Corrosion Behavior of Aluminized Steel Sheets in 50-Year Outdoor Exposure Test

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Aluminized steel sheets are very resistant to corrosion in the outdoor exposure environment. We evaluated the corrosion behavior of aluminized steel sheets with a Type 1 coating containing approximately 10% Si and a Type 2 coating not containing Si in a 50-year outdoor exposure test. Both specimens had strong perforation resistance, but those with Type 2 coating exhibited excellent perforation resistance. Type 2 aluminized steel sheets are known as a superior corrosion resistant materials compared to Type 1 aluminized steel sheets due to their thicker intermediate layer and higher coating weight. The Type 2 aluminized steel sheets in this exposure test included two sublayers composed of Fe2Al5 and FeAl2 as the intermediate layer between the aluminized layer and the steel substrate. The FeAl2 phase has less noble potential than the steel substrate and the Fe2Al5 phase in an artificial rain environment. As a result, this layer provided sacrificial corrosion protection for the steel substrate, and was the reason why the specimens with Type 2 coating exhibited better perforation resistance than those with Type 1 coating.

KEY WORDS: aluminized steel sheets; outdoor exposure test; corrosion resistance; intermetallic compound layer.

1. Introduction

Aluminized steel sheets are steel sheets primarily coated with aluminum and are known to have excellent heat resistance and corrosion resistance. They were commercialized in the 1960s in Japan.1) They have been used as materials for automobile exhaust systems since the 1980s2) and have been widely used in the manufacture of high-strength parts by hot stamping processes (such as hot forming, die quenching, and press hardening) since the 2000s.3)

In the manufacture of aluminized steel sheets, an intermetallic compound layer (hereinafter called the alloyed layer) forms at the interface between the aluminized layer and the steel substrate. This layer rapidly grows and inhibits the formability of the aluminized steel sheets. To hinder the growth of the alloyed layer, 8% to 10% Si is added to the bath. This type of aluminized steel sheet is referred to as Type 1. Aluminized steel sheets without Si addition are claimed to be superior in corrosion resistance and are called Type 2 sheets. Type 2 aluminized steel sheets are reportedly used in civil engineering structures and buildings such as corrugated steel pipes in the United States and Europe.

Type 1 aluminized steel sheets are used as high-grade building materials in roofs, walls, and other applications for their beautiful appearance and excellent corrosion resistance. Maki et al.4) reported the corrosion behavior of Type 1 aluminized steel sheet specimens after 31-year atmospheric exposure test. Uchiyama et al.5) carried out 31-year atmospheric exposure tests of Type 1 aluminized steel sheets in Singapore. The results of both tests were similar, and the color tones of the specimen surfaces tended to be darker. It was reported that corrosion of the specimens had hardly progressed, particularly in the thickness direction. The atmospheric exposure tests were continued thereafter for both Type 1 and Type 2 aluminized steel sheets in Japan. In 2015, after 50 years of atmospheric exposure, the corrosion conditions of Type 1 and Type 2 aluminized steel sheets were reexamined. The aluminized layer composition and the alloyed layer composition were studied to evaluate their effects on the corrosion conditions of the specimens in the atmospheric environment.

2. Experimental Methods

2.1. Materials

Low-carbon steels of the compositions shown in Table 1 were used as base materials for aluminizing purposes. Type 1 aluminized steel with 10% Si addition and Type 2 aluminized steel sheets were used as high-grade building materials in roofs, walls, and other applications for their beautiful appearance and excellent corrosion resistance. Maki et al.4) reported the corrosion behavior of Type 1 aluminized steel sheet specimens after 31-year atmospheric exposure test. Uchiyama et al.5) carried out 31-year atmospheric exposure tests of Type 1 aluminized steel sheets in Singapore. The results of both tests were similar, and the color tones of the specimen surfaces tended to be darker. It was reported that corrosion of the specimens had hardly progressed, particularly in the thickness direction. The atmospheric exposure tests were continued thereafter for both Type 1 and Type 2 aluminized steel sheets in Japan. In 2015, after 50 years of atmospheric exposure, the corrosion conditions of Type 1 and Type 2 aluminized steel sheets were reexamined. The aluminized layer composition and the alloyed layer composition were studied to evaluate their effects on the corrosion conditions of the specimens in the atmospheric environment.

