Short-term corrosion behavior of galvanized coatings in natural waters of the Greek territory

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Abstract The corrosion behavior of hot-dip galvanized steel immersed in domestic and seawater was investigated after an exposure period up to 10 days. The examination of the coatings was accomplished with optical microscopy, scanning electron microscopy and X-ray diffraction. From this investigation it was deduced that the corrosion process in domestic water is slow and mainly proceeds through pitting corrosion, while the corrosion phenomena in seawater are more intense. The main mechanisms in this environment are pitting and intergranular corrosion. In both waters the Cl^- and the O^{2-} ions diffuse in the coating up to the Fe/Zn interface. Especially in seawater the Cl^- ions seem to be very aggressive.

Introduction

Zinc hot-dip galvanized steel structures such as tubes, pipes and tanks are widely used in contact with different kind of natural waters. The term natural water refers to the water naturally occurred on the surface of earth including domestic, river, lake, sea etc. water and to the underground water. In any case the natural water is distinguished by the aqueous solutions which are waters containing artificially introduced salts or other compounds.

Galvanizing is successfully used to protect steel when immersed in natural waters [1]. However, the corrosion of zinc in natural waters is a complex process, which is lar-

gely controlled by impurities dissolved or suspended in the water. These substances and other factors such as pH, temperature and flow velocity affect the structure and composition of the corrosion products formed on the exposed zinc surface. Relatively small differences in these parameters can produce substantial changes in corrosion products and rate [2]. Thus, there is no simple rule governing the corrosion behavior of zinc in natural waters.

Numerous long-term studies concerning the zinc corrosion in different natural waters are reported [1–4 and references herein]. However these works are mainly focused on the determination of the corrosion rate and on the modeling of the phenomena. In the present work the initial steps of the zinc coating corrosion are examined after a short period of immersion ranging from 48 h up to 10 days. The corrosive medium was domestic water from three Greek cities and seawater from three different coasts of the Aegean. The main target of this project was a contribution to a better understanding of the corrosion process under these circumstances taking into account the special characteristics of the water used. Especially an effort was made to correlate the water composition with the corrosion performance of the galvanized coatings.

Experimental

The domestic water was collected from the public water supply network of Thessaloniki, Athens and Larisa situated, respectively, at the north, the south and the center of the Greek territory. The seawater was collected from the coast of Thessaloniki, Piraeus and Volos, which are also situated at almost equal intervals along the continental Greek coastline. The typical chemical analysis of these waters is presented in Table 1.

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Table 1 Typical analysis of Greek natural waters [5]

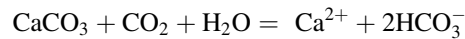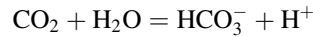| Element	Content (mg/L)	
	Aegean	Domestic
Ca^{2+}	400	81
Mg^{2+}	1,480	21
Na^+	12,000	34
K^+	580	2
NH_4^+	0.01	0
HCO_3^-	165	342
SO_4^{2-}	3,030	20
Cl^-	21,900	48
NO_3^-	0.5	4.5
Total dissolved solids	38,000	390
As	0.01	0
B	4.6	0
pH Value	7.0	7.4

From Table 1 it is deduced that the domestic water is slightly hard. This is a common phenomenon in Greece because the Greek territory is mainly composed by limestones and as a result the Ca^{2+} and Mg^{2+} concentration is higher than usual [5]. Regarding the salt content of the examined seawater is very close to the typical value [2].

Apart from the elements of Table 1 the natural waters contain also dissolved gases (oxygen and CO_2 [2]). Among them oxygen is the most significant in relation to the metal corrosion, owing to its cathodic depolarization effect [6], which leads to the formation of OH^- in accordance to the following reaction:

$$H_2O + 1/2O_2 + 2e^- = 2OH^-.$$
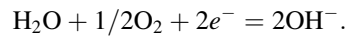
The effect of CO_2 is also complicated because it interacts with other water constituents, such as Ca^{2+}, Mg^{2+} and OH^- which originates from oxygen depolarization [2]. Finally scales are formed according to the following reactions [7]:

$$CO_2 + H_2O = HCO_3^- + H^+$$

$$CaCO_3 + CO_2 + H_2O = Ca^{2+} + 2HCO_3^-$$

$$Ca^{2+} + HCO_3^- + OH^- = CaCO_3 \downarrow + H_2O$$

$$Mg^{2+} + HCO_3^- + OH^- = MgCO_3 \downarrow + H_2O.$$

Oxygen depolarization induces also the formation of $Mg(OH)_2$ [7]:

$$Mg^{2+} + 2OH^- = Mg(OH)_2 \downarrow .$$
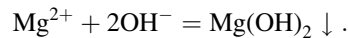
The examined samples were specimens of SAE 1010 steel galvanized in a laboratory scale facility following the standard industrial process [8]. The used Zn melt was composed by special high-grade zinc (99.999%), 0.5 wt.%

