In the condensate collected on the interior surface of the exhaust system, the potential increases in the aluminum coating, alloy layer, and steel base in that order[7]. Corrosion is thus least likely to occur in the steel base. Another reason is that the aluminized coating itself has improved corrosion resistance. As evident from the corrosion data on the 350th day shown in **Fig. 3**, the corrosion rate of the aluminized coating on the stainless steel is lower than that of the aluminized coating on the low-carbon steel. **Fig. 4** shows the cathodic polarization curves of aluminized coatings on the low-carbon steel and 11% chromium steel in a 5% sodium chloride (NaCl) solution[8]. The two steels do not appreciably differ before the onset of corrosion. With the progress of corrosion, the aluminized coating of the low-carbon steel decreases in polarization, but the shape of the polarization curve for the 11% chromium steel's aluminized coating changes little. When a chromium-containing steel is hot-dip aluminized, about 0.1% of the chromium from the base metal diffuses into the aluminized coating. **Fig. 5** shows the concentration behavior of chromium in corrosion products in the salt spray test[8]. The chromium is temporarily concentrated in the corrosion products with the progress of corrosion. The concentration of the chromium turns the aluminum corrosion products into amorphous substances with less defects. As these substances retard the diffusion of corrosive factors, cathodic polarization is maintained to ensure the corrosion resistance of the aluminized coating.

Table 2 Muffler interior surface corrosion test method

○ Specimen preparation: Chromating of aluminized steel

○ Test solution composition (ppm)

SO_4^{2-}	NO_3^-	Cl^-	CO_3^{2-}	NH_4^+	Formic acid	Acetic acid
1,100	150	300	4,000	3,000	1,000	1,000

The pH values of the above solutions were adjusted to 8 or 3 by adding ammonia water or sulfuric acid.

○ Test cycles (1 week/1 cycle)

No.	Test condition
1	Two cycles of heating (300°C, 30 min) → 2/3 immersion (pH 8, 80°C, 150 min)
2	Drying (100°C, 24 h)
3	2/3 immersion (pH 3, 80°C, 24 h)
4	Drying (100°C, 24 h)
5	2/3 immersion (pH 3, 80°C, 24 h)
6	Drying at room temperature (27°C, 66 h)

○ Test period: 20 weeks

3.2 Properties of aluminized stainless steel sheet as building material

Aluminized stainless steel sheet was originally developed for automotive exhaust systems. Thanks to its aesthetic appearance and excellent thermal reflectivity, aluminized stainless steel sheet has been gaining increasing usage as a high-grade building mate-