Table 1. Steel composition of specimens (mass%).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Al</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td>0.02</td>
<td>0.01</td>
<td>0.35</td>
<td>0.006</td>
<td>0.009</td>
<td>0.006</td>
<td>0.0024</td>
</tr>
<tr>
<td>Type 2</td>
<td>0.02</td>
<td>0.01</td>
<td>0.34</td>
<td>0.007</td>
<td>0.008</td>
<td>0.004</td>
<td>0.0033</td>
</tr>
</tbody>
</table>
nized steel without Si addition were used as specimens. The coating weight was 90 to 100 g/m² per side. Figure 1 shows the cross-sectional micrographs of the specimen regions, where little corrosion was evident. The exposed specimens were used because the specimens before exposure did not remain. The Type 1 aluminized layer exhibits a hypoeutectic structure. Acicular Si phase is observed in the aluminized layer. The alloyed layer thickness was approximately 7 µm. On the other hand, a 15 µm thick alloyed layer formed on Type 2 material. Minute precipitates were also observed in the aluminized layer and were found to be Al–Fe intermetallic compounds.

2.2. Atmospheric Exposure Test

Specimens measuring 50 by 200 mm were exposure tested with their skyward surfaces facing south at 30°. The exposure site was located in the Yawata Works, Kitakyushu; located approximately 500 m from the coast. The airborne salt concentration was 1.7 × 10⁻² g/m² s (0.15 mg/dm²/day when measured in 1997). Corrosion is known to rapidly progress in coastal areas and in heavy industry areas. The exposure site represents a relatively severe corrosion environment. The exposure test was started in 1965. The appearance, weight change, and other details of the specimens were periodically measured. All specimens were recovered and investigated in 2015 after 50 years of exposure.

2.3. Investigation of Corrosion Conditions

Surface color tone changes of the specimens after the atmospheric exposure test concluded were measured with a colorimeter according to JIS Z 8781. To investigate corrosion conditions, 50 mm square pieces were cut from the specimens, corrosion products were removed from the cut pieces, and the depth of corrosion in the cut pieces was measured with a micrometer. The corrosion conditions of the aluminized layer and the steel substrate were evaluated by cross-sectional observation. The corrosion products were analyzed for elements using an electron probe micro analyzer (EPMA) and the corrosion products were identified using x-ray diffraction (XRD). The EPMA was used with an acceleration voltage of 15 kV and 500 by 500 measurement points. The x-ray diffraction was performed with a Co target and a measurement angle, 2θ, of 10° to 100°. Area analysis was conducted with laser Raman spectroscopy. The area distribution by compound type was measured by assigning the detected peaks to specific compounds. The excitation wavelength was 532 nm, the observation wavelength was 1.495 cm⁻¹ to 145 cm⁻¹, the spot diameter was 1 µm, and the integration time was 15 s.

3. Results

3.1. Corrosion Conditions of Aluminized Layer and Steel Substrate after 50 Years of Exposure

Figure 2 shows the typical appearance of the specimens after 50 years of exposure. The lightness (L* value) of each specimen was also measured. The lightness of aluminized steel sheets before exposure was approximately 80. The lightness of the specimens after 50 years of exposure was 32 and 42 for Types 1 and 2, respectively. Type 1 already exhibited an L* value of 30 in the 31st year of exposure. Its color tone was close to dark brown and changed little thereafter. Type 2 appeared whiter than Type 1. From the investigation results of the specimens exposed for 31 years, this appearance change is estimated to have occurred because the steel substrate partly corroded and the resultant corrosion products covered the specimens’ surface.

