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INFLUENCE OF LEAD ON ZINC RESISTANCE TO ATMOSPHERIC CORROSION

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Lucrarea prezintă rezultatele cercetărilor proprii efectuate privind determinarea influenței eterogenității chimice a suprafeței metalice a zincului asupra rezistenței la coroziune atmosferică. Evidențierea modificărilor ce au avut loc la suprafață şi în structura materialului metalic, distribuția, adâncimea şi forma atacului coroziv precum şi microanaliza limitei de grăunte şi a suprafețelor adiacente corodate au condus la stabilirea rolului plumbului, în declanşarea şi evoluția procesului de coroziune tip "pitting" în zincul supus coroziunii atmosferice.

Results are presented on researches carried out to determine the influence of the chemical heterogeneity of the metallic surface on its resistance to atmospheric corrosion. By putting in evidence the transformations that take place at the surface and inside the structure of the metallic material, such as distribution, depth and form of corrosive attack and by performing a microanalysis of grain boundaries and of adjacent corroded areas it was possible to establish the role of lead to trigger and maintain a pitting corrosion process in zinc when exposed to atmospheric corrosion.

Keywords: chemical heterogeneity in zinc; pitting corrosion induced by lead.

Introduction

The field of atmospheric corrosion resistance of zinc was the object of many researches carried out all over the world: the corrosion rates in different types of atmospheres have been determined; the thermodynamics and kinetics of the physic-chemical processes at the zinc/atmosphere interface have been evaluated; the role played by the environmental and exposure conditions has been established. The major part of the tests carried out on long term (20-30 years) stated the fact that the purity degree of zinc does not influence in a significant measure the atmospheric corrosion rate of this metal; witness for this are the results of works conducted by researchers all along the time, [1- 6];

Concerning the influence of the metallic elements forming the inclusion state of zinc used as a structural material, on its resistance to atmospheric corrosion, it was established that magnesium, copper and titanium exert a positive influence. On the contrary aluminum, in small quantities, decrease the zinc corrosion resistance, especially if lead is also present. Lead, as a single metallic

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element, is considered inoffensive as concerns the chemical and electrochemical processes that could take place at the zinc/atmosphere interface, [3, 4], but having in mind the inclusion state of zinc, the influence of this element on the atmospheric corrosion resistance is not yet clear [6].

When studying the behavior of structural materials made of zinc to atmospheric corrosion, the distribution of corrosive attack zones is particular important. Indeed two types of corrosive attack can result in the following interactions zinc/atmosphere: uniform and local due to the differential aeration. The pitting corrosion attack represents the effect of the presence on the zinc metallic surface of some physical deposits or the existence of some isolated wet zones, which determine the differentiated access of oxygen, [6].

Our own researches have established the fact that lead determines a chemical heterogeneity of zinc metallic surface which facilitates the localization of corrosion partial reactions, the initiation and evolution of pitting corrosion process. The aggressiveness of this type of corrosive attack is influenced by the fact that the process localization takes place in the proximity of intergranular zones and on the boundary between crystals which determines high depths of corrosion attack having as a final result the breakdown of the metallic material and its premature taking out of service.

1. Experimental

In the Zn-Pb-Cd alloys used as structural materials, the lead has a role of structure modifier and controls the anisotropy index of the main mechanical characteristics of the product, as fracture resistance and elongation, due to the limiting of thermal range for optimal zinc processing. The chemical composition of such a zinc material that was exposed to atmosphere action more than 30 years is presented in Table 1.

Table 1

Chemical composition of the investigated zinc

Element %									Zn%
Pb	Cd	Fe	Cu	Ti	Sn	Sb	As	Al	
1.08 (max. 1.4)	0.2	0.0111	0.0056	-	0.0018	-	-	-	REST

At a concentration of 1.08 % lead is distributed in zinc as point inclusions, preferentially oriented, following the plastic deformation direction of the metallic material (Fig.1).

