Study of the corrosion products formed on carbon steels in the tropical atmosphere of Panama

J.A. Jaén*, M.S. de Villalaz**, L. de Araque**, C. Hernández** and A. de Bósquez**

Abstract
Mössbauer spectroscopy and X-ray powder diffraction (in selected samples) have been used to characterize corrosion products on carbon steels after atmospheric exposure to the tropical Panamanian locations of Panama and Colon, classified according to ISO 9223 as C3 and C5, respectively. Goethite ($\alpha$-FeOOH) of intermediate particle size (20-100 nm), lepidocrocite ($\gamma$-FeOOH), a spinel phase consisting of non-stoichiometric magnetite ($Fe_{1+x}O_4$) and/or maghemite ($\gamma'$-Fe$_2$O$_3$) and nano-sized particles were identified in the corrosion products. The spinel phase is related to short term atmospheric exposure transforms in time to other corrosion products. The corrosion resistance increased with fraction of goethite following a saturation-type behavior.

Keywords

1. INTRODUCTION

It is of interest the phase analysis of corrosion products to understand the effect of the environment on the corrosion rate and corrosion mechanisms of steels. In recent years, some studies have been performed on the analysis of rusts from carbon steel exposed to the tropical atmosphere using Mössbauer spectroscopy and several other techniques.$^{[1-7]}$

The usual reported atmospheric corrosion products on iron include $\alpha$-FeOOH (goethite) in various degrees of crystallinity, $\beta$-FeOOH (akaganeite) in marine environments, $\gamma$-FeOOH (lepidocrocite) main component of the initial rust layer, and the spinel phase magnetite ($Fe_{1+2}O_4$), maghemite ($\gamma$-$Fe_{2}O_3$) and non-stoichiometric magnetite ($Fe_{1+3}O_4$).

In the present work, the corrosion products formed on carbon steels exposed to tropical locations of Panama are systematically investigated.
2. EXPERIMENTAL

The experimental procedure for the preparation of test specimens and exposure to the atmosphere were described in a previous paper[4]. Two types of carbon steels were used, type 1020 and A-36. Corrosion products were collected after exposures to the atmosphere following the programs given in table I and II. The site Panama was located at the University Campus, whereas Colon is in a moderate industrial area near the seashore.

Table III presents the classification of test sites according to environmental levels (SO₂ = sulphation rate, Cl⁻ = chloride ion level and tₙ = time of wetness) using ISO 9223[8]. Corrosion products were separated mechanically before determining corrosion rates (corrosion penetration p) from weight losses[9 and 10]. They were characterized by conventional constant-acceleration ⁵⁷Fe Mössbauer spectroscopy at room temperature and some samples at 80 K. The Mössbauer spectra were fitted using the program NORMOS. X-ray powder diffraction (Rigaku diffractometer, Model RTP 300 RC) was used as a complementary technique in the analysis of selected samples.

3. RESULTS AND DISCUSSION

The results of corrosion rates and losses for both types of steel are summarized in table IV using bilogarithmic relationships. The difference between corrosion rates, specially at early stages, are due to the higher levels of sulphation rate ([SO₂]), chloride ion ([Cl⁻]) and time of wetness (tₙ) in Colon site as compared to Panama[4 and 8].

Representative XRD patterns of corrosion products from A-36 steel are shown in figures 1 and 2. The identified constituents were lepidocrocite (γ-FeOOH), goethite (α-FeOOH) and magnetite (Fe₃O₄). The peak intensity of the diffraction lines attributed to magnetite gradually decreases with exposure time, thus indicating that magnetite is a dominant crystalline constituent at the early stages of atmospheric corrosion in the tropical locations of Panama and Colon. It is important to note that under unfavorable conditions of peak width and intensity, it is difficult to ascertain the presence of magnetite, maghemite or both. Thus, even though we have identified the presence of magnetite, XRD does not exclude the possibility of maghemite. The same constituents were identified in the corrosion products from steel 1020, but the intensity of the magnetite peaks were very much...
Table IV. Bilogarithmic relationships between penetration values $p$ (μm) and exposure time $t$ (years), and their correlation coefficients (C.C.)

<table>
<thead>
<tr>
<th>Test site</th>
<th>Substrate</th>
<th>Equation</th>
<th>C.C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Panama</td>
<td>A-36</td>
<td>$\ln p = 3.908 + 0.438 \ln t$</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>1020</td>
<td>$\ln p = 3.423 + 0.576 \ln t^*$</td>
<td>0.882</td>
</tr>
<tr>
<td>Colon</td>
<td>A-36</td>
<td>$\ln p = 4.770 + 0.644 \ln t$</td>
<td>0.986</td>
</tr>
<tr>
<td></td>
<td>1020</td>
<td>$\ln p = 4.671 + 0.590 \ln t^*$</td>
<td>0.971</td>
</tr>
</tbody>
</table>

* Includes previous results using the same type of steel, in order to have more significance in the experimental equation.

