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Influence of a $CuSO_4$ Treatment on Atmospheric Steel Rust Formation A Mössbauer Spectroscopy Study*

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Abstract

Mössbauer spectroscopy has been used to analyze the rust layers formed on a weathering steel and a 1010 steel exposed for 10-1/2 months to an urban-industrial atmosphere. No significant difference was found comparing the rusts of both steels: they were composed by γ-FeOOH, superparamagnetic α-FeOOH, and an amorphous or gel-like compound. γ-FeOOH is more abundant in the internal rust layers, whereas the amount of α-FeOOH and the amorphous compound increase in the external rusts. Part of the samples received an initial copper deposit by immersion of the steel plates in a $CuSO_4$ bath. Mössbauer spectroscopy analysis showed that the amorphous substance was no longer present in the rusts of those specimens; that is, the rusts of both steels were formed only by γ-FeOOH and α-FeOOH.

Introduction

Low alloy steel corrosion is still a not well known field. Particular interest is focused on the so-called weathering steels which show a remarkable resistance to atmospheric corrosion once a stable rust is formed, especially in SO_2-containing atmospheres.[1]

Several analysis of the distribution of alloying elements in low alloy steels rust show an increase in copper and chromium concentration at the metal-oxide interface,[1-4] though some authors report a homogeneous distribution in the bulk rust with increasing concentration of alloying elements around pits and voids of the oxide layer.[5] Accordingly, it was supposed that the presence of copper and sulfate produces a change in the composition and/or morphology of the corrosion products of low alloy steels which would be responsible for their good corrosion resistance. This conclusion was reinforced by results of experimental research on the influence of Cu^{2+} and SO_4^{2-} ions on the formation of iron corrosion products.[6-9]

Furthermore, studies of steel corrosion products morphology detected the formation of two different layers when observed by reflected polarized light.[1,10,11] In low alloy steels, exposed to the atmosphere for more than a year, an internal optically isotropic layer was distinguished from an external optically active layer, while these two layers continued mixed in the rust of carbon steels, even after several years exposure. It was concluded that the internal optically isotropic layer would be responsible for the corrosion rate decrease of weathering steels. According to Miranda,[1] the internal rust would be a crack- and void-free compact layer, composed mainly by α-FeOOH. The presence of SO_4^{2-} would seem to play an important role in the process of α-FeOOH formation.[9] On the other hand, Missawa *et al*[12] propose that the metallic surface would be protected by an amorphous ferric oxyhydroxide compact layer with a considerable amount of bound water.

In the present work, the initial copper and sulfate contents on the surface of low alloy and 1010 steels waa increased by immersing in a $CuSO_4$ bath. By this method, the copper content increment at the metal-oxide interface can be obtained earlier than by the atmospheric weathering process. The influence of this procedure on the weathering steel patina formation could be studied. Analysis of the so-treated carbon steel corrosion products would allow to determine if, at initial corrosion stages, the effect of the copper deposited on the steel surface is comparable to that produced by copper as an alloying element in a weathering steel. The samples immersed in the $CuSO_4$ bath were exposed along with low alloy and 1010 steels blank specimens in an urban-industrial atmosphere.

Mössbauer spectroscopy was used for the analysis of the corrosion products.[13] This technique can give more information compared with other conventional techniques due to the fact that it is a very suitable tool in the study of crystalline or amorphous iron oxides and hydroxides in bulk and in ultrafine particles (< 100 Å).[14]

Experimental

Plates 30 cm long, 10 cm wide, and 0.2 cm thick of low alloy steel (see composition in Table 1) and 1010 steel were

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TABLE 1 — Low Alloy Steel Composition

Element	C	Mn	Si	S	P	Cr	Ni	Mo	Sn	Cu	Fe
% Weight	0.11	0.37	0.22	0.023	0.085	0.69	0.11	0.10	0.06	0.38	diff.