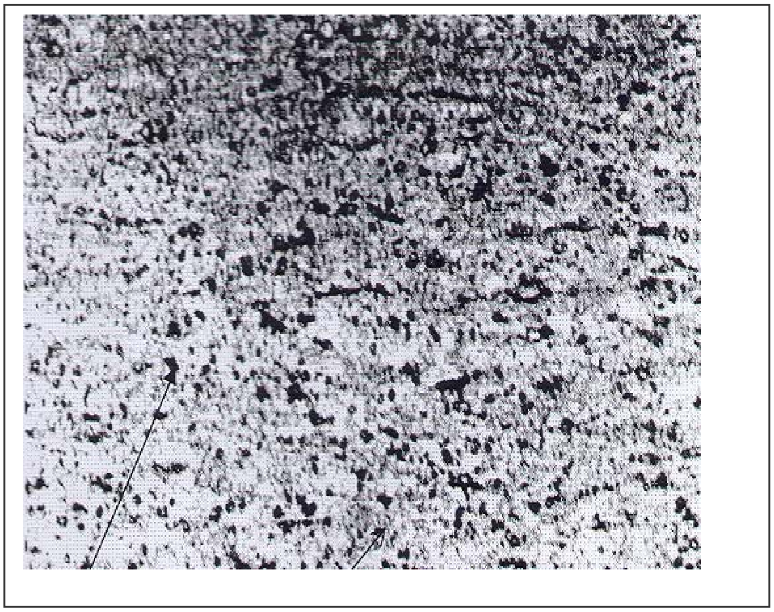
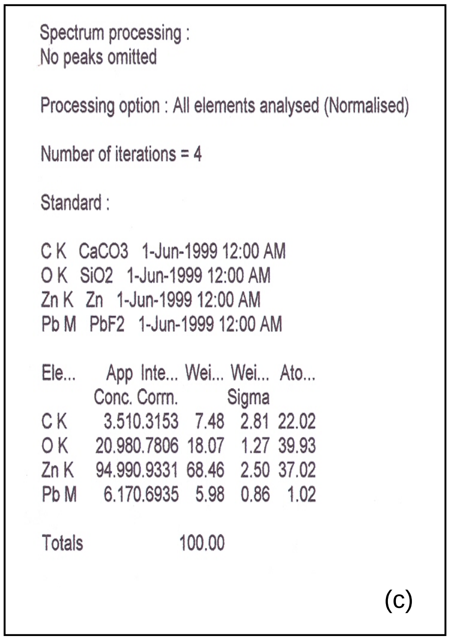


Fig.1. Optical micrograph of wrought zinc alloy from Table 1, x 200

In the cast zinc alloy the repartition of Pb on the metallic surface of Zn is non-uniform which leads to the existence of some areas with different lead concentrations (segregations) (Fig.2).

The EDAX spectrum confirms the non-uniform distribution of Pb on the zinc metallic surface, having as a result the variation of lead concentration between 1% and 6%, along the investigated zone, fact that points to a strong chemical heterogeneity (Fig.4).



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Spectrum processing :
No peaks omitted

Processing option : All elements analysed (Normalised)

Number of iterations = 4

Standard :

C K   CaCO3   1-Jun-1999 12:00 AM
O K   SiO2   1-Jun-1999 12:00 AM
Zn K   Zn   1-Jun-1999 12:00 AM
Pb M   PbF2   1-Jun-1999 12:00 AM

Ele...     App  Inte... Wei... Wei...  Ato...
          Conc. Corrn.         Sigma
C K        3.510.3153   7.48   2.81  22.02
O K       20.980.7806  18.07   1.27  39.93
Zn K      94.990.9331  68.46   2.50  37.02
Pb M       6.170.6935   5.98   0.86   1.02

Totals                 100.00
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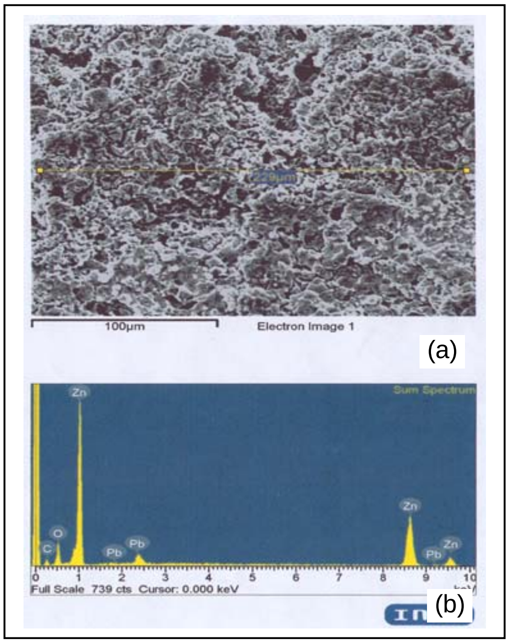


