Nature of the Corrosion Products Formed on Carbon Steel under Marine Atmosphere Environment Investigated by Vibration Spectroscopy

AUREL SOARE*, CRISTINA MANDRAVEL
Department of Physical-Chemistry, Faculty of Chemistry, University of Bucharest,4-12 Regina Elisabeta Blv., 030018, Bucharest, Romania

The corrosion of OL 37 carbon steel under marine environment was studied by means of the Fourier Transform vibrational spectroscopy methods (FT-IR and NIR-FT-Raman spectroscopy). The main components of the rust layer identified were goethite, lepidocrocite, amorphous ferric oxyhydroxide and magnetite. On this basis, a mechanism of formation of the corrosion products was proposed. This is important for further research in improvement of the carbon steel corrosion resistance.

Keywords: corrosion products, rust, marine environment, FT-IR and FT-Raman spectroscopy

The corrosion is defined as the destruction of the metal materials caused by the chemical or electro-chemical action of the surrounding environment. Particularly, the marine environment is very corrosive due to the high relative humidity, rainfall and time of wetness as well as high chloride content.

The chemical characterization of the rust formed on carbon steel [1, 2] and the understanding of rusting mechanism are very important factors both for the improvement of the steels corrosion resistance and the development of the anticorrosive protections [3, 4]. The applied methods for the corrosion study must fulfill the conditions of a rigorous control of the different factors characterizing the corrosion process [5]. Many authors [6-10] have studied the corrosion products formed on steel exposed to various environments by FTIR and Raman spectroscopy, scanning electron microscopy or X-ray diffraction. Iron oxyhydroxides and oxides are the main constituents of the rust generated by the corrosion of the steel surface in contact with aqueous phase.

The certain knowledge of the rust mixtures formed on the steel surface is very important whereas some of them, in time, convert to more protective and adherent modifications [2]. The main phases observed were lepidocrocite (γ-FeOOH), goethite (α-FeOOH), amorphous oxyhydroxide (β-FeOOH) and magnetite (Fe_3O_4). Green rust was observed, too. It was reported that out of the oxyhydroxides, goethite is the most stable phase [8, 10, 11]. During the initial stage, lepidocrocite is formed, but it is subsequently oxidized to goethite.

The phase composition of the rust depends on the physico-chemical factors of the corrosion process such as: electrolyte composition, *p*H, time of exposure, environment, type of steel and temperature.

In this paper we used vibration spectroscopy (FT-IR and NIR-FT Raman) data to evidence the nature of the corrosion products formed on carbon steel exposed to the marine environment. In this domain, there is still little information in Romania about the types of corrosion products formed in marine atmosphere conditions. Taking into account our previous studies [1, 2], the goal of this work was to study the nature of the corrosion products and to propose a mechanism of their formation on OL 37 steel exposed to the natural marine environment.

Experimental part

As tested material, OL 37 carbon steel was used. Samples of sheets of 200 x 100 x 2 mm dimensions were prepared using abrasive blasting with specific requirements (Sa 2□). Abrasive blasting represents the process of preparing and cleaning a metallic surface by an abrasive jet material such as grit, corundum or sand.

OL 37 steel composition, in accordance with Romanian STAS 500/2 [12], is shown in table 1.

Table 1
CHEMICAL COMPOSITION OF OL 37 STEEL

Steel mark	Chemical composition / %			
	C	Mn	P	S
OL 37	0.22	max. 0.85	0.055	max. 0.055

Carbon steel sheets were exposed to marine environment on the south-east coastline of Romania in a marine experimental site, near Constantza. The experimental site is located 50 meters away from the coastline and 7 m altitude in open area. The sheets were mounted on one meter high racks at an angle of 45 degrees to the vertical and facing south-east toward the Black Sea.

The exposure time of the OL 37 steel sheets was 2 years. After this period the exposed sheets were completely covered with a thick, brown coating of corrosion products. For analyses, the corrosion products, formed and developed in time, were sampled by scraping out of outer layer with a wire brush and inner layer with a razor. Then the samples were stored under laboratory conditions (about 23° C temperature and 60% relative humidity).