Next, the corrosion depth of the steel substrate was measured from the surface and the cross section. Specimens after 10 to 31 years of exposure exhibited corrosion depths exceeding 50 µm in the regions where the steel substrate was observed to be most severely corroded based on cross-sectional microscopic observations. Additionally, the corrosion products were removed from 50 mm square specimens after 50 years of exposure and corrosion depth was measured from the surface with a micrometer. The corrosion depth was measured at five points where the corrosion appeared to be deep, and the measured values were averaged. The averaged values of the corrosion depth included the aluminized layer thickness. The aluminized layer thickness was subtracted so that the measured values of the corrosion depth could be compared with those obtained in the past. The corrosion depth of the 50 mm specimens was also measured by cross-sectional microscopy. It was confirmed that the corrosion depth measured by micrometry roughly agreed with that measured by cross-sectional microscopy.

The results are shown in Fig. 3. It was reported that a corrosion depth of 50 µm was recognized in the steel substrate of Type 1 specimens after 31 years of exposure. The corrosion depth increased to 0.1 mm in the Type 1 specimens exposed for 50 years. Corrosion of the steel substrate mainly occurred near the cut edges. Figure 4 shows the cross-sectional micrographs near the cut edges of Type 1 and 2 specimens exposed for 50 years. Each micrograph shows a
region at approximately 10 mm from the edge. It is evident from Fig. 4 that the corrosion of the steel substrate was minor in Type 2, that the corrosion of the steel substrate progressed relatively easily in a region 5 mm from the edge in Type 1, and that the top surface (the exposed surface) was more likely to corrode than the bottom surface.

Figure 3 shows that the corrosion depth of Type 1 almost linearly increased with time. Given that its steel substrate corroded by only 0.1 mm near the edge after 50 years of exposure, Type 1 is considered to have sufficient durability in normal environments. The corrosion depth of Type 2 was much less than that of Type 1 and did not increase much after 31 years of exposure. Even after 50 years of exposure, the corrosion depth of Type 2 was extremely shallow (25 μm).

Next, the corrosion conditions of the aluminized layer and the steel substrate were observed by cross section. Figure 5 shows cross-sectional optical micrographs of typical corroded regions in Types 1 and 2. As indicated by the investigation results of the specimens exposed for 31 years (Type 1) in the referenced report, the corrosion of the aluminized layer reached the alloyed layer and the corrosion factors reached the steel substrate through cracks in the alloyed layer. The steel substrate consequently corroded and the resultant corrosion products built up and expanded to ultimately push up the alloyed layer locally. The corrosion

![Fig. 3. Corrosion depths of steel substrates after outdoor exposure tests.](image)

![Fig. 2. Visual appearances of specimens after 50 years of exposure. (Online version in color.)](image)

![Fig. 4. Cross sectional views of specimens near the cut edge after 50 years of exposure. (Online version in color.)](image)
of the steel substrate proceeded internally along the alloyed layer. For this reason, the progress of the corrosion was relatively low in the thickness direction of the steel sheet. In Type 2, on the other hand, the corrosion penetrated through the alloyed layer and some of the alloyed layer then preferentially corroded. The corrosion of the alloyed layer was present particularly in regions near the steel substrate and the corrosion of the steel substrate was inhibited to a greater extent than in Type 1. This supports the fact that the corrosion of the Type 2 steel sheet was hardly apparent in Fig. 3.

### 3.2. Analysis of Corrosion Products

Representative corroded regions were selected in both Types 1 and 2 and the distributions of elements in the selected corroded regions were measured and mapped with the EPMA. The distributions of the corrosion products in the corroded regions were analyzed by laser Raman mapping. The EPMA and Raman maps are shown in Figs. 6 and 7, respectively.

From the EPMA analytical results, it was found that the corrosion products in Type 1 consisted of the outer layer containing aluminized layer components, \textit{i.e.} Al, Si, and the inner layer consisting of mainly Fe corrosion products. The corrosion products in both outer and inner layers contained Ca, S, Cl, \textit{etc.} In Type 2, on the other hand, the alloyed layer remained and was partially corroded. The aluminized
layer was also partially corroded and the aluminized layer surface was covered with approximately 100 $\mu$m of Al corrosion products. S was specifically detected in the Al corrosion products. Uchiyama et al.\textsuperscript{5)} analyzed (using EPMA) the cross sections of long-term exposure Type 1 aluminized steel sheet specimens in Singapore. They similarly described that C, Ca, and Cl were detected as elements in addition to elements derived from the aluminized layer and the steel substrate. Their results are similar to ours. It is inferred that Ca and Cl were derived from sea salt particles and that S was derived from sulfate compounds.