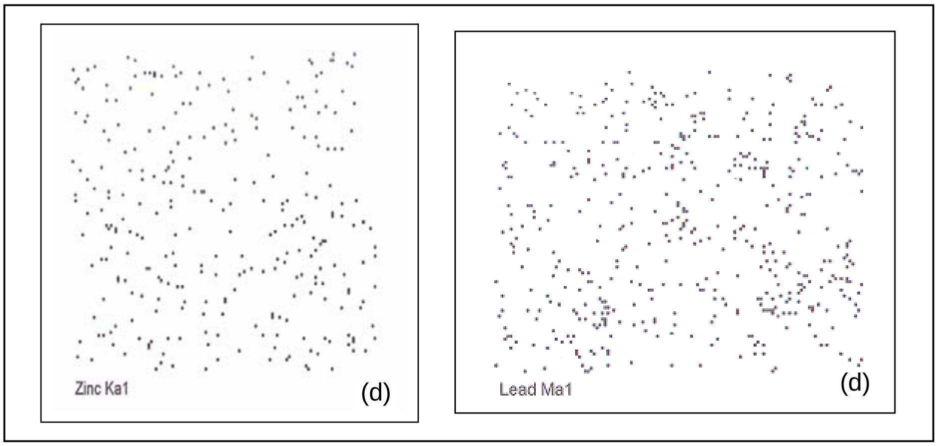


Fig. 2. The result of the EDS analysis performed on the surface of the metallic surface of zinc
(a) SEM image of the analized metallical surface
(b) The emision spectrum of the radiations
(c) The result of the quantitive analysis
(d) The distribution of the metallic elements: zinc, lead.

After zinc exposure in the atmosphere, corrosion products cover the whole metallic surface, in different depths and with a different arrangement, colored from white to grey and black (Fig.3).

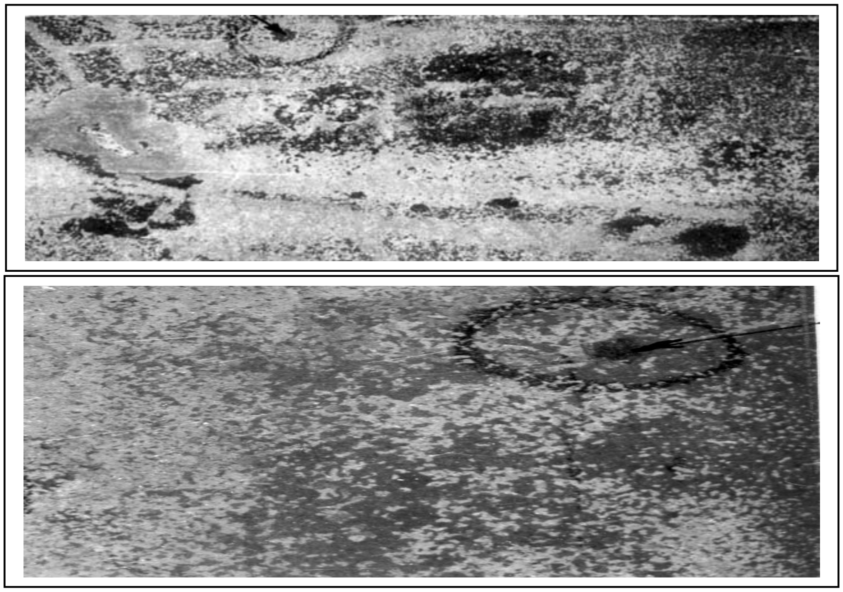
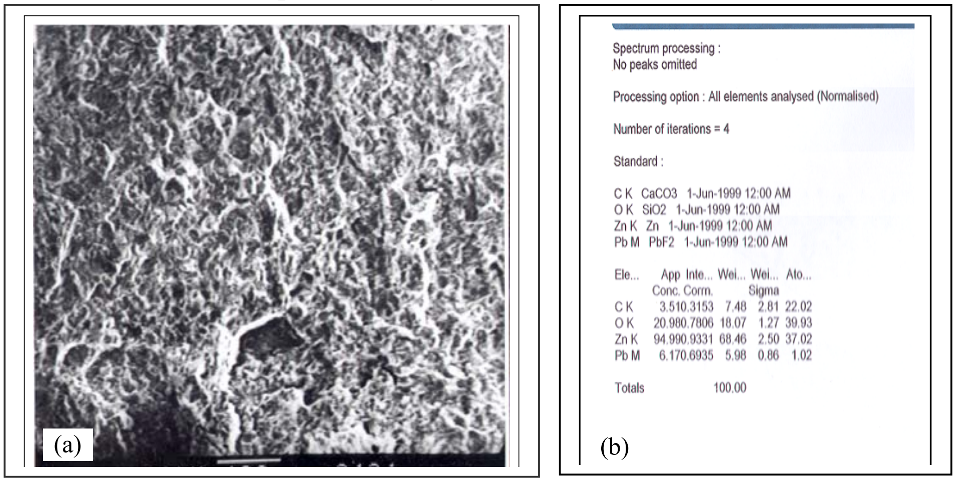