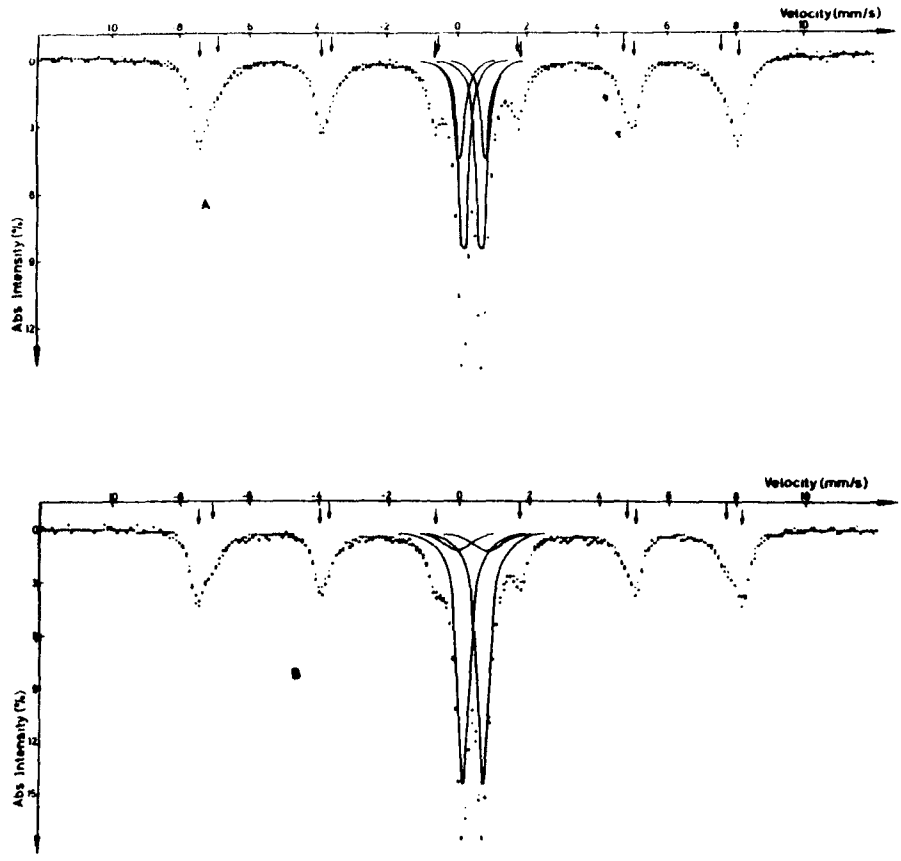

FIGURE 1 — Mössbauer spectra at L N temperature of 1010 steel rust. (A) external layer; (B) internal layer. ○ experimental points, • fitted points, + coincident points.

used. The samples were pickled with an hydrochloric acid solution (100 mL of HCl inhibited with 2 grams antimonious oxide and 2 grams stannous chloride per liter); next they were sandblasted and afterwards degreased with carbon tetrachloride. On half of the specimens, copper was deposited on the surface by immersing the plates in a 0.1% $CuSO_4$ solution for 4 minutes.

The plates were exposed for 10-1/2 months in the urban-industrial atmosphere of Buenos Aires City suburbs, facing north at a 30° angle. The exposition started at the end of autumn and finished in the middle of autumn the next year.

The samples of rust were taken from areas of the plates that were far away from the frames so that no water was caught in those zones during the drying periods. Samples of the external rust were taken by slightly scraping the surface with a razor. Then the bulk of the rust layer was removed by scraping and samples of the rust next to the metal surface were taken. The latter were called the internal rust samples.

Mössbauer spectra were measured using a constant acceleration spectrometer operated with a 256 channel analyzer in the time mode. The source was kept at room temperature and consisted of ^{57}Co in a Pd matrix. The iron content of the powder form samples was approximately 9 mg/cm^2. Measurements were carried out with the absorber at room and liquid nitrogen temperature. All spectra were analyzed by least squared computer fit,[15] using a pure Lorentzian shape. Parameters were constrained such that each component of a doublet as well as each pair of a magnetic sextet has equal width and area. Each spectrum has been fitted with different hypothesis and its quality was checked by χ^2 *test. Those whose* χ^2 values were statistically acceptable and showed physical consistency were selected. The corresponding χ^2 per degree of freedom are quoted in Table 3.