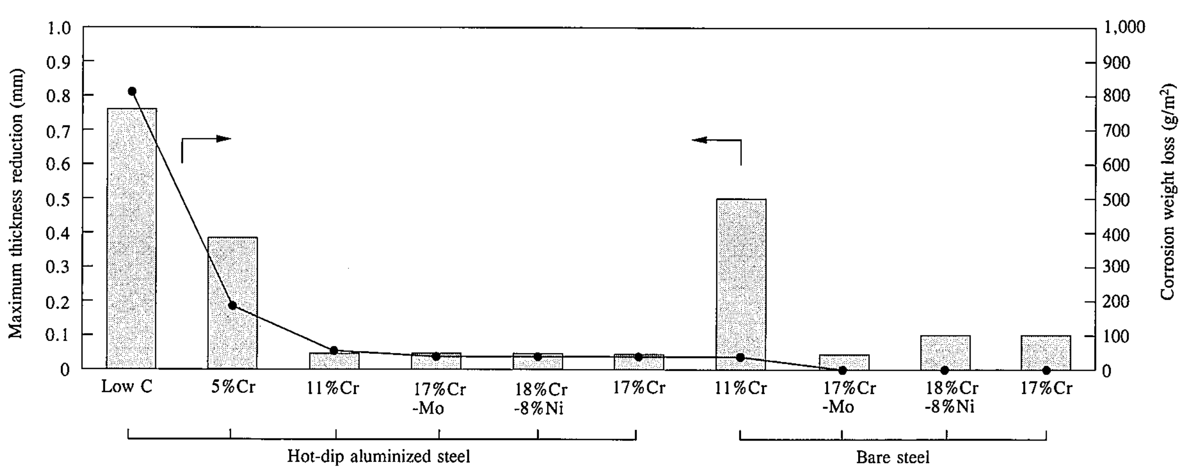


Fig. 2 Results of muffler interior surface corrosion test

Table 3 Muffler exterior surface corrosion test method

○ Specimen preparation: Chromating of aluminized steel
○ Test solution: 5% NaCl
○ Test cycles (1 day/1 cycle)

No.	Test condition
1	Salt spray (35°C, 6 h)
2	Drying (60% RH, 70°C, 4 h)
3	Wetting (95% RH, 49°C, 4 h)
4	Freezing (-20°C, 4 h)