Table 2 shows the corrosion products identified by x-ray diffraction. Goethite ($\alpha$-FeOOH), magnetite (Fe$_3$O$_4$), and silica were detected in Type 1. Goethite and magnetite alone were detected in Type 2. Cross-sectional EPMA detected Al corrosion products in Type 2 but x-ray diffraction did not. This suggests that the Al corrosion products were amorphous. Uchida et al.\textsuperscript{6)} analyzed the aluminized steel sheet edges and reported that amorphous corrosion products built up and suppressed the subsequent corrosion of the steel substrate. The phenomenon the present authors observed was considered similar to that reported by Uchida et al.

Figure 7 shows the distributions of compounds examined by laser Raman spectroscopy for the distributions of goethite and magnetite detected in Type 1 and of goethite alone detected in Type 2. In Type 1, goethite was detected in the corroded regions of the steel substrate inside the alloyed layer. Magnetite was also detected in the corroded regions of the steel substrate inside the alloyed layer, and in the corroded regions of the aluminized layer and the corrosion product build-up regions of the aluminized layer surface. As described in the previous report\textsuperscript{4)} regarding the aluminized steel specimens exposed for 31 years, it is known that when Fe corrosion products are formed, the presence of Al ions facilitates the formation of goethite. The detection of goethite in the corroded regions of the steel substrate inside the alloyed layer (where many Al ions are apparently supplied) agrees with the results of the report.\textsuperscript{4)} On the other hand, magnetite is increasingly formed toward the surface layer, where fewer Al ions are supplied. Goethite is known as stable rust on weathering steels, and may also contribute to the corrosion resistance of aluminized steel sheets.

Similarly, in Type 2, goethite was detected in the corroded regions of the alloyed layer. It was confirmed that a phenomenon similar to what is described above occurred. In Type 2, corrosion products containing Al build up on the aluminized layer surface, although the present analysis could not clarify their structure.

4. Discussion

4.1. Corrosion Behavior of Type 1

First, the corrosion behavior of Type 1 aluminized steel sheets is described. As shown in Fig. 1, the aluminized layer has acicular Si phases. The thickness of alloyed layer is normally less than 5 $\mu$m and this layer is composed of mainly Fe$_2$Al$_8$Si.$\textsuperscript{7)}$ The corrosion potential of Si is higher than that of Al.$\textsuperscript{8)}$ The preferential corrosion of Al near Si starts first. What remains in the corroded aluminized layer in the micrograph of Type 1 in Fig. 5 is Si. After the corrosion reaches the alloyed layer, the corrosion factors reach the steel substrate through cracks in the alloyed layer and initiate corrosion of the steel substrate. The corrosion potential of the alloyed layer is more noble than that of the steel substrate,$\textsuperscript{9)}$ so corrosion progresses at the interface between the steel substrate and the alloyed layer. These corrosion conditions are schematically illustrated in Fig. 8.

As shown in Fig. 3, the corrosion depth of the steel substrate tended to linearly increase with exposure time. Because the Type 1 aluminized layer has little capability to sacrificially protect the steel substrate in an atmospheric corrosion environment, local corrosion of the aluminized layer proceeds and some corrosion of the steel substrate below the alloyed layer also progresses, as shown in Fig. 5. The resultant corrosion products build up and expand to lift the alloyed layer and to facilitate the intrusion of any corrosion factors into the alloyed layer. It is inferred that
these influences cause the local corrosion to continue to progress over time.

