STUDYING THE ATMOSPHERIC CORROSION BEHAVIOR
OF WEATHERING STEELS AT A MILD MARINE ENVIRONMENT

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The atmospheric corrosion products on three types of weathering steels which were exposed at a marine
environment for sixteen years, have been analyzed by Mössbauer spectroscopy and Electron Probe Micro-Analysis. In
the region closer to the steel surface, silicon and chromium distributed with similar concentration to those in the steel
substrate. Increasing the silicon content resulted in increasing the relative fraction of superparamagnetic goethite.
Although the nickel content which gradually reduced toward the surface of the corrosion products was different, the
composition of corrosion products was almost the same.

1. INTRODUCTION

Studying the atmospheric corrosion of steel is very complicated since there are many active
parameters, such as composition of steel, environmental condition and exposure time¹⁻³. Some studies
have been performed to improve the understanding of the atmospheric corrosion behavior of steel as
a function of the steel composition⁴⁻⁵, in order to design steel with a better resistance against the
atmospheric corrosion. The better corrosion resistance can be obtained from the formation of a
protective layer which is densely packed with small-sized particles. It has been proposed in papers
that the alloying elements would have important roles in forming the protective layer⁶⁻⁷, although the
mechanisms are not clearly resolved. This study aims to understand the atmospheric corrosion
behavior of weathering steel exposed under a marine environment for the same exposure time. The
better understanding can be obtained by correlating the Mössbauer and electron probe micro-analyzer
data with the steel composition and the distribution of alloying elements in the corrosion products.

2. EXPERIMENTAL PROCEDURES

Table 1 lists the compositions of the three A588-type weathering steels, which were
investigated in this study. Comparing to the contents of silicon and nickel of the coupon A52, the
coupon A45 was lower in silicon, but the coupon A50 was lower in nickel. The coupons had been
exposed for sixteen years at Kure Beach NC, USA, 250 m from the shoreline of the Atlantic Ocean. The atmospheric concentrations of chlorine and sulfur dioxides were 39 g/m² yr and 4.1 g/m² yr. The Mössbauer spectroscopic samples were prepared from the corrosion products, which were scraped from the surface region of about 1x2 cm² on the steel substrate. The transmission spectra were recorded at 300K and 77K. After fitting the Mössbauer spectrum, the absorption area fraction of each iron oxide was converted to relative atomic fraction using the relative recoilless fractions⁸. The distribution of alloying elements across the intact corrosion layer was characterized by compositional mapping and line profile using an electron probe micro-analyzer (EPMA). The cross-sectional sample for the microanalysis was prepared by the conventional metallographic sample preparation method, i.e., mounting in epoxy, grinding and polishing. Although XRD data is not included in this paper, x-ray diffraction pattern was recorded, in order to identify whether or not akaganeite was present.

3. RESULTS

The Mössbauer spectra of the corrosion products formed on the coupon A50 are shown in Fig. 1, where goethite (α-FeOOH), lepidocrocite (γ-FeOOH) and superparamagnetic maghemite (γ Fe₂O₃(s)) were identified using Mössbauer spectroscopy. No akaganeite was detected. The XRD analysis for the identification of akaganeite will be published soon. In the 300K Mössbauer spectrum, the superparamagnetic component of goethite (α-FeOOH(s)) which comprised the doublet together with lepidocrocite and superparamagnetic maghemite, were present. Goethite in Fig. 1(a) is classified as follows⁹⁻¹⁰: (1) α-FeOOH(m) : goethite particle of >15 nm, which is magnetic both at 300K and 77K, and (2) α-FeOOH(s) : goethite particle of <15 nm, which is superparamagnetic at 300K. The 300K subspectrum of magnetic goethite (α-FeOOH(m)) showed the distribution of hyperfine field with the most probable value of about 30 Tesla. Comparing to Cabral and Reyes' data¹¹, it was estimated that the mean particle size of goethite was approximately 20-30 nm. Also, it may be inferred that the contribution of the superparamagnetic goethite particles, <15 nm, were possibly present in the doublet.

Table 1. Composition of the three A588-type weathering steel coupons. (Wt. %)

<table>
<thead>
<tr>
<th>Coupon</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Cu</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>A45</td>
<td>0.14</td>
<td>0.97</td>
<td>0.012</td>
<td>0.016</td>
<td>0.12</td>
<td>0.31</td>
<td>0.59</td>
<td>0.36</td>
<td>0.037</td>
</tr>
<tr>
<td>A50</td>
<td>0.12</td>
<td>1.06</td>
<td>0.006</td>
<td>0.013</td>
<td>0.77</td>
<td>0.01</td>
<td>0.59</td>
<td>0.33</td>
<td>0.038</td>
</tr>
<tr>
<td>A52</td>
<td>0.14</td>
<td>1.00</td>
<td>0.009</td>
<td>0.018</td>
<td>0.75</td>
<td>0.31</td>
<td>0.57</td>
<td>0.35</td>
<td>0.052</td>
</tr>
</tbody>
</table>
At 77K, α-FeOOH(s) is subclassified as follows\textsuperscript{8-10} : (1) α-FeOOH(s1) : goethite particle of 8-15 nm, which is superparamagnetic at 300K, but magnetic at 77K, and (2) α-FeOOH(s2) : goethite particle of <8 nm, which is superparamagnetic at both temperatures. Using Kundig's data\textsuperscript{12}, the relative fraction of superparamagnetic goethite, α-FeOOH(s2), was estimated 8%. The Mössbauer spectra of the corrosion products on the other coupons, A45 and A52, were very similar to those in Fig. 1. Table 2 lists the iron oxide phases and their relative fractions identified in the corrosion products formed on the three weathering steel coupons. The relative fraction of each iron oxide was

![Mössbauer spectra](image_url)

**Fig. 1.** Mössbauer spectra of corrosion products formed on coupon A50 exposed at the marine site of Kure Beach, NC for sixteen years.