Fig. 1 Light micrographs of the corroded specimens after (**a**) 48 h, (**b**) 4 days, (**c**) 6 days and (**d**) 10 days of exposure in domestic water
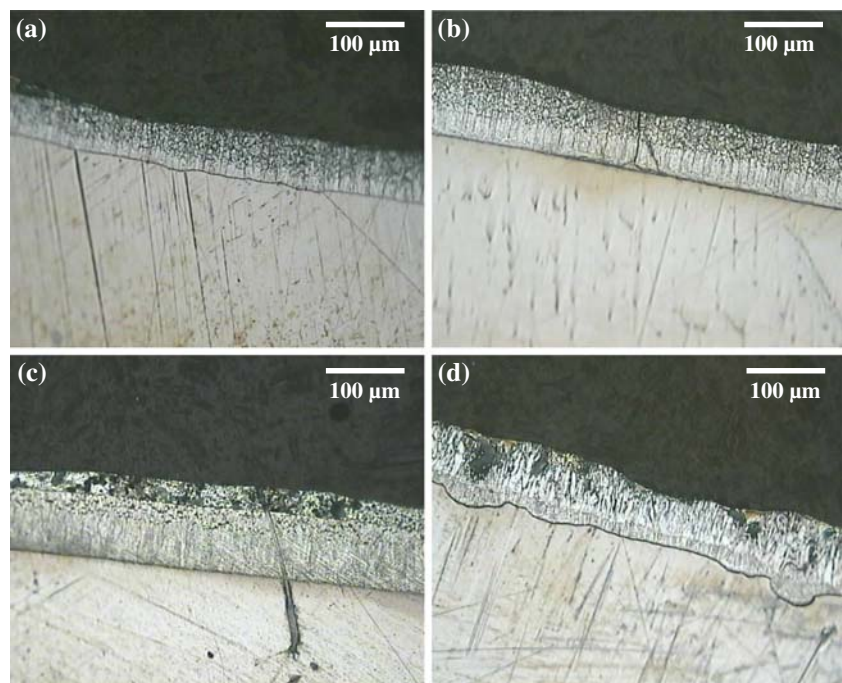
aluminum and 0.5 wt.% lead, while all the other chemicals used were of technical grade.

After hot-dipping the as-cast samples were cleaned with ethyl alcohol and acetone with ultrasonic stirring, in order to remove from their surface fatty phases or other contaminants that could interfere with the corrosion mechanism. For the corrosion study the coupons were hanged with nylon fibers in containers from polystyrene in order to be totally immersed in the different waters but without coming in contact with the container walls and with each other. The maximum exposure time was 10 days. However samples were retrieved every 2 days. The water was also replaced every 2 days in order to avoid equilibrium conditions between the coating and the water.

The as-corroded samples were examined with Optical Microscopy (OM), Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). They were also microscopically photographed with a Zeiss M8 stereoscope. For the examination with OM cross-sections of each specimen were cut, mounted in bakelite, polished down to 5 μm alumina emulsion and etched in a 2% Nital. The observations were made with an Olympus BX60 optical microscope connected with a CCD camera (JVC TK-C1381). SEM observations took place in a 20 kV JEOL JSM 840A SEM associated with an EDS analyzer (OXFORD ISIS 300) and the necessary software, to perform linear microanalysis and chemical mapping of the material under examination. The XRD study of the samples was accomplished with a Seiffert 3003 TT diffractometer with Bragg–Brentano geometry where Cu K_α radiation ($\lambda = 1.54406$ Å) was used.

Results

Some typical light micrographs of the corroded samples are presented in Figs. 1 and 4 and some SE micrographs are presented in Figs. 2 and 5. Figures 1 and 2 refer to samples exposed in domestic water, while Figs. 4 and 5 in samples exposed in seawater.

The basic morphology of the non-corroded coatings is the same in every case. The delta phase is observed close to the steel substrate while the needle-like crystals of the zeta phase and the eta phase compose the rest of the coating [3]. Small variations in the coating thickness or the relative thickness of each phase are attributed to the coating procedure which is not automated as in industrial scale facilities.

