DEVELOPMENT OF NANO-PHASE IRON OXIDES FROM SHORT-TERM ATMOSPHERIC CORROSION OF CARBON STEEL

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ABSTRACT

The performance of steels used for structural and industrial applications is affected by atmospheric corrosion. The study of development of corrosion products in atmospherically exposed steels is very important to understand the corrosion process. A systematic study has been made of the development of corrosion products formed on carbon steel atmospherically exposed for short times along the Gulf of México. Carbon steel coupons were exposed between 1 and 12 months at a marine location in Campeche, México, to study the corrosion as a function of time. The environmental parameters were monitored during the exposure period. The resulting corrosion products were analyzed by Mössbauer Spectroscopy, Micro-Raman Spectrometry and X-ray diffraction in order to completely identify the oxides and map their location in the corrosion coating. The most abundant oxides present in the corrosion products were lepidocrocite and goethite as evidenced by in-situ X-ray diffraction and transmission Mössbauer and micro-Raman analysis of the corroded coupons. Akaganeite was absent in the corrosion coatings even though the exposure site was in a marine environment. In a similar exposure of carbon steel coupons at one of the marine sites prior to this exposure, akaganeite was detected in the corrosion products. However during this present exposure the average chloride concentration was measured to be only 12 mg/m²/day as opposed to an average chloride concentration of 45 mg/m²/day measured in the previous exposure. Mössbauer analysis at 300 K and 77 K showed the presence of lepidocrocite and superparamagnetic goethite in amounts dependent on the exposure time. The average particle size of goethite in the corrosion coating was found to lie in the range of 7-10 nm. Mössbauer spectra of the corrosion products recorded at 4 K, showed the presence of an x-ray amorphous phase whose hyperfine parameters corresponded to ferrihydrite with particle size < 8 nm. The ratio of α-FeOOH/γ-FeOOH, measured by Mössbauer spectroscopy was found to be nearly 3.5 in carbon steel for short-term exposures, compared to the reported ratio of 1.5 for weathering steel for similar exposure periods from X-ray diffraction measurements. Micro-Raman analysis showed that the corrosion coatings were multi-layered with lepidocrocite closer to the surface and goethite closer to the steel.

Keywords: Goethite, Lepidocrocite, Mössbauer spectroscopy, Micro-Raman spectrometry, Superparamagnetism, Oxide layering
INTRODUCTION

"One small step for man, and one giant leap for mankind" the famous quote of astronaut Neil Armstrong, can be used to describe the complexity of corrosion research, where the contribution from every aspect of research addressing corrosion problems would immensely help develop corrosion resistant materials. Steel has been the most widely used alloy for structural and industrial applications, since the beginning of the industrial revolution. The lifetime of steel is directly related to its performance against corrosion. In the U.S.A. alone, estimated costs of corrosion are $500 b/yr. Maintenance of steel structures costs on an average of about $2000/person/year. Corrosion of steel caused by environmental conditions is termed as atmospheric corrosion.

Systematic studies on the formation and transformation of corrosion products and their correlation to the environmental parameters is very important to understand the processes that lead to the atmospheric corrosion of steels. It is of utmost importance to use a precise characterization technique which not only identifies the oxides uniquely but also can quantify the amount of each oxide present in a typical corrosion coating. One such method is the resonant recoil-less nuclear emission and absorption of \(\gamma\)-rays, also popularly known as the Mössbauer effect.

The oft quoted values of fraction of the different hydroxyoxides of iron in a corrosion coating are evaluated by such characterization techniques like X-ray diffraction, which cannot be successfully used when the particle size is less than 20nm. It turns out that the oxides formed during initial periods of exposure have particle size less than 15 nm. Hence Mössbauer spectroscopy is the most effective technique for characterization of such oxides. Research on the accurate characterization of the initial iron oxides formed on carbon steel atmospherically exposed for short-term would contribute immensely to the better understanding of the oxide formation and transformation. This new perspective in corrosion research involving accurate oxide characterization will highlight those corrosion processes which lead to a better understanding of the corrosion mechanism which eventually would lead to improving the performance of steels in highly corrosive environments.

Many regions along the Gulf of México have extremely corrosive environments due to high mean annual temperature, humidity, time-of-wetness and very high atmospheric pollutants. We have addressed the effect of short-term atmospheric corrosion on carbon steel exposed along the Gulf of México from micro-crystalline point of view of the oxides. The process of formation and the possible transformation of corrosion products resulting from short-term exposure of carbon steel, both as a function of environmental conditions and exposure time, has been investigated. This paper presents the results of the study of atmospheric corrosion of carbon steel, exposed in a marine location in México for up to 9 months.

SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

Standard 1010 grade Mexican carbon steel coupons measuring 150 x 100 x 6 mm (6 x 4 x 0.25") were exposed at Programa de Corrosion del Golfo de México (PCGM) in Campeche, México with a site identification tag CP1. Table 1 presents the chemical composition of the carbon steel coupons. The exposure site PCGM, located 300 m inland from the coast, was classified as a marine site having ISO site corrosion class C2 (T4, S1, P0). The carbon steel coupons were subjected to atmospheric exposure for 1, 2, 3, 6 and 9 months. Additional sets of coupons were exposed during the different seasons as well, to monitor the effect of seasonal variation on atmospheric corrosion. Various critical environmental factors like, temperature, humidity, chloride and sulfur-dioxide concentrations were measured during the exposure period. Table 2 presents the environmental conditions at the site monitored during the exposure of the carbon steel coupons. The corrosion coatings were carefully observed using optical microscope with a 50 X objective and a 10 X eyepiece, in combination with cross polarizers. In-situ X-ray diffraction analysis was performed to identify the oxide phases present. Cu K\(_\alpha\) radiation of wavelength of 1.54056 \(\AA\) was used to record the X-ray diffraction patterns of the corroded coupons. Transmission Mössbauer Spectroscopy (TMS) was used to record the spectra of hyperfine interactions, characteristic of the oxides, both at room temperature (300 K), and at liquid nitrogen temperature (77 K). For the TMS analysis, the corrosion coatings were removed from a 50 x 25 mm (2 x 1") piece of the exposed coupons, by carefully scraping the rust layer off the steel substrate. About 15 mg of the coating was mixed with 150 mg of boron nitride binder, and pressed into a 1 cm diameter tablet. The Mössbauer spectra were recorded at 300 K and 77 K using a 50 mCi Co/Rh source. Micro-Raman spectrometry was performed to identify the location of the different oxides within the corrosion coating. For Raman analysis, the corrosion products formed on the exposed steel coupons were prepared by shearing the steel and mounting the strips in room temperature-curing epoxy. The surface of the metallographic cross-section mount was then ground repeatedly with fine silicon carbide paper and finally polished with 0.25 \(\mu\)m diamond paste. The Raman spectra were recorded using a micro-Raman spectrometer, consisting of 25 mW helium-neon laser (\(\lambda = 632.817\) nm) for excitation.
and a grating of 1800 lines/mm. The laser power was reduced to an optimal value of 6 mW using neutral density filters to prevent the phase transformation of the different oxides due to laser heating.

RESULTS AND DISCUSSION

Optical microscopy measurements revealed that the corrosion coating was a well layered system even for exposure times as low as 2 months. The thickness of the coating was estimated to be 10 μm for the sample exposed for 2 months. Figure 1 shows the optical microscopy image of the sample CP1-14, exposed for 6 months, in PCGM. The corrosion coating was distinctly bi-layered with the outer layer composed of alternating bright orange bands characteristic of lepidocrocite and reddish brown bands characteristic of goethite (1). The inner layer was characterized predominantly by a dark brown hue.

In order to obtain a basic identification of the oxides present in the corrosion coating, in-situ X-ray diffraction patterns for all the coupons were recorded in the angular range of 10-120 deg. Figure 2 shows the X-ray diffraction patterns for the four corroded coupons in the angular range of 45-65 degrees. Comparison of the X-ray patterns of the coatings with those of standard oxides, indicated that lepidocrocite, and goethite were the dominant oxides present in the coatings (2). X-ray diffraction peaks corresponding to the steel substrate were also observed, and they corresponded to the regions where the corrosion coating was thin. The mean peak width of the X-ray patterns of the coupons showed an increase, as compared to pure standard oxides. This clearly suggested that the particle size was much smaller than the standards whose average particle size was 100 nm. The absence of the diffraction peak at 55.9 degrees, characteristic of the akaganite phase was very interesting indicating that akaganite did not form even though the exposure site was classified as a marine site. In prior exposures of carbon steel coupons at two other Campeche sites (closer to the Gulf of Mexico), akaganite was detected in the corrosion products. However, during this present exposure the average chloride concentration was measured to be only 12 mg/m²/day at CP1 as opposed to an average chloride concentration of 45 mg/m²/day measured in the previous exposure at CP2 (3). A map of the exposure sites in Mexico is available at reference (4).