Two complementary, FT-IR and NIR-FT-Raman spectroscopic methods were used. FT-IR spectra were carried out on Vertex 70 – Brucker spectrometer with spectral resolution better than 0.5 cm^{-1} , wave number accuracy better than 0,01 cm^{-1} and photometric accuracy

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* *email: aurel_soare@yahoo.co.uk: Tel.: 0727 71 88.22*

better than 0.1%T at room temperature. Specimens were pressed into a spectroscopic pure KBr matrix (with KBr: Probe = 300:1 ratio).

NIR-FT-Raman spectra of the analyzed samples were recorded with a Bruker VERTEX 70 NIR-FT-Raman instrument with a spectral range of 3500-50 cm^{-1}, wave number accuracy better than 0,1 cm^{-1}, spectral resolution better than 0.8 cm^{-1}. A Nd: YAG laser with an exciting power between 1 mW to 500 mW at a wavelength of 1064 nm was used. For each sample 50 scans were accumulated at a resolution of 4 cm^{-1}; Ge detector and integral preamplifier were cooled to 77 K by liquid nitrogen for all measurements.

Both FT-IR and NIR-FT-Raman spectrometers operated with OPUS program, which permits a fine treatment of the spectra.

Results and discussions

The FT-IR spectra of the inner and outer rust layers formed on OL 37 steel exposed to marine environment are shown in figures 1 and 2, and Raman spectra are shown in figures 3 and 4.

FT-IR analysis

The main product identified for inner rust layer was lepidocrocite (peak appearing at 1024 cm^{-1}). Goethite (with its characteristic peaks at 890 and 798 cm^{-1}), magnetite (590 cm^{-1}) and amorphous oxyhydroxid (feroxite) (465 cm^{-1} and 1450 cm^{-1}) were found, too [1, 13]. The weak peaks from 2925 and 2854 cm^{-1} correspond to green rust I. The broad band seen in the region 3000–3600 cm^{-1} corresponds to O–H stretching mode of vibration and the medium band observed in the region 1600 – 1680 corresponds to O–H bending type.

In the case of the outer rust layer magnetite (588 cm^{-1}), amorphous ferric oxyhydroxide (1425 cm^{-1}) and goethite (peak appearing at 885 and 800 cm^{-1}) were identified; lepidocrocite (1023 cm^{-1}) was observed, too. The characteristic frequencies are mentioned in parentheses. In this case green rust was not observed.

Raman analysis

The products identified for both inner and outer rust layers formed on OL 37 steel exposed to marine conditions were lepidocrocite (245 cm^{-1}), goethite (298 cm^{-1}), amorphous ferric oxyhydroxide (399 cm^{-1}) and magnetite (630 cm^{-1}). The observed bands of Raman spectra have been compared with the characteristic frequencies of the corrosion products according to other authors [7-9, 15]. Green rust was not observed.

The very large bands appeared in the Raman spectrum in the domain 3500-2000 cm^{-1} for the inner rust layer and

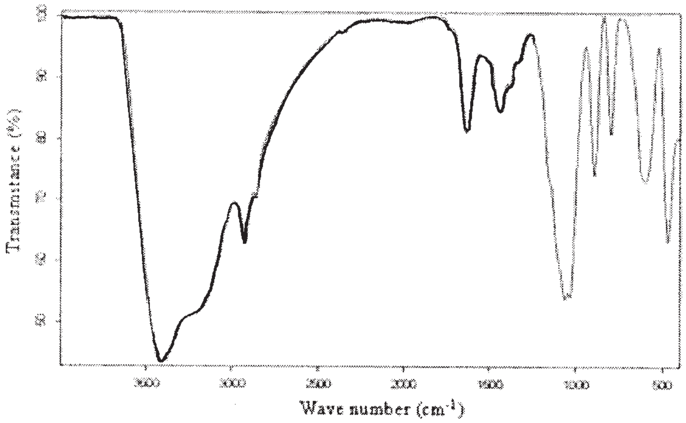

Fig. 1. FT-IR spectrum of the inner rust layer formed on OL 37 steel exposed to marine environment