Results and Discussion

Mössbauer spectra of all the samples showed similar characteristics: at room temperature, they consist of peaks in the central region and a slight indication of a magnetic hyperfine interaction. At 77 K, a magnetic hyperfine spectrum appears superimposed with the paramagnetic peaks (Figures 1 to 4). The Mössbauer parameters obtained are summarized in Table 2, where at room temperature we have indicated only the values corresponding to the paramagnetic region. For

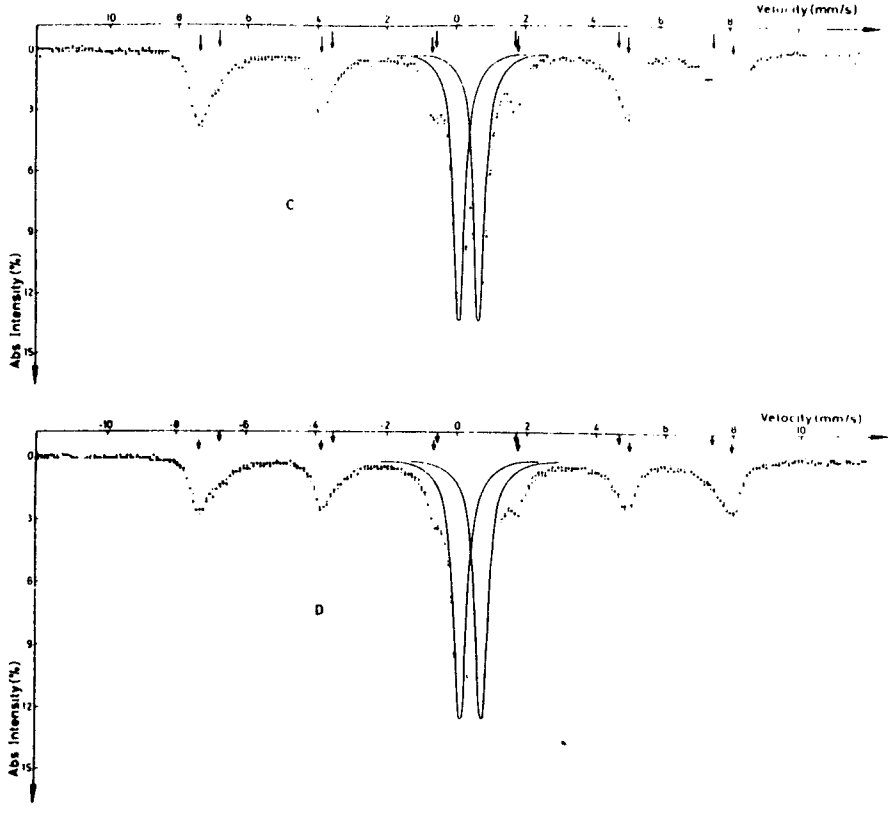

FIGURE 2 — Mössbauer spectra at L N temperature of 1010 steel with $CuSO_4$ bath rust. (C) external layer; (D) internal layer. For key, see legend to Figure 1.