Fig. 3. Distribution and particularities of corrosion products on zinc, x 50

The compactness of the corrosion products that cover the metallic surface is different; so, there are some surface zones covered with compact layers of carbonate rich corrosion products (Fig.4).



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Spectrum processing :
No peaks omitted

Processing option : All elements analysed (Normalised)

Number of iterations = 4

Standard :

C K   CaCO3   1-Jun-1999 12:00 AM
O K   SiO2   1-Jun-1999 12:00 AM
Zn K   Zn   1-Jun-1999 12:00 AM
Pb M   PbF2   1-Jun-1999 12:00 AM

Ele...      App  Inte... Wei... Wei...  Ato...
          Conc. Corrn.         Sigma
C K        3.510.3153   7.48   2.81  22.02
O K       20.980.7806  18.07   1.27  39.93
Zn K      94.990.9331  68.46   2.50  37.02
Pb M       6.170.6935   5.98   0.86   1.02

Totals              100.00
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Fig. 4. The chemical composition of the carbonate layer on zinc;
(a) SEM image of the analysed surface, x 650;
(b) The results of the quantitive analysis

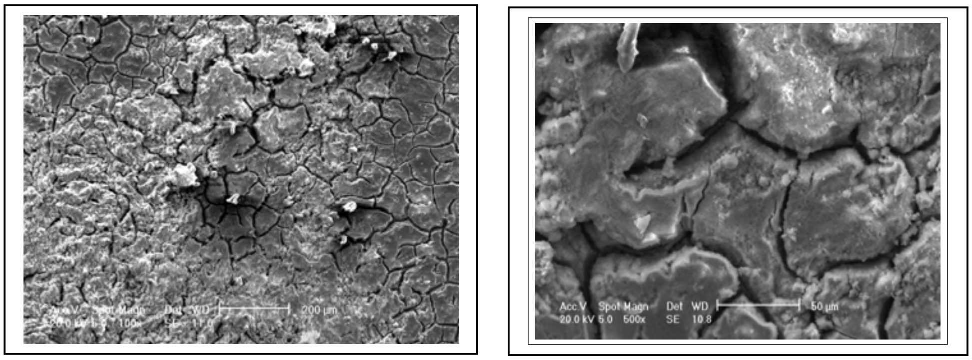
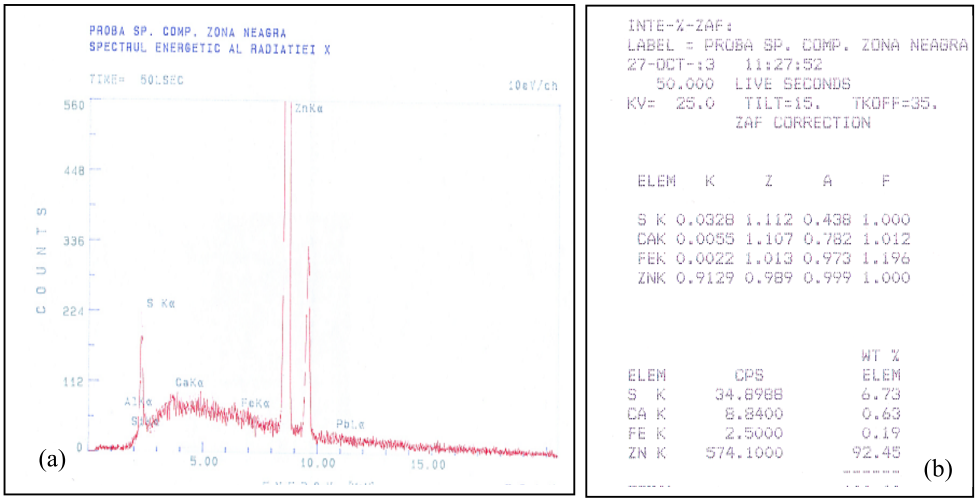