4.2. Alloyed Layer Composition of Type 2

With the Type 2 aluminized steel sheets, it is observed that the alloyed layer is preferentially corroded with respect to the steel substrate in the atmospheric exposure environment, as shown in Fig. 5. In Fig. 3, the corrosion depth of the steel substrate was minor and exhibited little difference between the specimens exposed for 31 and 50 years. Because the corrosion of Type 2 proceeded on the steel substrate side of the alloyed layer, the alloyed layer composition was point analyzed by SEM-EDS. The results are shown in Fig. 9. This figure shows a backscattered electron image. The image confirms that the intermetallic compounds near the center consist of two layers. The EDS analytical results (five-point average values) shown in Fig. 9 were compared with those of an Al–Fe binary phase diagram. The composition of the alloyed layer on the aluminized layer side agreed with the composition of Fe2Al5 closest to Fe (Fe2Al5 has a detectable composition width) and the composition of the alloyed layer on the steel substrate side agreed with the composition of FeAl2. Namely, this means that Fe2Al is most susceptible to corrosion when the steel substrate, Fe2Al, and Fe2Al5 exist together.

The alloyed layer formed on the Type 2 aluminized steel sheets is reported to usually be Fe2Al5. However, some references report that FeAl3 or FeAl2 forms in addition to Fe2Al5. In the Al–Fe binary phase diagram, FeAl2, Fe2Al5, and FeAl3 are stable phases from room to high temperatures, and all can form. It is logical to consider that some kinetic factors are responsible for the ease with which specific phases form when steel sheets are aluminized. Fe2Al5 has an orthorhombic crystal structure and contains many lattice defects in the c-axis direction. For this reason, its growth rate is said to be high in the c-axis direction and thus is expected to be most frequently observed. Over 50 years have passed since the Type 2 aluminized steel sheets described in the present report were first manufactured and atmospherically exposed. Operating conditions and other details at that time are not clear, and the references cited above are not clear regarding the conditions under which FeAl2 forms easily.
4.3. Corrosion Potential of Al–Fe Intermetallic Compounds

The present study indicated that an alloyed layer consisting of FeAl$_2$ is preferentially corroded with respect to Fe$_2$Al$_5$ and to the steel substrate in an atmospheric exposure environment. Ingots of such Al–Fe compositions were prepared and evaluated for their electrochemical properties. A small arc furnace was used to prepare the ingots. FeAl$_3$, Fe$_2$Al$_5$, FeAl$_2$, and FeAl were selected as major compounds to appear in the Al–Fe binary phase diagram. The chemical composition of the ingots was adjusted to reproduce the respective compounds. Ingots measuring 20 to 25 mm and 7 mm thick were prepared by melting and cooling, were then surface polished and sealed except for a 10 mm square in their center and were subjected to electrochemical measurements.

Artificial rain was used as the measurement environment to mimic the environment of the specimens exposed for 31 years. The composition of the artificial rain was adjusted to include 200 ppm Cl$^-$ and 200 ppm SO$_4^{2-}$ by using NaCl and Na$_2$SO$_4$, respectively. The immersion potential and polarization curve of each specimen were measured at room temperature in air. The sweep rate was 1 mV/s. Similar measurements were taken for plain steel sheet specimens and Type 1 aluminized steel sheet specimens.

The corrosion potential measurements of the intermetallic compounds were arranged with respect to Fe composition and are shown in Fig. 10. It was recognized that the corrosion potential of FeAl$_3$ was most noble and that the corrosion potential tended to change in a less noble direction as the intermetallic compounds increased in the Fe concentration in the order of Fe$_2$Al$_5$, FeAl$_2$, and FeAl. The corrosion potential of the steel substrate was near the middle between FeAl$_3$ and Fe$_2$Al$_5$. The corrosion potential of the aluminized layer was almost the same as that of FeAl$_3$.

Al is an active metal and its corrosion potential is initially low. It forms a passive film on the surface and usually has a more noble corrosion potential than steel. Al is known to exhibit a less noble corrosion potential than steel in an environment with the presence of chloride ions that disrupt the passivation. Thus, the measurement environment influences the corrosion potential of Al or intermetallic compounds containing Al.