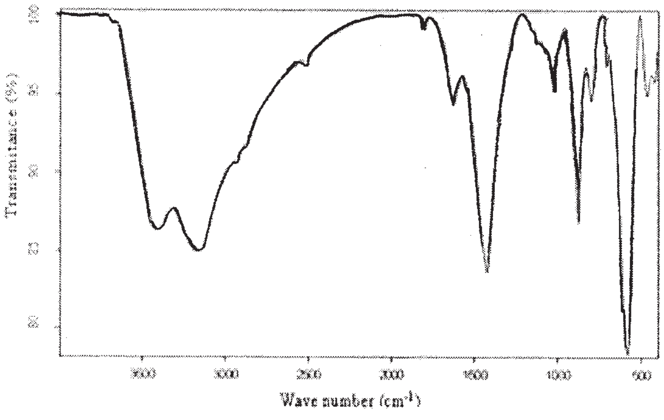

Fig. 2. FT-IR spectrum of the outer rust layer formed on OL 37 steel exposed to marine environment

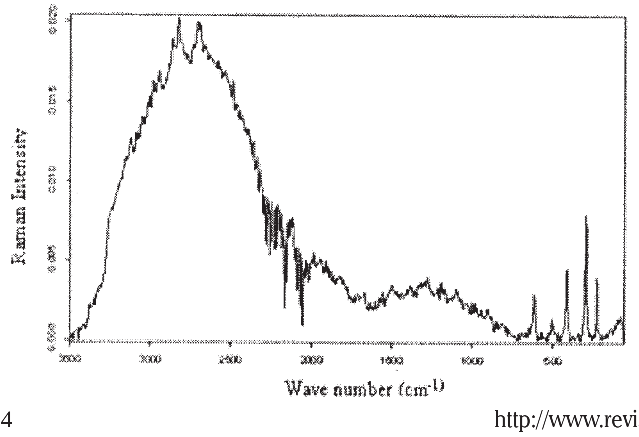

Fig. 3. Raman spectrum of the inner rust layer formed on OL 37 steel exposed to marine environment

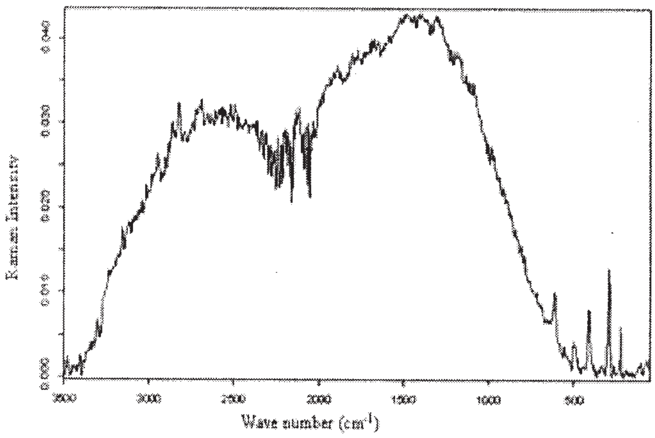

Fig. 4. Raman spectrum of the outer rust layer formed on OL 37 steel exposed to marine environment

at 3500-1000 cm^{-1} in the case of the outer rust layer, respectively, are due to the fluorescence effect; however, it is important that fluorescence band did not cover the characteristic vibration bands for the iron corrosion products.

The possible mechanism of the marine corrosion

The corrosion of the steel in marine environment is influenced by the following factors: *p*H of the environment solution, the concentration of oxidant, the type and concentration of anions, wet-dry cycle, the action of the atmospheric factors (wind, solar rays, dust etc.)

It is obvious that corrosion in the marine environment is of the type of wet atmospheric corrosion where the relative humidity value exceeds the critical humidity. In other words, it can be regarded as iron corrosion under a thin film of water containing corrosive agents, and the result is the formation of a rust layer due to the oxidation of metal surface by anodic reaction in the corrosive environment. Thus, the metal / corrosion product interface works as anode and the corrosion product / corrosive environment interface works as cathode site.

The results obtained from the exposure test of the OL 37 steel in marine atmosphere can be explained by the mechanism of formation of the identified corrosion products, presented in figure 5.

The corrosion process begins by dissolving the metal surface with the formation of Fe^{2+} ions. In the presence of the humidity and chlorine anions, by processes of hydrolysis and precipitation, the chlorinated green rust (GR I) is formed. This shows a structure where layers of iron hydroxides alternate with layers of chloride anions and water [16]. Then, in the conditions of a nearly neutral pH and of an increased intake of oxygen from environment, green rust oxidizes forming lepidocrocite. This is transformed to feroxite (amorphous ferric oxyhydroxide) by dissolution and precipitation. Amorphous ferric oxyhydroxide is converted to goethite by a solid state reaction [17].