**Table 2.** The relative fraction of iron oxides on the three coupons.

<table>
<thead>
<tr>
<th>Coupon</th>
<th>α-FeOOH (m)</th>
<th>α-FeOOH (s1)</th>
<th>α-FeOOH (s2)</th>
<th>α-FeOOH (s1+s2)</th>
<th>α-FeOOH (m+s1+s2)</th>
<th>γ-FeOOH</th>
<th>γ-FeOOH(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A45</td>
<td>25</td>
<td>47</td>
<td>8</td>
<td>55</td>
<td>80</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>A50</td>
<td>21</td>
<td>51</td>
<td>8</td>
<td>59</td>
<td>80</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>A52</td>
<td>20</td>
<td>53</td>
<td>8</td>
<td>61</td>
<td>81</td>
<td>14</td>
<td>5</td>
</tr>
</tbody>
</table>
determined after subtracting the contribution of the steel powder, which was due to mechanically scraping from the steel substrate while the corrosion products were being removed.

The line scanning for studying the depth profiles of alloying elements was accomplished along the line in the middle of EPMA image, as shown in Fig. 2(a). The line scanning for probing the presence of chromium, nickel and silicon in the corrosion products is shown in Fig. 2(b). In the region of corrosion products closer to the steel surface, chromium and silicon concentrated with roughly similar density to those in the steel substrate, as shown in Fig. 3(b), where the larger dot density in Fig. 3(b) corresponds to the higher relative intensity in Fig. 2(b). The concentration did not appear in the region near the surface of the corrosion products. It is shown in Fig. 3(b) that silicon randomly aggregated as the form of small islands in the outer region of the corrosion coating contacting with
air, but not chromium. The nickel content gradually decreased toward the surface of the corrosion products formed on the coupons A45 and A52, as shown in Fig. 2(b), except for the coupon A50 due to the insignificant content of nickel in the steel substrate.

4. DISCUSSION

The coupons A45 and A52 with different silicon content, Table 1, had almost the same relative fractions of constituent phases, i.e., goethite(m+s1+s2), lepidocrocite and superparamagnetic maghemite, as listed in Table 2. However, the relative fraction, 61%, of the small-sized goethite(s1+s2) on A52, which was higher in silicon content, was larger than that, 55%, on A45. It was indicated that increasing the silicon content in the steel substrate resulted in the increase the relative fraction of small-sized goethite particles exhibiting superparamagnetism. Increasing the fraction of small-size goethite could be helpful in the formation of the complete protective layer to prevent water and oxygen penetration to the steel substrate by densely compacting the small particles. Fig. 3(b) shows that the concentrations of silicon and chromium appeared to drop at the similar position in the corrosion products. Also, although the mapping of silicon and chromium on the coupon A52 do not appear in Fig. 3, it is revealed that their concentrations dropped at the similar position, as appeared on the coupon A50. However, although the chromium distribution was similar to others, the behavior of silicon in the coupon A45 could not be confirmed due to low concentration. The behaviors of chromium and silicon are interesting, since it may be inferred that they could have a certain interaction with iron oxides in the corrosion products, together. It was reported by Yamashita et al.\textsuperscript{13} that increasing the chromium content in the synthetic chromium-substituted goethite ((α-Fe\textsubscript{1-x}Cr\textsubscript{x})OOH) up to x=22wt.% resulted in the decrease of the goethite particle size from 90 nm for no chromium to 10 nm for greater than 3 wt.% chromium. However, it is not clear whether or not chromium and/or silicon, which diffused from the steel substrate, refined the goethite particles in the atmospheric corrosion products investigated in this study. The refining mechanism of iron oxide particles in atmospheric corrosion products will be a subject of further study.

Fig 2(b) shows that nickel content gradually decreased toward the surface of the corrosion products. The composition of corrosion products on the coupons A50 and A52 with different nickel content were very similar to each other in every aspect, i.e., the constituent phases, their relative fractions and particle size distribution, as listed in Table 2. An extensive research\textsuperscript{4} revealed that increasing the nickel content in steel substrate resulted in decreasing corrosion rate of steel, which did not necessarily mean the particle size refinement. Unfortunately, the decrease of the corrosion rate
with increasing nickel content could not be explained in this study.

5. CONCLUSIONS

Nickel had negative gradient toward the surface of the corrosion products and had no detectable influence on the composition of corrosion products. In the region closer to the steel surface, silicon and chromium distributed with similar concentration to those in the steel substrate. Increasing the silicon content resulted in increasing the relative fraction of superparamagnetic goethite(s₁+s₂) in the corrosion products. The refining mechanism of iron oxide particles which formed in atmosphere, will be a subject of further study.

6. ACKNOWLEDGMENTS

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Reference