From the micrographs of Fig. 1 it is obvious that even after 4 days of exposure in domestic water the coating degradation is negligible. However as the exposure time in domestic water increases the coating attack is heavier. After 6 days cavities are formed on top of the coating and after 10 days the cavities reach the zeta phase.

The form of the cavities implies that a pitting corrosion mechanism is predominant [9]. This phenomenon is highly affected by the oxygen content of the domestic water [2]. Usually, domestic water, because of the constant flow and the pretreatment at which it is submitted, is saturated in oxygen [5] which in turn enhances pitting procedure. The presence of Cl⁻ ions is also another factor that facilitates the same phenomenon. Cl⁻ can cause breakdown of the passive film which covers galvanized coatings when exposed in the open air [2].

Fig. 2 SEM micrographs of the corroded specimens after (**a**) 48 h, (**b**) 6 days and (**c**) 10 days of exposure in domestic water
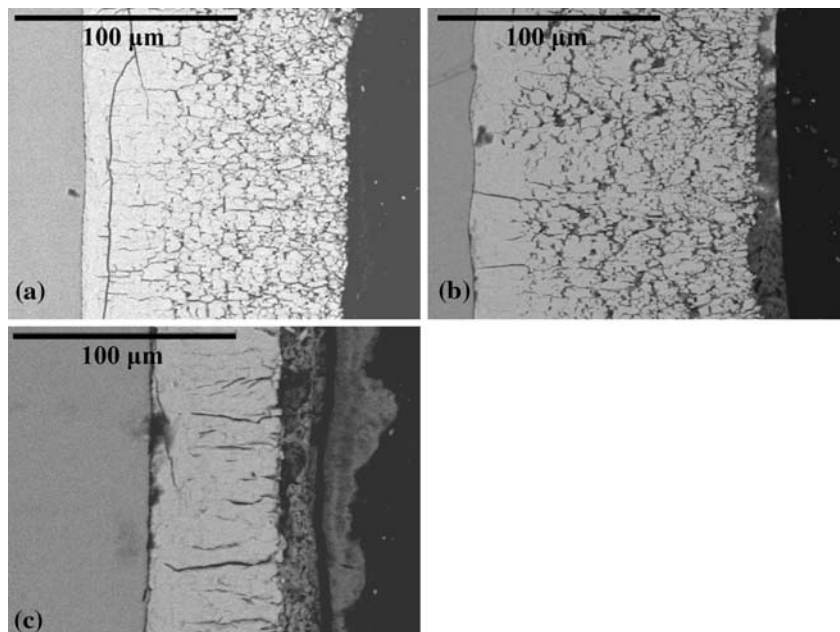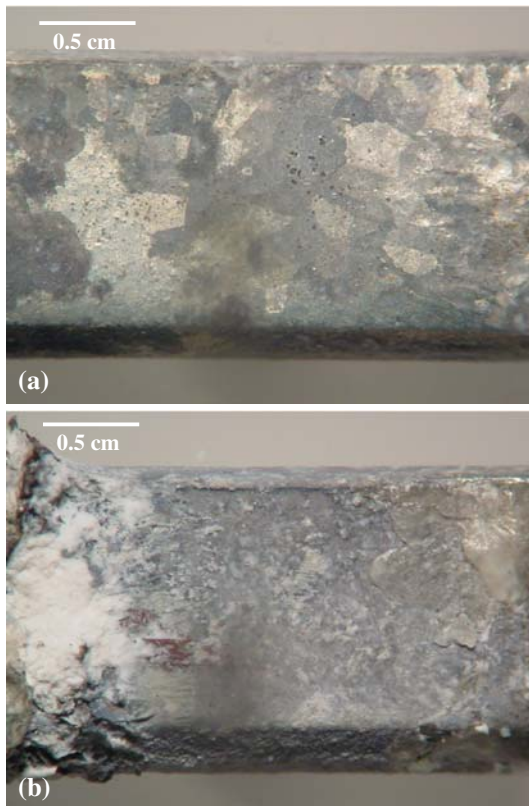
Fig. 3 Stereoscopic photograph of the corroded coating after 10 days of exposure in domestic water (**a**) and in seawater (**b**)

If we take into account the rate of the pitting corrosion, as it could be determined from the above-mentioned micrographs, the life-time of the galvanized tubes should be very low, ranging from a few months up to a couple of

years. However the corrosion rate is much lower resulting to a service life of a few decades [1]. This is explained by the fact that the water hardness protects zinc through the precipitation of Ca^{2+} and Mg^{2+} salts, which form a dense and adherent scale at the tube surface [2]. This phenomenon is expected to be more intense in Greece since domestic water is harder than usual and thus the quantity of the different phases that precipitate is expected to be larger.