Fig. 5. Electron micrographs showing cracks in the brittle, porous layer of corrosion products

This hypothesis is also confirmed by the chemical micro-analysis of porous corrosion products which demonstrates that the activation of corrosion the process was determined by the presence of an aggressive environment, with variable acid pH. In these conditions the chemical compounds with a protective role, consisting especially of carbonates begin to dissolve and thus allow the starting of the corrosion process (Fig.6).



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27-OCT-:3    11:27:52
   50.000  LIVE SECONDS
KV=  25.0    TILT=15.    TKOFF=35.
           ZAF CORRECTION


 ELEM   K      Z      A      F

 S K 0.0328 1.112 0.438 1.000
 CAK 0.0055 1.107 0.782 1.012
 FEK 0.0022 1.013 0.973 1.196
 ZNK 0.9129 0.989 0.999 1.000


                        WT %
ELEM       CPS          ELEM
S  K     34.8988        6.73
CA K      8.8400        0.63
FE K      2.5000        0.19
ZN K    574.1000       92.45
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Fig.6. The results of the EDS analysis performed on the porous corrosion products

(a) The EDS spectrum

(b) The results of the quantitive analysis

After the removal of the corrosion products from the zinc metallic surface, pitting corrosion points were put in evidence on the whole metallic surface. These pitting corrosion points were non-uniformly distributed, with an average density between 37 and 75 points/cm^2 (Fig.7).

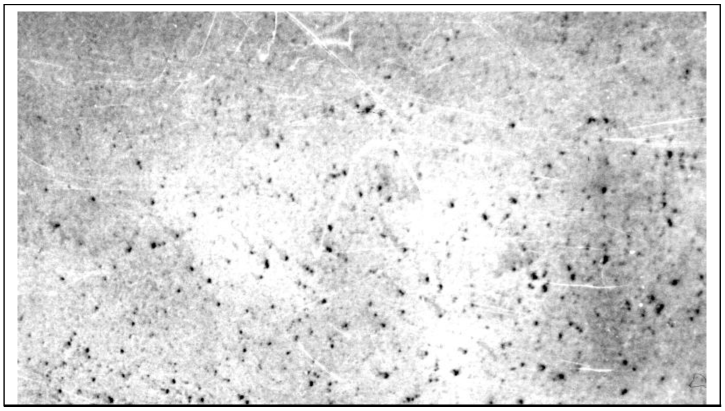


Fig. 7.Aspect of the metallical surface tested in the corrosion process.
Points of localized corrosion with non-uniform distribution on the zinc metallic surface, x 50

The micro-analysis of the surface confirms the specific aspects of *pitting* corrosion attack, focused on small surface areas, relatively round, with small diameter and high depth (Fig.8, Fig.9).

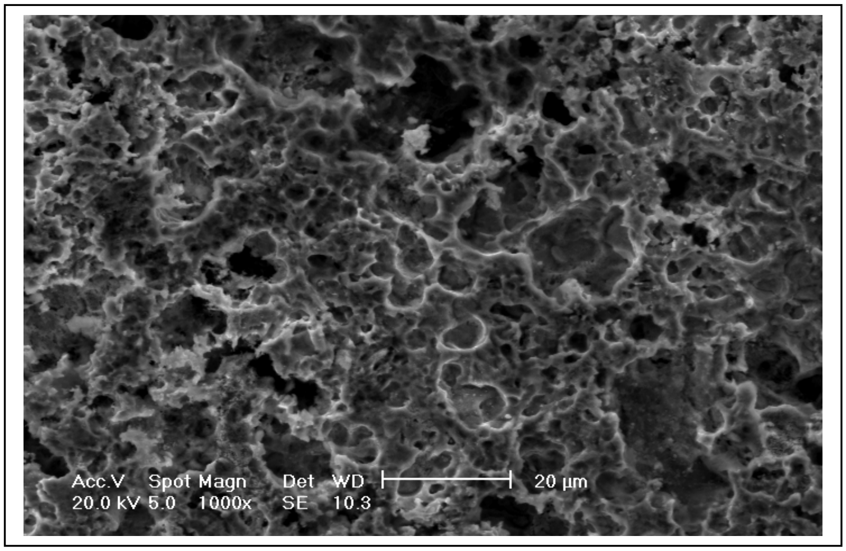


Fig. 8. Image of electron micro-analysis obtained on the corrosion tested surface in the process of corosion

The micro structural analysis of the metallic material surface on which points of localized corrosion were put in evidence has indicated different depths of corrosion attack on the studied area, the measured values being: 85µm, 225µm and 325µm (Fig.9, 10).