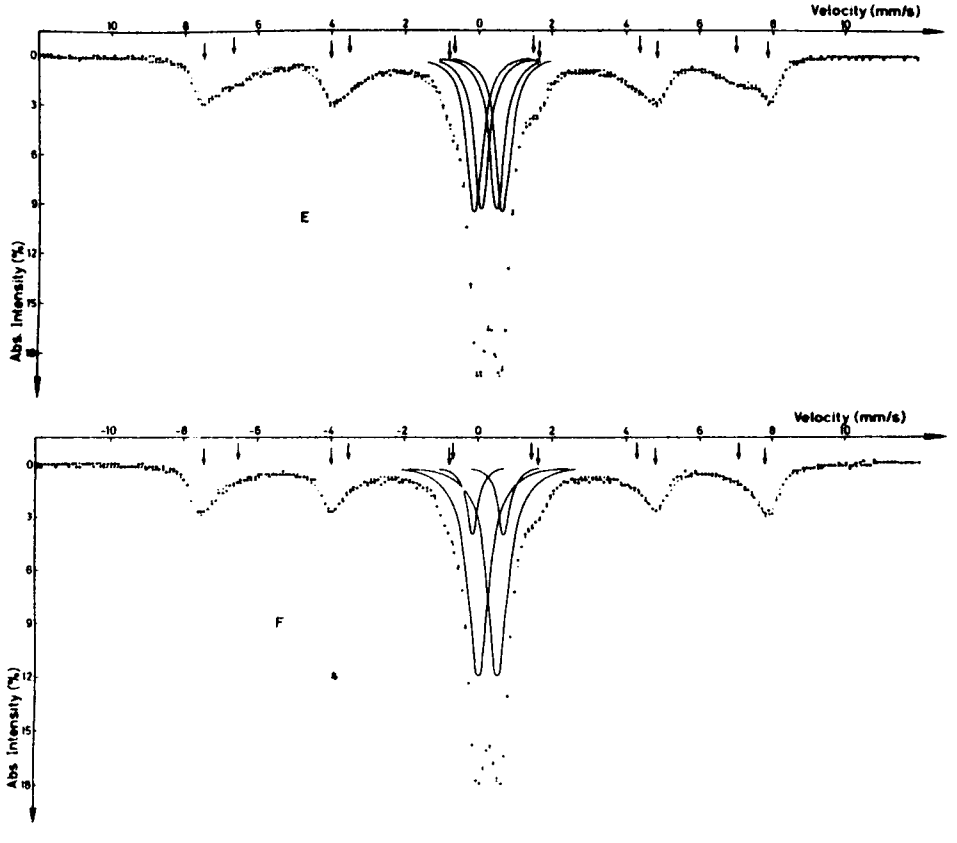

FIGURE 3 — Mössbauer spectra at L N temperature of weathering steel rust. (E) external layer; (F) internal layer. For key see, legend to Figure 1.

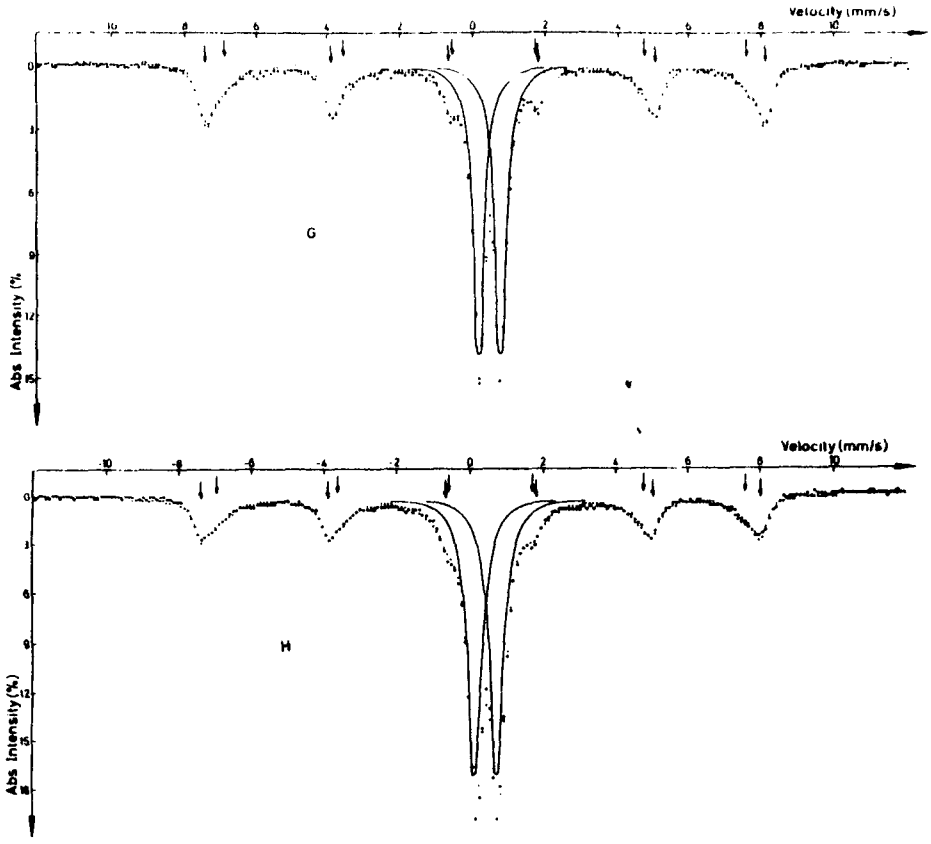

FIGURE 4 — Mössbauer spectra at L N temperature of weathering steel with $CuSO_4$ bath rust. (G) external layer; (H) internal layer. For key, see legend to Figure 1.

TABLE 2(a) — Mössbauer Parameters of the Fitted Spectra at Room Temperature

Steel	layer	γ-FeOOH Doublet		II Doublet	
		△mm/s	IS[(1)]mm/s	△mm/s	IS[(1)]mm/s
1010	external	0.55(4)	0.22(5)	0.65(6)	0.26(6)
	internal	0.54(4)	0.23(5)	0.65(6)	0.27(6)
1010 with $CuSO_4$ bath	external	0.54(4)	0.23(5)	0.67(6)	0.22(6)
	internal	0.56(4)	0.23(5)	0.70(6)	0.22(6)
Weathering st.	external	0.61(4)	0.20(5)	0.64(6)	0.28(6)
	internal	0.61(4)	0.22(5)	0.65(6)	0.27(6)
Weathering st. with $CuSO_4$ bath	external	0.60(4)	0.20(5)	0.69(6)	0.21(6)
	internal	0.54(4)	0.23(5)	0.70(6)	0.22(6)