Transmission Mössbauer analysis at room temperature of the corroded coupons was characterized by only a doublet. The doublet observed at room temperature is indicative of the presence of lepidocrocite and/or akaganite and/or superparamagnetic goethite. But the X-ray analysis indicated the absence of akaganite in the corrosion products. Transmission Mössbauer analysis of the corrosion products was carried out at 77 K, in order to distinguish the two oxide phases that were suspected to be present. Figure 3 shows the TMS spectra at 77 K of the corrosion products on the four coupons. The low temperature spectra consisted of two components namely, a doublet and a broadened sextet. The doublet was fitted with a broadened doublet, and the fit parameters yielded an average quadrupole splitting of Δ = 2ε = 0.62±0.03 mm/s, with a distribution of σ(0) = 0.2+0.1 mm/s that corresponded to lepidocrocite and very fine particle goethite. The final fit parameters for the broadened sextet corresponded to that of magnetically ordered goethite having a distribution of particle size. Table 3 presents the Mössbauer fit parameters of the spectra recorded at 77 K. The low temperature Mössbauer results, clearly showed that goethite displayed a distribution of magnetic field, which then indicated a distribution of particle size. Since the magnetic order for the goethite was absent at room temperature, the particle size was estimated to be in the range of 8-15 nm. Also the distribution of the doublet measured at 77 K strongly indicated the presence of nano-phase goethite with particle size < 8 nm (5). TMS analysis at 4K was performed on the sample CP1-18. The resulting spectrum was fitted to three iron sites. The fit parameters showed a unique magnetically split site corresponding lepidocrocite with hyperfine field value of 446.9 kOe, and a hyperfine field distribution corresponding to goethite, with an average hyperfine field of 500.2 kOe. Of interest was the third site whose hyperfine field was 456.1 kOe, with an enormous distribution of 43.2 kOe. This phase was not identified by X-ray analysis. This X-ray amorphous phase whose hyperfine parameters corresponded to ferrihydrite (6), could be identified only by Mössbauer spectroscopy due to its poor crystallinity. The relative contribution of goethite and lepidocrocite to the 4 K spectra were 38.1 % and 11.5 %, while that of the X-ray amorphous phase was 50.4 %. The ratio of α-FeOOH/γ-FeOOH, measured by Mössbauer spectroscopy was found to be nearly 5.5 in carbon steel for short-term exposures, compared to the reported ratio of 1.5 for weathering steel for similar exposure periods from X-ray diffraction measurements (7). Figure 4 shows the variation of mean field of magnetic goethite measured at 77 K as a function of exposure time. The superparamagnetic relaxation model was used to estimate the particle size of nano-phase goethite (8). Accordingly, the mean particle size of goethite, increased from 6 nm to about 10 nm as the exposure time increased from 2 months to 9 months. A decrease in the distribution of particle size was observed as a function of exposure time. This clearly indicated that the particle size became more uniform as the exposure time increased.

Micro-Raman analysis confirmed the layering of oxides as observed from optical microscopy. The layering of oxides in the coating was very similar to those observed in weathering steel. Figure 5 shows the line scan micro-Raman spectra of the
sample CP1-04, exposed for 2 months. The line scan was recorded from the coating surface inward toward the steel. The outer layer was composed of a mixture of lepidocrocite and goethite, while the inner layer was predominantly small particle goethite. A gradual decrease in the Raman signal was observed as the line scan proceeded from the outer layer to the inner layer lying closer to the steel substrate. This indicated that the inner layer was composed of mainly of a mixture of nano-phase goethite and/ some superparamagnetic maghemite and/or ferrihydrite.

CONCLUSIONS

The corrosion products formed on carbon steel coupons following short term atmospheric exposure at marine site along the Gulf of México were studied. In-situ X-ray diffraction and transmission Mössbauer and micro-Raman analysis of the coupons showed that lepidocrocite and goethite were the dominant oxides present in the corrosion products. Akaganeite was absent in the corrosion coatings. The corrosion coating was very well layered even for short-term exposures. Transmission Mössbauer analysis at room temperature identified the presence of lepidocrocite and superparamagnetic goethite. In addition, transmission Mössbauer analysis showed that the superparamagnetic component became magnetically ordered at 77 K, which then indicated the particle size of goethite to be in the range of 8-15 nm. The doublet measured at 77 K comprised of lepidocrocite and nano-phase goethite whose particle size was less than 8 nm. As a function of exposure time, the mean particle size increased from 6 nm-10 nm as evidenced by Mössbauer measurements. Furthermore the particle size became more uniform as the exposure time increased. The ratio of α-FeOOH/γ-FeOOH was found to be nearly 3.5 for carbon steel atmospherically exposed for short times. Of importance is the detection of the X-ray amorphous phase whose hyperfine parameters corresponded to ferrihydrite, only by Mossbauer spectroscopy due to its poor crystallinity. This phase could not be detected by other characterization techniques used. Micro-Raman measurements indicated the presence of nano-phase goethite closer to the steel substrate. Hence the use of highly specialized characterization techniques like Mössbauer spectroscopy and micro-Raman spectrometry is strongly emphasized for precise characterization of the various oxides formed in the corrosion coating.