Several reports have been published regarding the electrochemical properties of Al-bearing steel in a dilute solution. For example, F. E. Heakal et al. measured the polarization of Al-free steel and 1.3% Al steel in a 0.05M NaCl solution and found that the corrosion potentials were approximately $-0.62$ and $-0.68$ V (SCE), respectively. X. H. Chen et al. measured the polarization of steels with an Al content of 0 to 1.85% in a 0.3% NaCl solution and reported that the corrosion potentials of the Al-free steel and the 0.96% Al steel were approximately $-0.49$ and $-0.58$ V (SCE), respectively. These authors indicated the tendency of the corrosion potential of the Al-bearing steels to decrease. The reasons involved were not clarified. When the anode reaction does not appreciably change and the cathode reaction manifests with difficulty, for example, the corrosion potential determined by the balance between the two reactions should decrease. If the addition of a small amount of Al to steel is assumed to facilitate the formation of a passive film of Al on the surface, the cathode reaction is presumed to slow down. So if the anode reaction does not significantly change because of the small amount of Al added, then the decrease in the corrosion potential can be explained.

When the cathode reaction does not greatly change and the anode reaction becomes more likely to occur, conversely, the corrosion potential should also drop. The corrosion potential decreased in the order of FeAl$_3$, Fe$_2$Al$_5$, FeAl$_2$, and FeAl in the present study. This can be accounted for by the ease with which these intermetallic compounds can dissolve in dilute solutions in that order. Figure 11 shows the polarization curves of these compounds. It was confirmed that the rate of the anode reaction actually increased in the above order. No great difference was observed in the cathode reaction. This is because the film formed on the surface of each intermetallic compound is similar in composition to the passive film of Al.

When the Type 1 aluminized steel sheets are used in the
hot stamping process, heating to around 900°C changes the aluminized layer into Al–Fe intermetallic compounds containing Si. The main phase formed at this time is said to be Fe₂Al₅. It is reported that the corrosion potentials of the Fe₂Al₅ phase containing some Si and that of plain steel in a 5% NaCl solution are approximately −0.4 and −0.45 V (SCE), respectively. These values correspond to −0.35 and −0.4 V, respectively, relative to the Ag/AgCl reference electrode. As compared with the measured results of the present study, the corrosion potential difference was not greatly different for the steel substrate but was 0.17 V for Fe₂Al₅. The differences between the results of the present study and the results previously reported are mainly due to the measurement environments (artificial rain and 5% NaCl) and the presence or absence of Si. In a salt water environment, the Al passive film tends to be destroyed and it is difficult to expect the corrosion potential to rise. It is conceivable that the 1% to 2% Si content may affect the corrosion potential.

From the above study results, it was revealed that Fe₆Al₇ may form in the alloyed layer formed in Type 2 aluminized steel sheets, depending on the aluminizing conditions, and that this Fe₆Al₇ preferentially corrodes because its corrosion potential is less noble than that of the steel substrate in an atmosphere environment. The corrosion potential of Fe₂Al₅, said to normally form, is slightly less noble than that of the steel substrate. Thus, it is possible that an alloyed layer consisting only of Fe₂Al₅ may preferentially corrode relative to the steel substrate.

5. Conclusions

Specimens of Type 1 and 2 aluminized steel sheets were atmospherically exposed for 50 years in Kitakyushu. The specimens were investigated for their corrosion conditions, corrosion products, and corrosion behavior after 50 years of exposure. The following results were obtained:

(1) The steel substrate of Type 1 aluminized steel sheets generally produced in Japan was mainly corroded at its edges and the maximum corrosion depth was 0.1 mm. The Type 1 aluminized steel sheets are thus judged to have sufficient weatherability for practical use.

(2) The corrosion resistance of Type 2 aluminized steel sheets is much superior. The maximum corrosion of the steel substrate was approximately 0.025 mm in depth after 50 years of exposure and rarely progressed after 31 years of exposure.

(3) The principal corrosion product formed on the corroded steel substrate is goethite (α-FeOOH). This is considered to form under the action of Al dissolved from the aluminized layer or in the alloyed layer.

(4) The alloyed layer of Type 2 is formed in two layers. The Fe₆Al₇ layer on the steel substrate side is preferentially corroded with respect to the steel substrate. This is considered to occur because the corrosion potential of this compound is less noble than that of the steel substrate in the atmospheric exposure environment.

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