The SE micrographs of Fig. 2 verify the same observations. In these micrographs the layer of the corrosion products is also visible. Furthermore, apart from pitting corrosion (Fig. 2b) uniform corrosion is also present, as Fig. 2c shows.

These phenomena are more intense in seawater, since the concentration of aggressive ions is much higher than in domestic water. This is could be observed also in the stereographic photographs of Fig. 3. The volume of the corrosion products formed on the surface of the coating immersed in seawater is much bigger. In the case of the domestic water the corrosion progress is clearly visible in the form of gray areas covered by corrosion products. However there are still brighter areas of the coating which are less attacked probably due to different crystallographic orientation.

More information about the coatings exposed in seawater could be drawn by their light micrographs (Fig. 4). As Fig. 4 shows, after 4 days of exposure pit formation is observed at the surface, while after 10 days the coating degradation is severe and intergranular corrosion is also present (Fig. 4d). In this case the Cl^- ions diffuse preferentially through the grain boundaries of the coating and react with zinc forming different water-soluble zinc com-

Fig. 4 Light micrographs of the corroded specimens after (**a**) 48 h, (**b**) 4 days, (**c**) 6 days and (**d**) 10 days of exposure in seawater
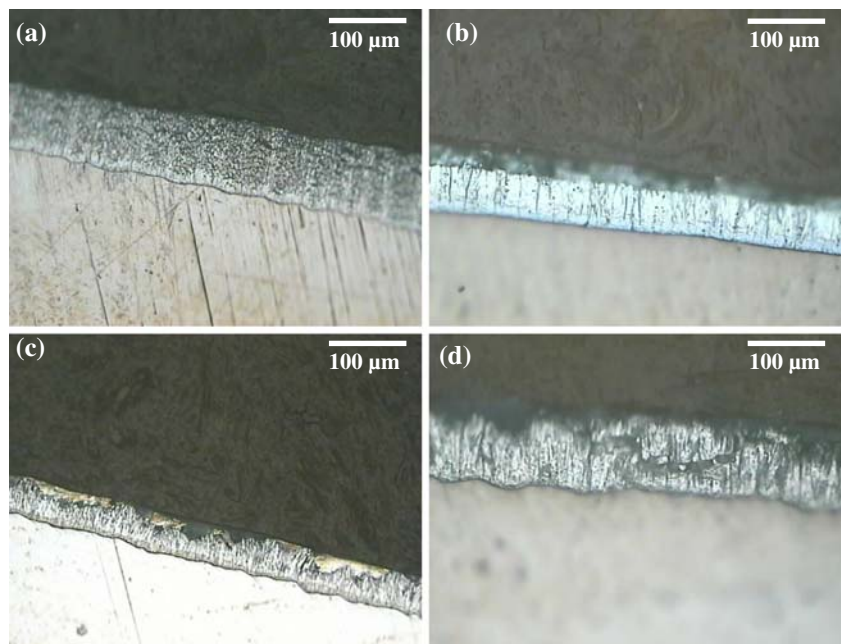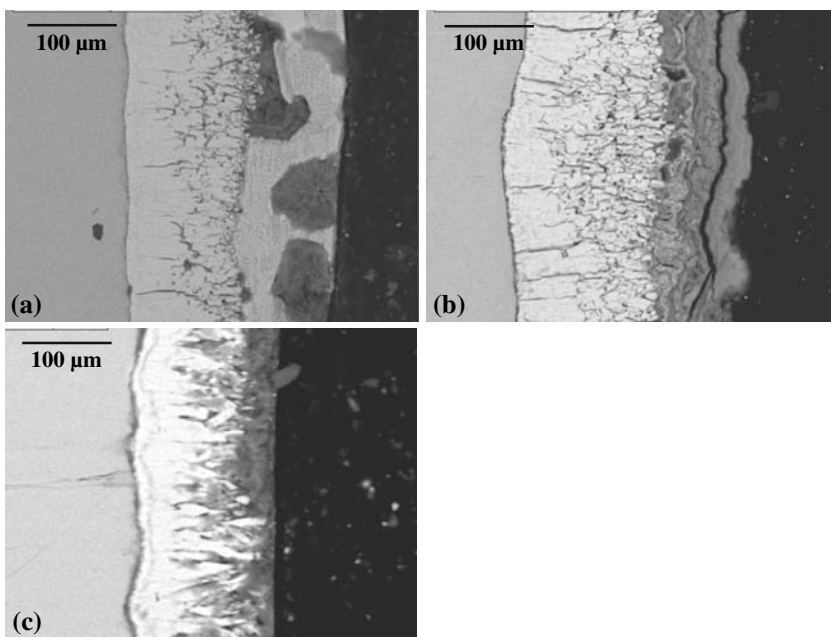
Fig. 5 SEM micrographs of the corroded specimens after (**a**) 4 h, (**b**) 6 days and (**c**) 10 days of exposure in seawater