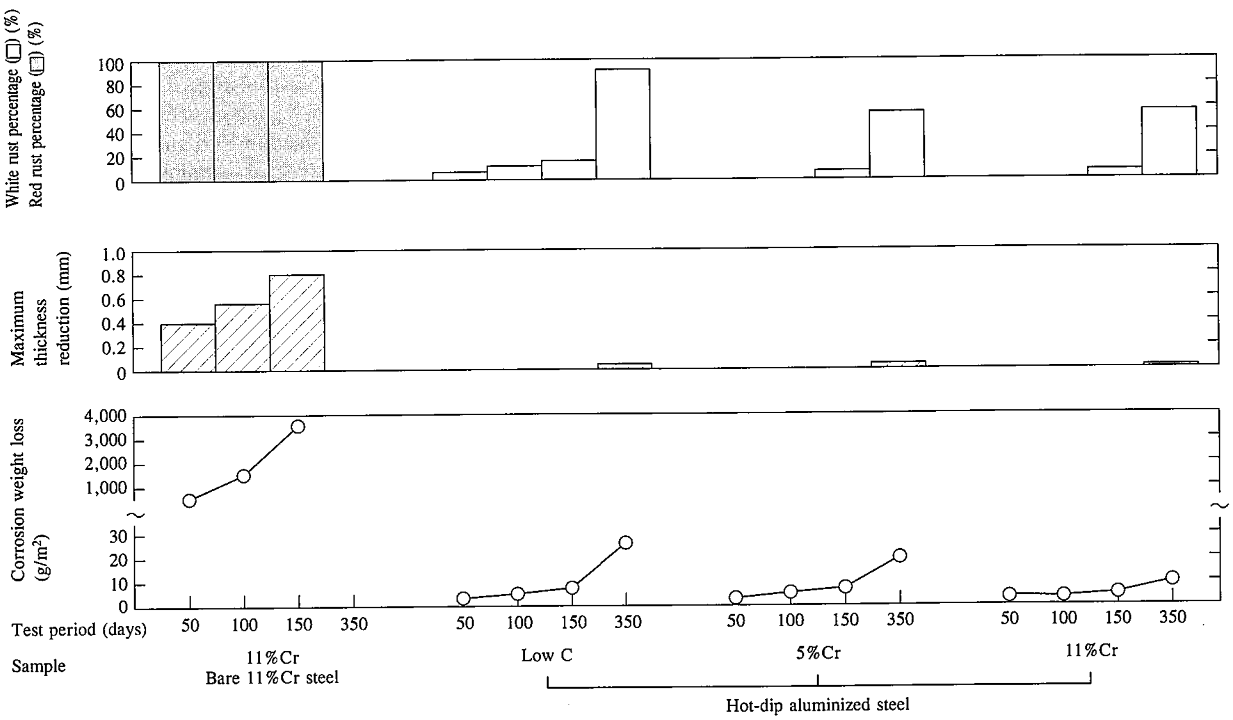


Fig. 3 Results of muffler exterior surface corrosion test

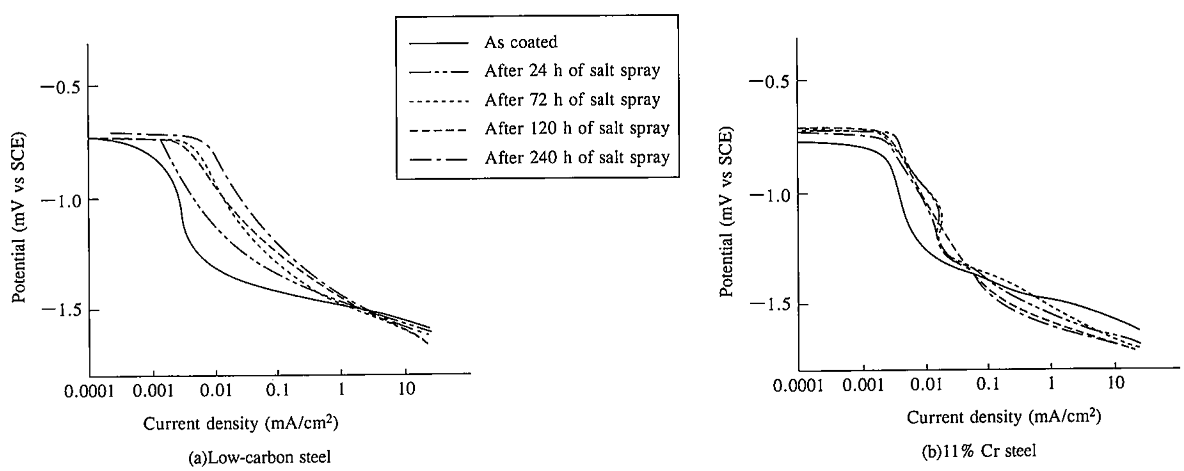


Fig. 4 Cathodic polarization curves of aluminized coatings

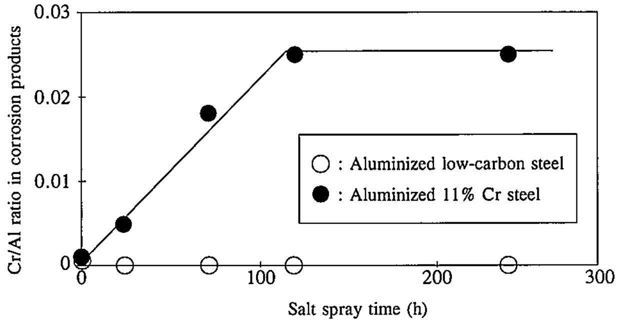


Fig. 5 Chromium concentration behavior in corrosion products

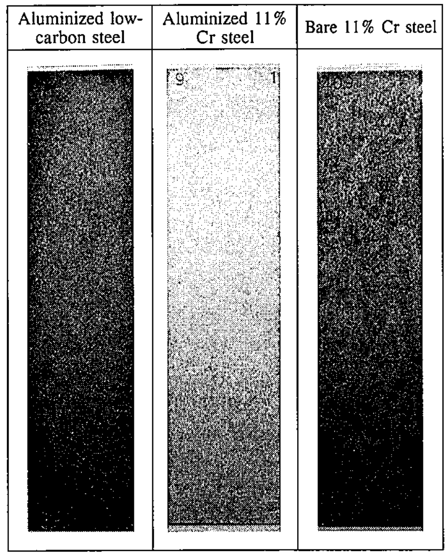


Photo 3 Appearance of specimens after 5 years of exposure

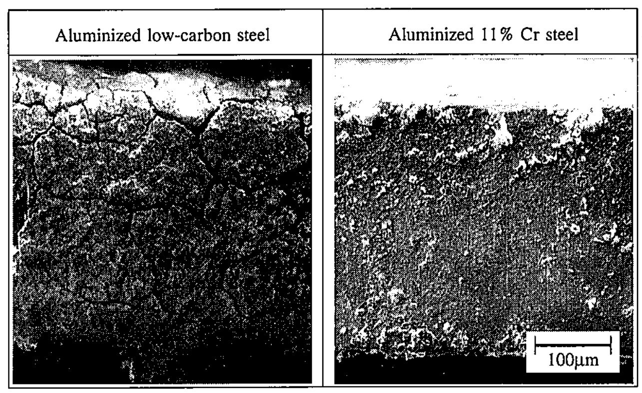


Photo 4 Secondary electron images of the edges of aluminized steel specimens after 5 years of exposure