Figure 1. XRD patterns of A-36 steel corroded samples (a) P-3-2 and (b) P-6 exposed at Panama site (monochromatic radiation Cu-Kα). Descriptions: L = lepidocrocite, G = goethite and M = magnetite.

Reduced, indicating lower magnetite content in the rust.

Corrosion products were also characterized using Mössbauer spectroscopy (Figs. 3-4). Figure 3 show the Mössbauer spectra of the adherent rust formed in the 1020 steel in test site Panama. It is worth noting that adherent and non-adherent rust showed similar Mössbauer spectra. They were fitted to a quadrupole doublet ($\delta_{Fe} = 0.34-0.41$ mm s$^{-1}$, $\Delta = 0.53-0.56$ mm s$^{-1}$ and $\Gamma = 0.54-0.56$ mm s$^{-1}$) and three sextets with hyperfine magnetic fields, $H_1 = 49.2-50.0$ T, $H_2 = 45.9-46.6$ T and $H_3 = 34-36$ T. The fit parameters suggested that the corrosion products could contain lepidocrocite and nano-sized particles. Akaganeite was exclude since it could not be observed in the X-ray analysis and in the 80 K Mössbauer spectra. Hyperfine magnetic fields $H_1$ and $H_2$ can be ascribed to the spinel non-stoichiometric-magnetite ($Fe_{3-x}O_4$). In some cases, for samples of two or three years exposure only the outer sextet was observed due to the total oxidation to the spinel better characterized as maghemite ($γ-Fe_2O_3$). The remaining sextet of broad asymmetrical lines has hyperfine parameters corresponding to goethite of intermediate particle size (20-100 nm).[1]

Figure 4 shows the Mössbauer spectra of the rust formed in the case of steel A-36 in test site Panama, which were deconvoluted practically using the same fitting model; i.e. a quadrupole doublet ($\delta_{Fe} = 0.33-0.36$ mm s$^{-1}$, $\Delta = 0.57-0.62$ mm s$^{-1}$ and $\Gamma = 0.40-0.47$ mm s$^{-1}$) and the three sextets assigned to non-stoichiometric magnetite/maghemite and to goethite of intermediate particle size. The slight increase of quadrupole splitting hint to a decrease of the fraction of $γ$-FeOOH phases in the rust. It should be pointed out that the relative amount of the spinel phase is larger at the initial stages of corrosion, but decreases during period of the test.

The Mössbauer spectra of the rust from Colon test site showed a quadrupole doublet with two
collapsing sextets fitted as distributions of hyperfine fields, corresponding to lepidocrocite and/or nanosized particles, goethite and a spinel phase. Again, more spinel phase is observed at the beginning of corrosion, diminishing after prolonged exposure to the atmosphere. The shape of the spectra strongly suggests a highly distorted, defective and oxidized spinel structure in the rust from Colon.

In order to know the change of rust composition with exposure period, and the increase of corrosion penetration, a ternary diagram with the fractions (Mössbauer areas) of the three type of corrosion products was used, as seen in figure 5. It is clear that for short exposure periods rust contains large amount of the spinel phase, thus, the initially high corrosion rates could be related to the presence of the spinel phase. Oh et al. related the formation of bulk γ-Fe₂O₃ to the high corrosion rate of carbon steel. The spinel phase has smaller contributions in the samples of Colon as compared to those of Panama. This was explained elsewhere as due to the high precipitation and humidity (lack of wet-dry cycles) prevailing in Colon, but it might be that this phase initially formed as a result of the reduction of rust layer via a solid state reaction. With the decrease of the amount of the spinel phase with exposure period, there is an increment of the other corrosion products, goethite for Panama test site and lepidocrocite (plus nano-sized particles) for Colon. In the latter case, there is also a slight increment of the goethite component.

According to the conclusions of a previous study, goethite of intermediate particle size is related to corrosion penetration (p) by a saturation behavior, following a Langmuir type of relationship.
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Using this approach, it could be obtained the relationships \( \text{p/Ag} = 0.258 + 0.0171 \text{ p} \) for rust from steel 1020, and \( \text{p/Ag} = 0.492 + 0.0141 \text{ p} \) for steel A-36; here \( \text{AQ} \) es the room temperature Mössbauer area of goethite of intermediate particle size. This goethite confers carbon steel certain degree of protection up to a limit given by the saturation surface coverage by goethite particles.

4. CONCLUSION

The main constituents of rust formed on carbon steels 1020 and A-36 after exposure at two sites in the tropical atmosphere of Panama are lepidocrocite, nano-sized particles, goethite of intermediate particle size and a spinel phase.

The spinel phase, consisting of \( \text{Fe}_{3-x}\text{O}_4 \) / \( \gamma\text{-Fe}_2\text{O}_3 \) is related to short term atmospheric exposure. This phase transforms in time to other
corrosion products. It is proposed that goethite of intermediate particle size gives some corrosion resistance up to a limit given by a saturation of this component on the surface.

REFERENCES