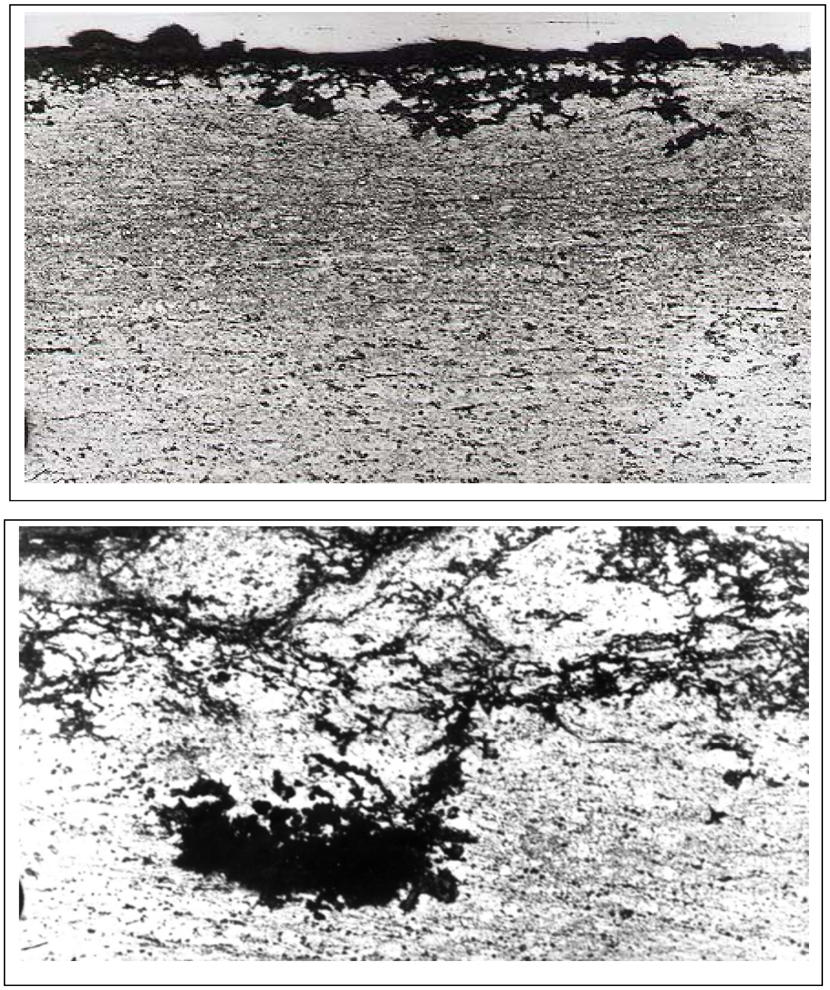
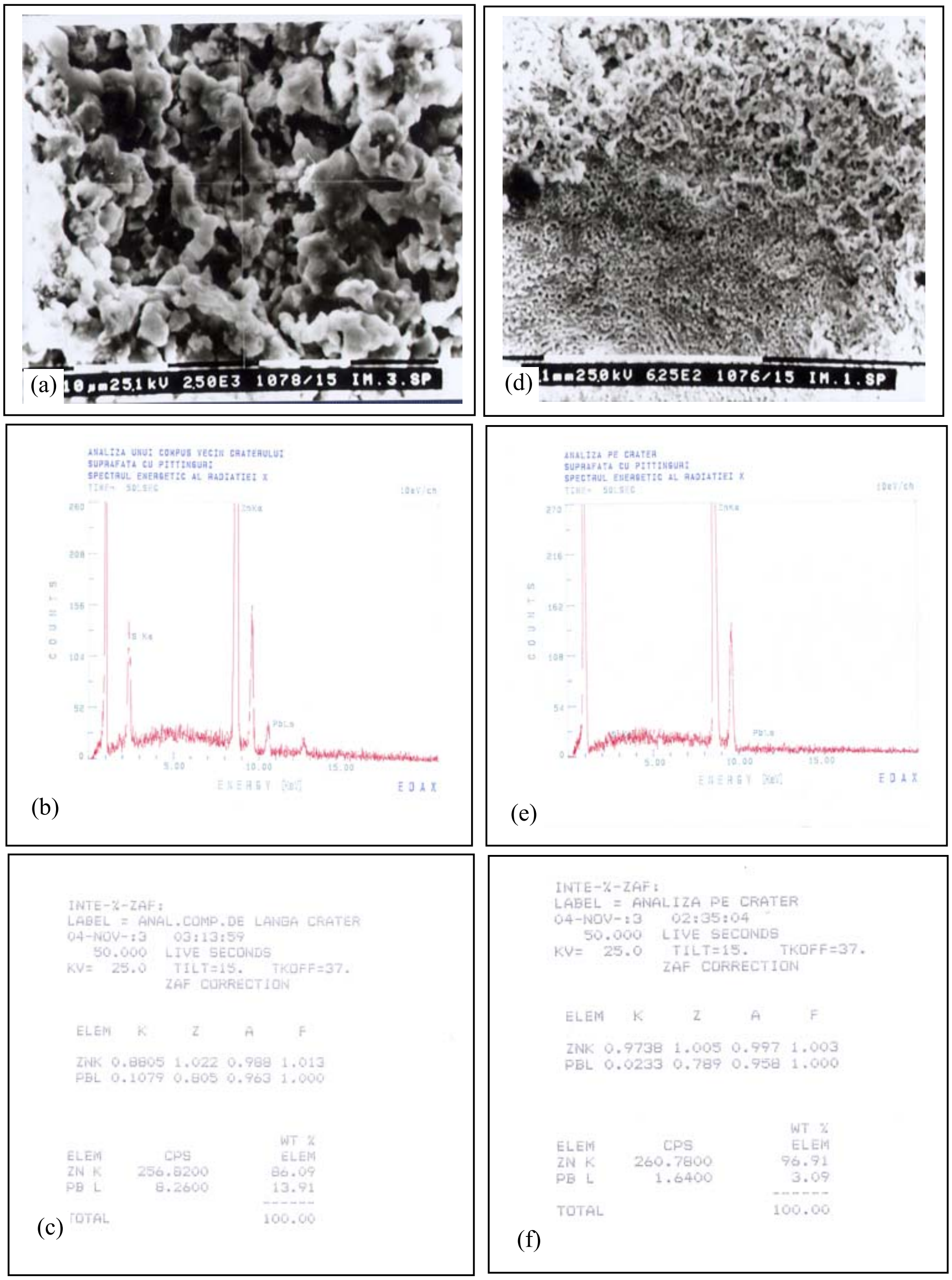