[(1)]Referred to Pd matrix at room temperature.

doublet I, these values are typical for γ-FeOOH.[16] The corresponding line widths are within 0.31-0.35 mm/s. When doublet II is present, the parameters are characteristic of an amorphous FeOOH or gel.[17] Besides we cannot discard the presence of α-FeOOH smaller than 40 Å, but to confirm that, it would be necessary to analyze the samples at lower temperature. At the magnetic region, the corresponding parameters indicate that α-FeOOH ultrafine particles are present[18] with distributions of sizes centered about 85 Å and finer. The presence of β does not seem probable because it has been shown that β-FeOOH is the least stable of all types of FeOOH. Only considerable concentration of chloride ions stabilizee it.[19]

The approximate relative concentrations of each oxyhydroxide, calculated from the area ratios of the corresponding spectra at liquid nitrogen temperature, are shown in Table

TABLE 2(b) — Mössbauer Parameters of the Fitted Spectra at Liquid Nitrogen Temperatures

Steel	Layer	Superimposed Hyperfine Spectra						γ-FeOOH Doublet			II Doublet		
		H Koe	QS mm/s	IS mm/s	Γ mm/s	H Koe	QS mm/s	IS mm/s	Γ mm/s	Δ mm/s	IS mm/s	Δ mm/s	IS mm/s	Γ mm/s
1010	ext.	483(3)	−0.12(3)	0.33(3)	0.4	452(6)	−0.12(6)	0.31(6)	0.8	0.57(4)	0.40(4)	0.79(6)	0.37(6)	0.45
	int.	487(3)	−0.12(3)	0.33(3)	0.4	456(6)	−0.11(6)	0.33(6)	0.8	0.57(4)	0.40(4)	0.74(6)	0.34(6)	0.45
1010 + $CuSO_4$	ext.	483(3)	−0.12(3)	0.33(3)	0.4	449(6)	−0.12(6)	0.33(6)	0.8	0.60(4)	0.40(4)	—	—	—
	int.	474(3)	−0.12(3)	0.32(3)	0.4	440(6)	−0.13(6)	0.33(6)	0.9	0.60(4)	0.39(4)	—	—	—
Weath.	ext.	477(3)	−0.11(3)	0.30(3)	0.4	426(6)	−0.12(6)	0.29(6)	0.9	0.62(4)	0.37(4)	0.66(6)	0.37(6)	0.49
	int.	477(3)	−0.12(3)	0.31(3)	0.4	425(6)	−0.09(6)	0.33(6)	1.0	0.58(4)	0.30(4)	0.68(6)	0.30(6)	0.47
Weath. + $CuSO_4$	ext.	482(3)	−0.11(3)	0.33(3)	0.4	449(6)	−0.12(6)	0.32(6)	0.9	0.58(4)	0.39(4)	—	—	—
	int.	479(3)	−0.13(3)	0.32(3)	0.4	452(6)	−0.12(6)	0.33(6)	0.8	0.58(4)	0.39(4)	—	—	—

The isomer shifts are referred to Pd matrix at room temperature

$$QS = \frac{e^2 qQ}{8}(1-3\cos^2\Phi)$$

3. It was assumed that the recoil free fraction for all components are equal.[13] The "f" values in amorphous materials are reduced when comparing with their values in the crystalline state, with a temperature dependence consistent with the harmonic model and a smaller θ_D.[20] This fact does not invalidate the general tendencies shown in Table 3. The figures corresponding to the amorphous compound could be somewhat greater and in this case, the other figures should be smaller.

For the weathering and 1010 steel plates without the $CuSO_4$ treatment, a larger quantity of γ-FeOOH is found in the internal layers than in the external ones, whereas α-FeOOH as well as the amorphous compound are more abundant in the external layers.

Comparing the external layers and the internal ones of both steels, no significant differences in the composition of the corresponding rusts are observed; the 1010 external layer contains a somewhat larger amount of α-FeOOH and a smaller quantity of the doublet II compounds than the low alloy steel rust, while the 1010 steel internal layer has a larger proportion of α-FeOOH and a smaller proportion of γ-FeOOH than the other internal layer.