pounds leading to the detachment of grains. This phenomenon is facilitated by the presence of aluminum in the zinc kettle [2]. Furthermore under these circumstances diffusion of the corroded species through the inherent crack network of the delta phase is possible [10].

The SEM examination of the same samples verifies the previous conclusions. The micrograph of Fig. 5a is characteristic for pitting corrosion of the coating. The pits are clearly observed as spherical inclusions, while their content is mainly composed by zinc, chlorine and oxygen as their EDS analysis showed. As corrosion proceeds the attack is more uniform, leading finally to the decomposition of the eta phase (Fig. 5c). Actually, after 10 days of immersion in seawater even the corrosion of the zeta phase is starting up (Fig. 5c).

More information could be withdrawn by the EDS analysis of the coatings (Fig. 6). From the diagram of Fig. 6 it is deduced that the outer part of the coating is composed by zinc, iron, oxygen and chlorine. In fact the non-metallic elements seem to replace the Zn atoms in the stoichiometric profile. Moreover oxygen and chlorine are also detected in the coating up to the Fe/Zn interface. This phenomenon implies a mechanism of intergranular corrosion, since the diffusion of these elements is an essential step to the progress of this corrosion form. These observations concern a coating exposed in seawater. However the profile is similar for the coatings exposed in domestic water, although the penetration of the aggressive species is not so deep.

The chemical compounds resulting from the corrosion process were determined more precisely with XRD (Fig. 7). In the diffraction pattern of the coating immersed

in seawater for 10 days peaks referring to ZnO and hydrated Zn chlorides were detected along with peaks referring to pure Zn, Fe oxides and hydrated Fe chlorides. The formation of the Fe compounds is probably due to the iron content of the coating which ranges from 0.03 up to 27% with regard to the distance from the Fe/Zn interface [3]. The composition of the corrosion products is almost the same for the coating immersed in domestic water for 10 days, with only quantitatively differences.

The data of the EDS analysis could also offer useful information about the aggressiveness of the Cl$^-$ ions with regard to the time of exposure. To calculate this value their compositional profile was measured with EDS for the samples immersed in seawater as Fig. 8 shows. From this
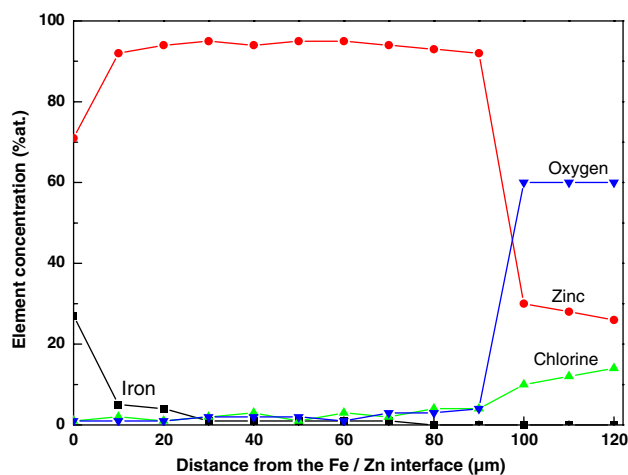

Fig. 6 Element distribution at the cross-section of the Zn coating after 10 days of exposure in seawater