rial in recent years. For architectural use, the aluminized coating weight is set at 200 g/m² for both sides, and a clear resin paint is applied to each surface to protect against scratching.

Corrosion test methods are not yet developed for building materials. The corrosion resistance of aluminized stainless steel sheet is mostly evaluated by an outdoor exposure test. Among the environmental factors that affect the corrosion resistance of aluminized stainless steel are the amount of rainfall, the condition of dew condensation, wind speed, the duration of sunshine, the composition of rain, and airborne matter. To investigate its performance as a building material, aluminized stainless steel was exposure tested within the premises of Nippon Steel's Yawata Works about 500 m from the coast, a comparatively severe environment. To evaluate the corrosion resistance of the material, clear resin paint was not applied to specimens. The appearance of the specimens after five years of exposure at an angle of 30°C facing the south is shown in **Photo 3**. Aluminized low-carbon steel and bare 11% chromium steel were also evaluated as control materials. As evident from **Photo 3**, corrosion gradually proceeded inward from the edges for the aluminized low-carbon steel. The corrosion turned the color tone of the steel darker. Red rust formed on the surface of the bare 11% chromium steel in a relatively short time and became conspicuous after five years of exposure. The aluminized 11% chromium steel had no or little edge and color tone change after five years of exposure. **Photo 4** shows the secondary electron images of the edges of the aluminized low-carbon steel and the aluminized 11% chromium steel. Thick iron rust had formed on the aluminized low-carbon steel, while the aluminized 11% chromium steel had no or little corrosion products appearing at the edges. A whitish substance found in very small amounts was identified as aluminum corrosion by electron probe X-ray microanalysis (EPMA). This substance occurs near the aluminized coating on the top and bottom surfaces and this suggests that red rust formation is inhibited by the aluminum's cathodic protection.

Fig. 6 shows the corrosion weight loss and color tone change measurements. The corrosion rate of the aluminized 11% chromium steel is about 25% lower than that of the aluminized low-carbon steel. This is probably due to the effect of chromium being diffused into the aluminized coating as described in the preceding section. The change in the color tone (lightness) of the aluminized coating surface with the time of exposure may be explained by the deposition of external airborne substances and products formed by the corrosion of the aluminized coating. An aluminized coating with higher corrosion resistance is predicted to have a smaller change in color variation. As shown in **Fig. 6**(b), the aluminized 11% chromium steel inhibits the corrosion of the aluminized coating than the aluminized low-carbon steel, so that the drop in its color (L* value) is correspondingly checked.

4. Example of Application as Building Material

As noted in the previous section, aluminized stainless steel sheet has very good corrosion resistance in automotive exhaust and exposed outdoor environments. When used as a building material, its aluminized coating offers a cathodic protection effect. Since the aluminized coating corrodes at a very low rate of about 0.5 g/m²/year/side, it is expected to last some decades when applied at a weight of 100 g/m² per side. The aluminized coating is especially resistant to chloride environments. In coastal environments where red rust is likely to occur on stainless steels such as SUS 304, the aluminized coating itself is thought to display good corrosion resistance. In recent years, the excellent corrosion resistance and aesthetic appearance of aluminized stainless steel