A remarkable difference is obtained for the rusts formed on the plates immersed in the $CuSO_4$ bath: the doublet corresponding to the amorphous oxyhydroxide is no longer present in the rusts of both steels. Along with the disappearance of the amorphous compound in the corrosion products, an increase in the proportion of γ-FeOOH is observed, while the amount of α-FeOOH in the rust is similar to that obtained for the steels without the $CuSO_4$ treatment.

According to the model proposed by Meisel,[21] it is most probable that the oxidation of Fe^0 to Fe^{2+} initially would lead to the formation of FeO islands and, by surface diffusion, to the formation of one or a few monolayers of wüstite. As the oxidation process continues, Fe_3O_4 and/or γ-Fe_2O_3 are formed in layers of thickness between 50 and 100 Å. These compounds have similar structures and little difference between their lattice parameters, and this fact would allow an epitactical growth of 10 to 30 atomic layers. The oxides that form this protective layer are not stable enough. Under the influence of water vapor, Fe_2O_3 is converted to the orthorhombic compound γ-FeOOH. The other products have a cubic structure. This phase transformation is accompanied by a large increase in molar volume and leads to a disruption of the oxide layer into small particles which behave as amorphous or gel-like compounds. The destruction of the oxide layer allows the progress of the oxidation process. On the other hand, the corrosive environmental conditions provide the activation energy (heat, radiation) necessary to transform γ-FeOOH to α-FeOOH and later to α-Fe_2O_3, which are more stable corrosion products.

It should be also considered that the metal surface exposed to the atmosphere is covered during certain periods by an electrolyte layer originated by rain water or condensed humidity. Partial dissolution of the corrosion products already formed takes place, which helps in the formation of α-FeOOH[22] and to further metal corrosion.

For the steels studied, our results show that the external layer of the rust, which is the most exposed to the corrosive environment, presents a larger proportion of α-FeOOH than γ-FeOOH and a greater amount of amorphous compounds. These facts agree with the ideas exposed above.

It should be noted that this behavior is very similar for the 1010 and the weathering steels. The eventual influence of the microalloying elements would not be evident yet, as the exposure period is short and the rust would have not consolidated.

A similar tendency, although less marked, for the ratio of α-FeOOH to γ-FeOOH, is observed in the steel plates with the copper deposit. Another important fact is the disappearance of the amorphous substance or gel from both layers. This result contradicts the hypothesis that the observed copper enrichment[1-4] in the metal-oxide interface favors the formation of an amorphous layer in the internal rust.

TABLE 3 — Relative Concentration of Oxyhydroxides

Steel	Layer	Magnetic Component	γ-FeOOH	II Doublet	χ^2_δ
1010	external	53%	27%	20%	1.08
	internal	46%	44%	10%	1.22
1010 with $CuSO_4$	external	54%	46%	—	1.18
	internal	48%	52%	—	0.95
Weathering st.	external	47%	26%	27%	1.11
	internal	40%	50%	10%	0.98
Weathering st. with $CuSO_4$ bath	external	47%	53%	—	1.05
	internal	40%	60%	—	1.20

χ^2_δ: χ^2 per degree of freedom.

In a previous work,[23] analyzing the rust of the same weathering steel exposed for 10 months in Buenos Aires urban-industrial atmosphere, we found a somewhat different distribution of the oxyhydroxides in the rust layers. The exposure period started in summer and ended in spring, and this fact might have some influence in the rust formation process. The composition of the external rust layer of our first samples was similar to that obtained for the weathering steel in the present experiment. The most important difference was observed comparing the internal layers composition: in the former test, no amorphous compounds were found in the internal rust layer and the proportion of α-FeOOH ultrafine particles was larger than in the present samples.

Conclusions

Our results show that there is a larger proportion of α-FeOOH to γ-FeOOH and a greater amount of amorphous compounds in the external rust layers of weathering and 1010 steels. This fact is in accordance with the models proposed[21,22] for atmospheric corrosion processes.

The present work also demonstrates that a copper deposit on low alloy steel and carbon steel surfaces produces a change in their atmospheric rust composition: the amorphous or gel-like corrosion products present in rusts of blank plates of both steels, disappears.

Even though the effect of immersing the steel plates in a $CuSO_4$ bath cannot be considered identical to the effect produced by the copper enrichment at the metal-oxide interface of a weathering steel exposed to the atmosphere, our results suggest that copper would not favor the formation of an amorphous protective layer on the metal surface.

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