

## CORROSION MECHANISM UNDER ACCELERATED ATMOSPHERIC CONDITIONS

G. Vourlias, N. Pistofidis, G. Stergioudis, E. K. Polychroniadis<sup>\*</sup>, D. Tsipas<sup>a</sup>

Department of Physics, Aristotle University of Thessaloniki, Greece

<sup>a</sup>Mechanical Engineering Department, Aristotle University of Thessaloniki, Greece

Corrosion experiments, which were conducted under accelerated atmospheric conditions, are presented and discussed. A salt spray chamber (Alternative Climate Test Chamber type SC-450) equipped with a saltwater tank and water or steam injector was chosen for this purpose. Series of ferrous and non-ferrous materials were subjected to a controlled corrosion lasted at least 4 and at maximum 12 days. As parameters the temperature of the test room and the temperature of the humidified air were chosen. The as corroded specimens after a rough observation with optical microscope (Olympus BX60) were examined by means of X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). Results are discussed on the basis of passivity of the films of corrosion products formed on the surface of the specimens and their breakdown and a mechanism is proposed. According to this, in spite that protective films are formed during oxidation process, these films do not ensure a sufficient protection to the materials, as corrosion mechanism and especially pit corrosion propagation destroy the continuity of the passive films.

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### 1. Introduction

Corrosion is an electrochemical process in which a metal reacts with its environment to form an oxide or other contaminant compound. The cell, which causes this process, has three essential constituents: an anode, a cathode and an electrolyte (an electrically conducting solution). The anode is the site where corrosion takes place, the electrolyte is the corrosive medium and the cathode is the second electrode of the cell, which is not corroded. Usually the pairs of anodes and cathodes (corrosion cells) are very small and scattered everywhere at the surface of a metallic component. The different electrodes may arise from differences in the constituent phases of the metal itself, from variations in surface deposits or coatings on the metal or from variations in the electrolyte [1-2].

In the case of a given substrate exposed in the atmosphere, the water, which is condensed on it from the atmosphere, acts as an electrolyte. The corrosion rate under these circumstances is mainly determined by the temperature, the relative humidity and the composition of the water, which is condensed, since corrosion is accelerated by dissolution of soluble ions in the electrolyte. Very usual contaminants, especially in areas close to the sea, are the Cl<sup>-</sup> ions, which even at relatively low concentration destabilize the passive films and cause pitting corrosion [3-8].

Despite the great interest towards understanding pitting corrosion, its mechanism has not been totally clarified yet; therefore predictions for the extent of corrosion of any metal in a particular situation are rather limited. In the present work experiments were conducted in a salt spray chamber in order to study the corrosion mechanism of aluminum, copper, carbonsteel St-37, stainless steel 304 and galvanized steel. Efforts were also made to elucidate the role of the concentration of NaCl particles contained in the environment of the indoor corrosion.

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<sup>\*</sup> Corresponding author: polychr@auth.gr

## 2. Experimental

The materials studied were pieces of aluminum, copper, stainless steel 304, carbon-steel St-37 and galvanized steel. Every sample was sandblasted and ultrasonically cleaned before the corrosion experiments, which were carried out in a Salt Spray Chamber (Alternative Climate Test Chamber type SC-450) with a solution of 5% wt. NaCl in distilled water as a corrosive medium. The specimens were examined after 4 and 12 days in the chamber under the conditions of Table 1.

Table 1. Conditions in the salt spray chamber.

Time (days)	Chamber temperature (°C)	Humidifier temperature (°C)
0-4	0-25	35
5-12	25-40	49

The samples after being cross-sectionally cut, were mounted in bakelite, polished, etched and examined with an optical microscope (Olympus BX60), a scanning electron microscope (20 kV JEOL 840A equipped with an OXFORD ISIS 300 EDAX analyzer) and a 2-cycle diffractometer (SEIFERT 3003 TT) with  $\text{FeK}\alpha$  radiation ( $\lambda = 1.936 \text{ \AA}$ ).