ACKNOWLEDGMENT

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REFERENCES

4. Map of Exposure sites in Mexico, URL: www.physics.odu.edu/~cnpml/mx/
### TABLE 1.
CHEMICAL COMPOSITION OF CARBON STEEL COUPONS.

<table>
<thead>
<tr>
<th>Grade</th>
<th>C (%)</th>
<th>Mn (%)</th>
<th>P Max. (%)</th>
<th>S Max.(%)</th>
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<tr>
<td>1010</td>
<td>0.08 - 0.13</td>
<td>0.30 - 0.60</td>
<td>0.040</td>
<td>0.050</td>
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</tbody>
</table>

### TABLE 2.
ENVIRONMENTAL CONDITIONS AT PCGM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Location</th>
<th>Exposure Time</th>
<th>Exposure Period</th>
<th>Average Temp. (°C)</th>
<th>Humidity</th>
<th>Chloride Conc. (mg/m²/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP1-04</td>
<td>PCGM</td>
<td>2 Months</td>
<td>May 97-June 97</td>
<td>29.7</td>
<td>67.0 %</td>
<td>5.12</td>
</tr>
<tr>
<td>CP1-08</td>
<td>PCGM</td>
<td>3 Months</td>
<td>May 97-July 97</td>
<td>29.2</td>
<td>70.0 %</td>
<td>13.60</td>
</tr>
<tr>
<td>CP1-14</td>
<td>PCGM</td>
<td>6 Months</td>
<td>May 97-Oct 97</td>
<td>28.6</td>
<td>74.5%</td>
<td>12.50</td>
</tr>
<tr>
<td>CP1-18</td>
<td>PCGM</td>
<td>9 Months</td>
<td>May 97-Jan 98</td>
<td>27.3</td>
<td>75.7%</td>
<td>12.00</td>
</tr>
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</table>

### TABLE 3.
TRANSMISSION MÖSSBAUER FIT PARAMETERS RECORDED AT 77 K FOR MAGNETIC GOETHITE PRESENT IN THE CARBON STEEL COUPONS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>IS (mm/s)</th>
<th>Δ (2ε) (mm/s)</th>
<th>B (kOe)</th>
<th>σ (kOe)</th>
<th>Sextet Area(%)</th>
<th>Doublet Area(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP1-04</td>
<td>0.473</td>
<td>-0.168</td>
<td>384.3</td>
<td>124.0</td>
<td>79.06</td>
<td>20.89</td>
</tr>
<tr>
<td>CP1-08</td>
<td>0.476</td>
<td>-0.190</td>
<td>386.8</td>
<td>137.5</td>
<td>63.68</td>
<td>36.39</td>
</tr>
<tr>
<td>CP1-14</td>
<td>0.473</td>
<td>-0.201</td>
<td>408.1</td>
<td>126.6</td>
<td>64.69</td>
<td>35.30</td>
</tr>
<tr>
<td>CP1-18</td>
<td>0.476</td>
<td>-0.214</td>
<td>433.9</td>
<td>103.7</td>
<td>62.10</td>
<td>37.89</td>
</tr>
<tr>
<td>Bulk Goethite (2)</td>
<td>0.475</td>
<td>-0.240</td>
<td>496.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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FIGURE 1. Optical image of the corrosion coating of the sample CP1-14, exposed for 6 months.

FIGURE 2. X-ray diffraction patterns of the corroded carbon steel coupons exposed.

L = Lepidocrocite
G = Goethite
FIGURE 3. Transmission Mössbauer spectra recorded at 77 K for the carbon steel coupons exposed.
FIGURE 4. Variation of the mean hyperfine field of goethite at 77 K as a function of exposure time, indicating the increasing particle size with exposure time.
FIGURE 5. Micro-Raman line scan for sample CP1-04, exposed for 2 months