Taking into account that the *p*H of the solution is nearly neutral to weak acid (*p*H ~5-7) it may be supposed that these oxyhydroxides are formed and transformed according to the mechanism presented in figure 5 on one hand, lepidocrocite is not possible to be formed in ferric solution without ferrous ions and on the other hand, goethite and amorphous ferric oxyhydroxide cannot be obtained directly by oxidation of ferrous ions, unless in a strongly acidic solution (pH~1), which is unlikely to form on steel only as a result of rain or pollutants in natural marine atmosphere [17].

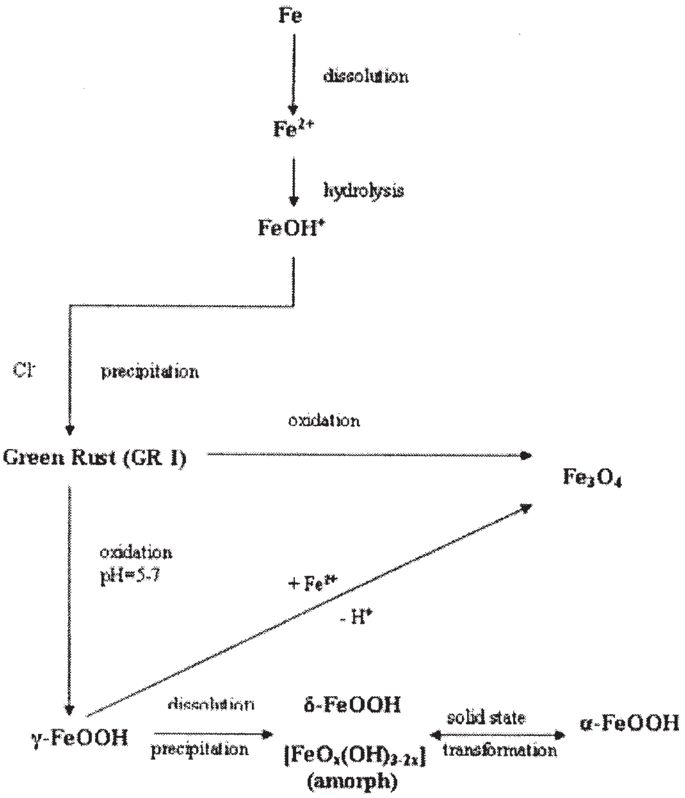

Fig. 5. Schematic mechanism of formation of the corrosion products in the marine environment

As can be seen in figures 1 and 2, lepidocrocite and green rust were found mainly in the inner rust layer while goethite and feroxite exist in the outer rust layer. The formation of the green rust as intermediate during rusting may be sustained by the presence of the magnetite in the rust layer. Magnetite detected by FT-IR spectroscopy at the rust-steel interface is regarded as formed under poor oxygen supply, after the covering of steel surface with a dense iron oxyhydroxides layer (amorphous oxyhydroxide and goethite). Therefore, magnetite was also identified in the outer layer. This could be sustained by the direct oxidation of the green rust. It is known that the humidity dissolves impurities existing in atmosphere, including SO_2, and thus there is a trend of slight decrease of the *p*H value until 4 or 5 [17]. At this *p*H value, the water film in contact with the rust / environment interface, dissolves lepidocrocite and a precipitate of amorphous ferric oxyhydroxide results. The amorphous ferric oxyhydroxide converts to goethite due to the deprotonation by hydroxyl ions provided by rain [17].

The alternative wet-dry cycles accelerate the process of precipitation and dissolution of the lepidocrocite.

At the metal / corrosion product interface, in the presence of Fe^{2+} ions and due to a lower intake of oxygen, lepidocrocite is transformed into magnetite, by deprotonation.

When an adherent and protective layer of magnetite, goethite and amorphous oxyhydroxide is formed, the corrosion process becomes with a very slow rate.

Conclusions

Our work evidenced that the main chemical components of the corrosion products layer formed on OL 37 steel exposed to the marine atmosphere conditions were goethite, lepidocrocite, amorphous ferric oxyhydroxide and magnetite.

Green rust was identified using FT-IR spectroscopy only in the inner rust layer as intermediate product.

As a result of our spectral investigations, a mechanism of formation of the corrosion products on OL 37 steel exposed to marine environment was proposed.

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