## 3. Results and discussion

### 3.1. Aluminum

When aluminum is exposed in the atmosphere under usual circumstances, it is covered by a film of  $\text{Al}_2\text{O}_3$ , which is formed in a very short period of time and protects the substrate from further corrosion by isolating it from the compounds of the atmosphere [9]. However after the exposure in the salt spray chamber, the  $\text{Al}_2\text{O}_3$  film is heavily influenced by the  $\text{Cl}^-$  ions (Fig. 6a and 6b). XRD patterns (Fig. 1a and 1b) and SEM microanalysis (Fig. 5a) revealed the penetration of  $\text{Cl}^-$  and  $\text{Na}^+$  ions to a depth more than  $10 \mu\text{m}$  after 4 days. This phenomenon was more intense after 12 days in the same environment and could cause pitting corrosion. The mechanism proposed was based on the fact that a sufficient amount of chloride ions was found at  $\text{Al}_2\text{O}_3/\text{Al}$  interface. Therefore the internal oxidation [10-13] of the substrate was proposed.

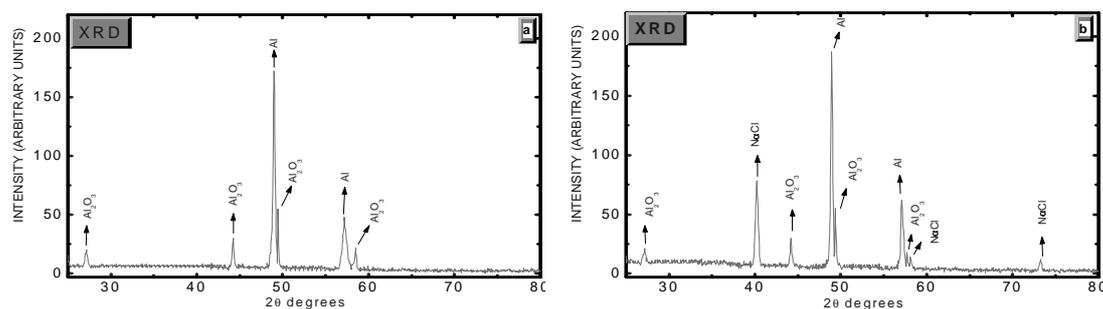


Fig. 1. X-Ray Diffraction pattern of Al after 4 (a) and 12 days (b).

### 3.2. Copper

Copper seems to be corroded uniformly (Fig. 6c and 6d). During the initial stage of exposure in the salt spray chamber  $\text{Cu}_2\text{O}$  (Cuprite) and Cu chlorides were formed (Fig. 2a). After a prolonged period of time in the chamber new corrosion products such as  $\text{Cu}(\text{OH})\text{Cl}$  (Fig. 2b) were formed. SEM analysis showed that salt ions penetrated the copper matrix to a depth of about  $40 \mu\text{m}$ . All the observations concerning Cu corrosion lead to the conclusion that the main factor which influences the

mechanism of this phenomenon is the high concentration and the high mobility of chloride ions (Fig. 5b).

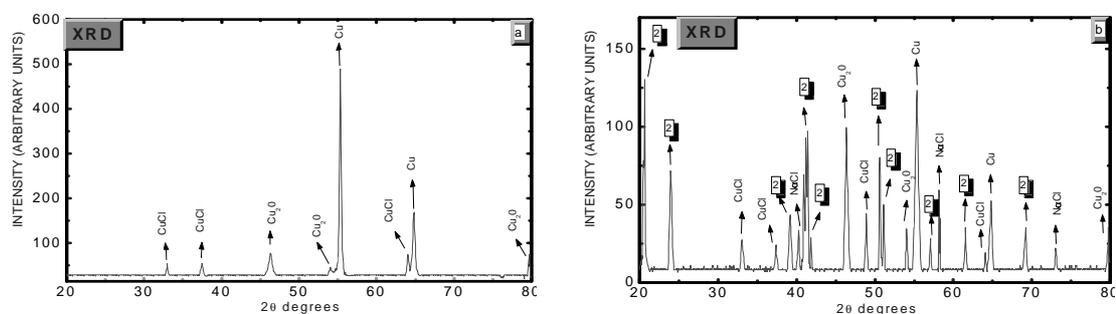


Fig. 2. X-Ray Diffraction pattern of Cu after 4 (a) and 12 days (b). The peaks noted with (2) refer to Cu(OH)Cl.

### 3.3. Ferrous metals

In the case of stainless steel (Fig. 6g and 6h) it seems that a barrier mainly consisting of Fe oxides, adjacent to the substrate was first formed, followed by another layer comprised of precipitated phases, which incorporate metal cations and chloride anions (Fig. 3a). The diffusion of alloying elements into the upper layer growing outwards from the barrier probably delays the transmission of ions through the barrier. So after an extended induced corrosion exposure, the structure of the layers does not change essentially (Fig. 3b). Due to the fact that both layers are formed in bulk form the formation and description of the mechanism in details is rather impossible so only a rough analysis was attempted.