Fig. 7 XRD pattern of the corroded coating after 10 days of immersion in seawater. The peaks noted with (1) refer to different hydrated Zn chlorides, the peaks with (2) to different hydrated Fe chlorides, the peaks with (3) to different Fe and Zn hydroxides, the peaks with (4) to different Fe oxides, the peaks with (5) to ZnO, the peaks with (6) to Zn
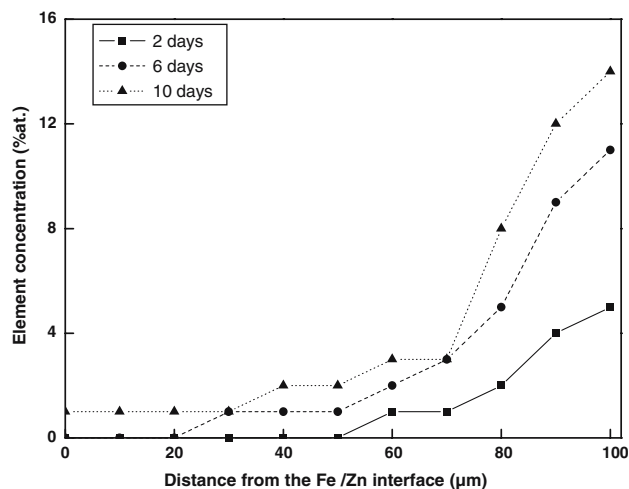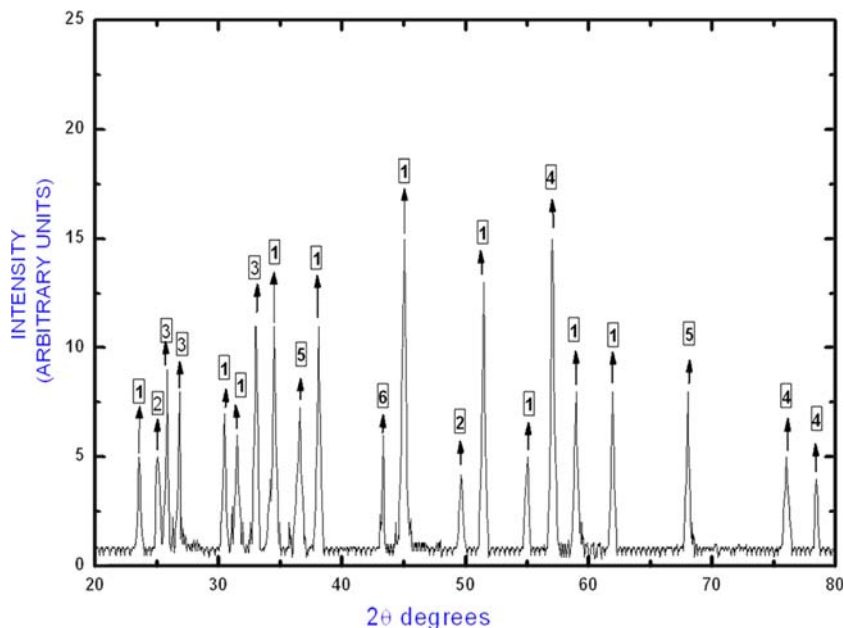

Fig. 8 Distribution of the Cl^- ions at the cross-section of the Zn coating after different periods of exposure in seawater

diagram it is obvious that the Cl^- concentration in the coating increases constantly as a function of the time of exposure. Furthermore the Cl^- ions are spread up to the Fe/Zn interface, although at the beginning they are present only at the outer part of the coating. Hence, it could be deduced the lack of a phase acting as a barrier to the Cl^- ions, which penetrate up to the ferrous substrate. This phenomenon could be detrimental for the coating performance because the penetration of the Cl^- ions is necessary for the progress of pitting and intergranular corrosion. The above observations concern the samples exposed in seawater. However similar behavior was observed in the case of the specimens exposed in domestic water, even though the concentration of the Cl^- ions is much lower.

Conclusions

From the above investigation it was concluded that:

1. The corrosion process in domestic water is slow and mainly proceeds through pitting corrosion, while the coating is also uniformly attacked. Possibly intergranular corrosion takes also place.
2. The corrosion phenomena in seawater are more intense. The main mechanisms in this environment are pitting and intergranular corrosion, along with uniform corrosion.
3. In both waters the corrosion products consist of ZnO, hydrated Zn chlorides, Fe oxides and hydrated Fe chlorides.
4. The Cl^- ions and the O^{2-} ions diffuse in the coating up to the Fe/Zn interface. Especially in seawater the Cl^- ions seem to be very aggressive. Thus in this corrosive medium the circumstances are proper for pitting and especially intergranular corrosion.

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