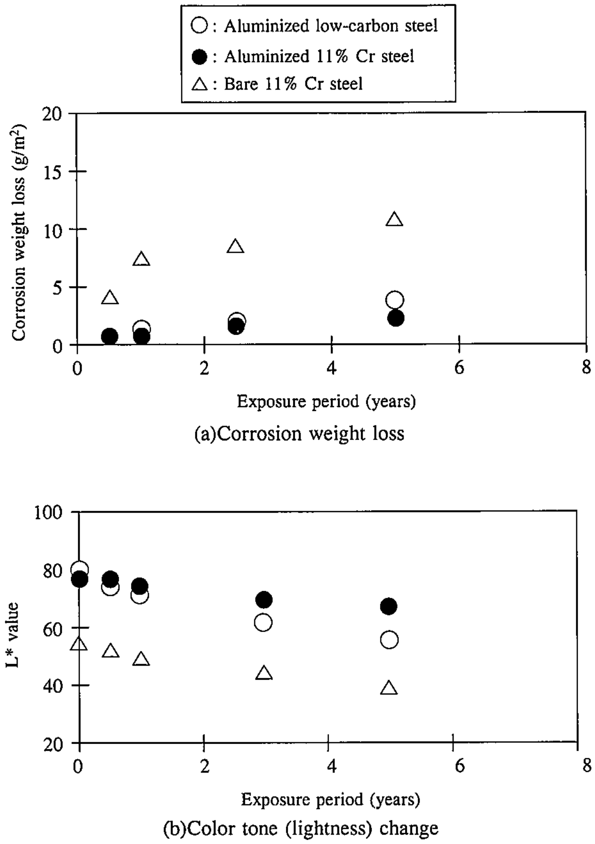


Fig. 6 Results of atmospheric corrosion resistance evaluation by outdoor exposure test

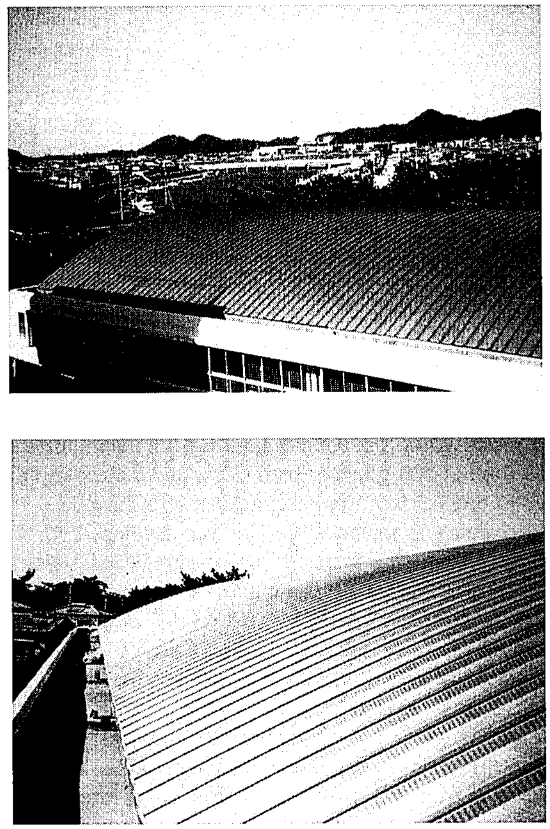


Photo 5 Application example of hot-dip aluminized stainless steel (11% Cr steel)

has accelerated its application as a building material, particularly for roofing. Aluminized stainless steel sheet was used in a total of about 20 buildings as of June 1996, with the oldest having a service record of about six years. The corrosion for aluminized stainless steel in service is as good as indicated by the results of outdoor exposure testing. **Photo** 5 shows a recent example in which aluminized 11% chromium steel is used in the roofing of a building.

5. Conclusions

Aluminized stainless steel sheet was developed as a coated stainless steel product. The pitting corrosion of and red rust formation in stainless steel are inhibited by coating with aluminum, a metal whose potential is less noble than that of stainless steel. The diffusion of chromium from the steel base into the aluminized coating sharply improves the corrosion resistance of the aluminized coating itself. As a result, the aluminized coating displays very good corrosion resistance in automotive exhaust and exposed outdoor environments. The new coated steel product is being extensively applied to automotive exhaust system components and building materials, and is expected to find widespread usage in many new applications.

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