Regarding St-37 (Fig. 6e and 6f) a complex multilayer scale was formed (Fig. 4a), even from the early stage of corrosion, which undergoes a further degradation (Fig. 4b). In both cases water absorption plays a decisive role in the mechanism of oxidation, facilitating the diffusivity of the ions (Fig. 5c and 5d) through the corrosion products towards the metal/corroded layer interface.

In the case of the galvanized steel (Fig. 6i and 6j) the ferrous substrate is protected by a zinc coating, which acts as a barrier and a sacrificial anode [14]. However this coating is heavily affected by the aggressive environment as the XRD patterns imply (Fig. 5a and b). The Cl<sup>-</sup> ions penetration is very intense (Fig. 7e). This phenomenon could destabilize the layer of zinc compounds, which protects the galvanized coating.

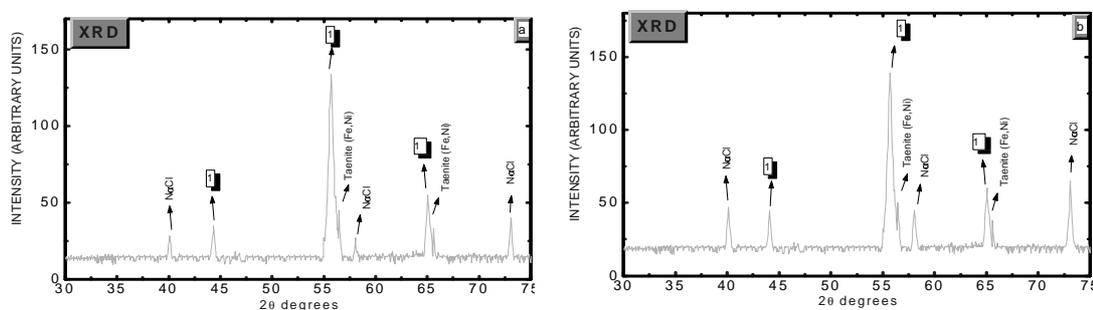


Fig. 3. X-Ray Diffraction pattern of stainless steel 304 after 4 (a) and 12 days (b). The peaks noted with (1) refer to Fe chlorides.

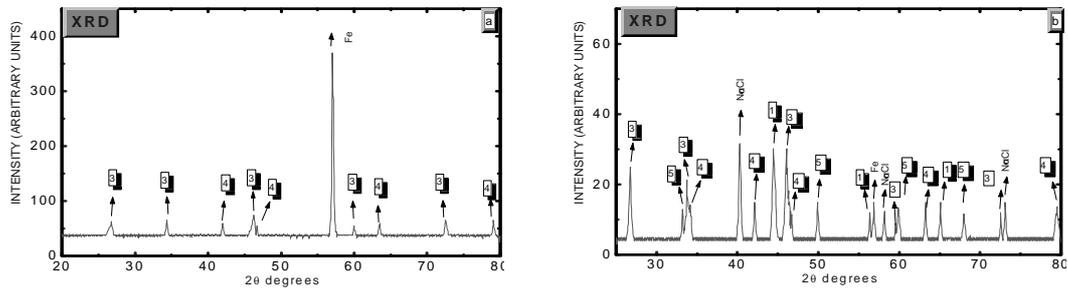


Fig. 4. X-Ray Diffraction pattern of St-37 after 4 (a) and 12 days (b). The peaks noted with (1) refer to Fe chlorides, with (3) to Fe hydroxy chlorides, with (4) to Fe oxides and with (5) to Fe hydroxides.

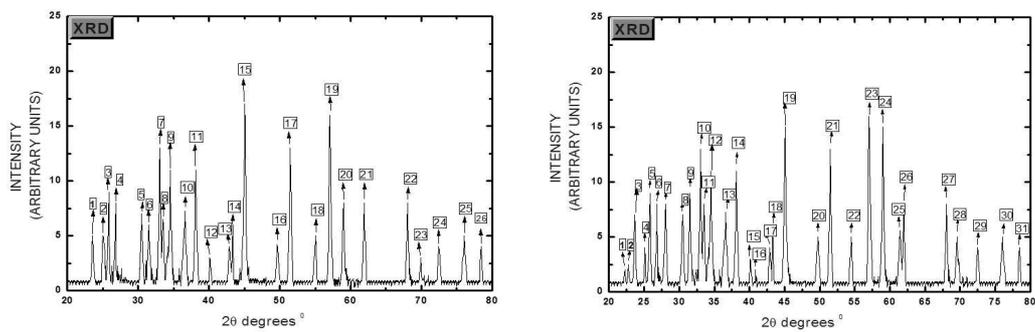


Fig. 5. X-Ray Diffraction pattern of galvanized steel after 4 (a) and 12 days (b). The peaks noted refer to hydroxy Zn chlorides, to Zn oxides, Fe oxides and Fe hydroxyl chlorides.

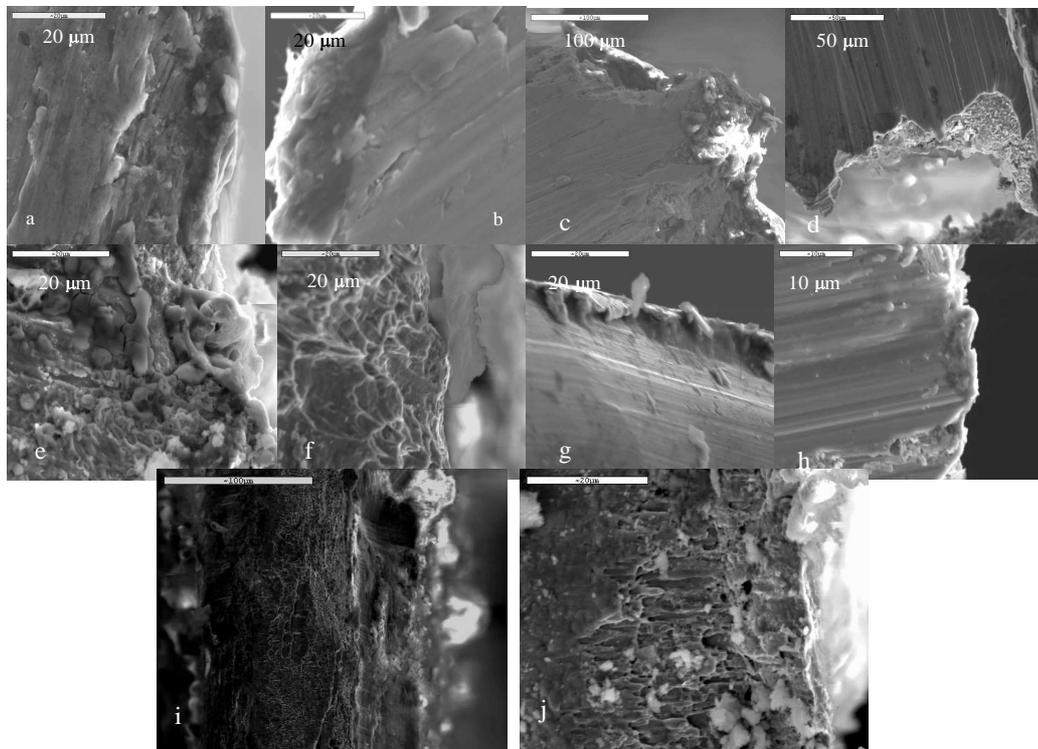


Fig. 6. SEM micrographs of the following metals: a) Al after 4 days, b) Al after 12 days, c) Cu after 4 days, d) Cu after 12 days, e) St-37 after 4 days, f) St-37 after 12 days, g) SS-304 after 4 days, h) SS-304 after 12 days, i) galvanized steel after 4 days and j) galvanized steel after 12 days.

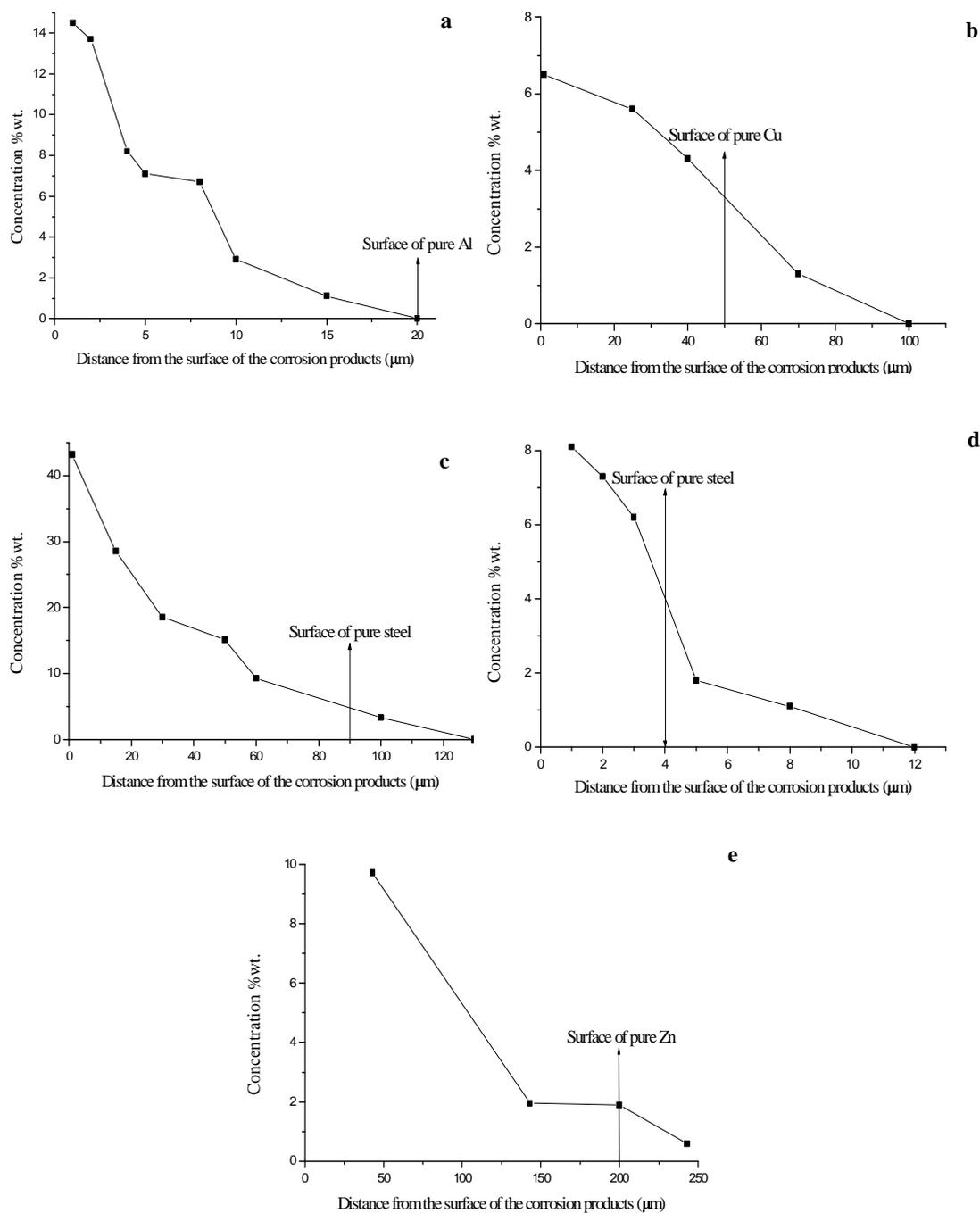


Fig. 7. Concentration (wt%) of the  $\text{Cl}^-$  ions in the layer of the corrosion products for a) Al, b) Cu, c) St-37, d) SS-304 and e) galvanized steel.

#### 4. Conclusions

- In the case of Al, the  $\text{Cl}^-$  ions penetrate in the  $\text{Al}_2\text{O}_3$  layer that protects the substrate and destabilize it, leading to pitting corrosion.

- Cu corrodes uniformly. The corrosion products are mainly composed by  $\text{Cu}_2\text{O}$  and  $\text{Cu}^{1+}$  chlorides, which are later oxidized to  $\text{Cu}^{2+}$  compounds such as  $\text{Cu}(\text{OH})\text{Cl}$ .  $\text{Cl}^-$  ions are also highly diffused in the scale layer of copper.
- Stainless steel is protected from a barrier consisting mainly of Fe oxides. Corrosion is also delayed by the diffusion of the alloying elements to the outer surface of the metal.  $\text{Cl}^-$  ions have the same behaviour as in the case of Cu and Al.
- A layer composed mainly by hydrated Fe chlorides and oxides covers St-37.

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