Fig. 9. Microstructure of the surface corrosion tested ; the preferential location of corrosion attack crystals boundaries and its evolution until the perforation of the metallic material, x 200; x 500

The chemical micro-analysis carried out on the areas close to the corrosion points, inside them as well as on the limit between crystals, has indicated the presence of sulphur and in the same time variations of composition for lead and zinc (Fig.10, 11).



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LABEL = ANAL.COMP.DE LANGA CRATER
04-NOV-:3   03:13:59
   50.000  LIVE SECONDS
KV=  25.0   TILT=15.   TKOFF=37.
            ZAF CORRECTION

 ELEM   K      Z     A     F

 ZNK 0.8805 1.022 0.988 1.013
 PBL 0.1079 0.805 0.963 1.000


                        WT %
ELEM       CPS          ELEM
ZN K     256.8200       86.09
PB L       8.2600       13.91
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TOTAL                  100.00
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LABEL = ANALIZA PE CRATER
04-NOV-:3   02:35:04
   50.000  LIVE SECONDS
KV=  25.0   TILT=15.   TKOFF=37.
            ZAF CORRECTION

 ELEM   K      Z     A     F

 ZNK 0.9738 1.005 0.997 1.003
 PBL 0.0233 0.789 0.958 1.000


                        WT %
ELEM       CPS          ELEM
ZN K     260.7800       96.91
PB L       1.6400        3.09
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TOTAL                  100.00
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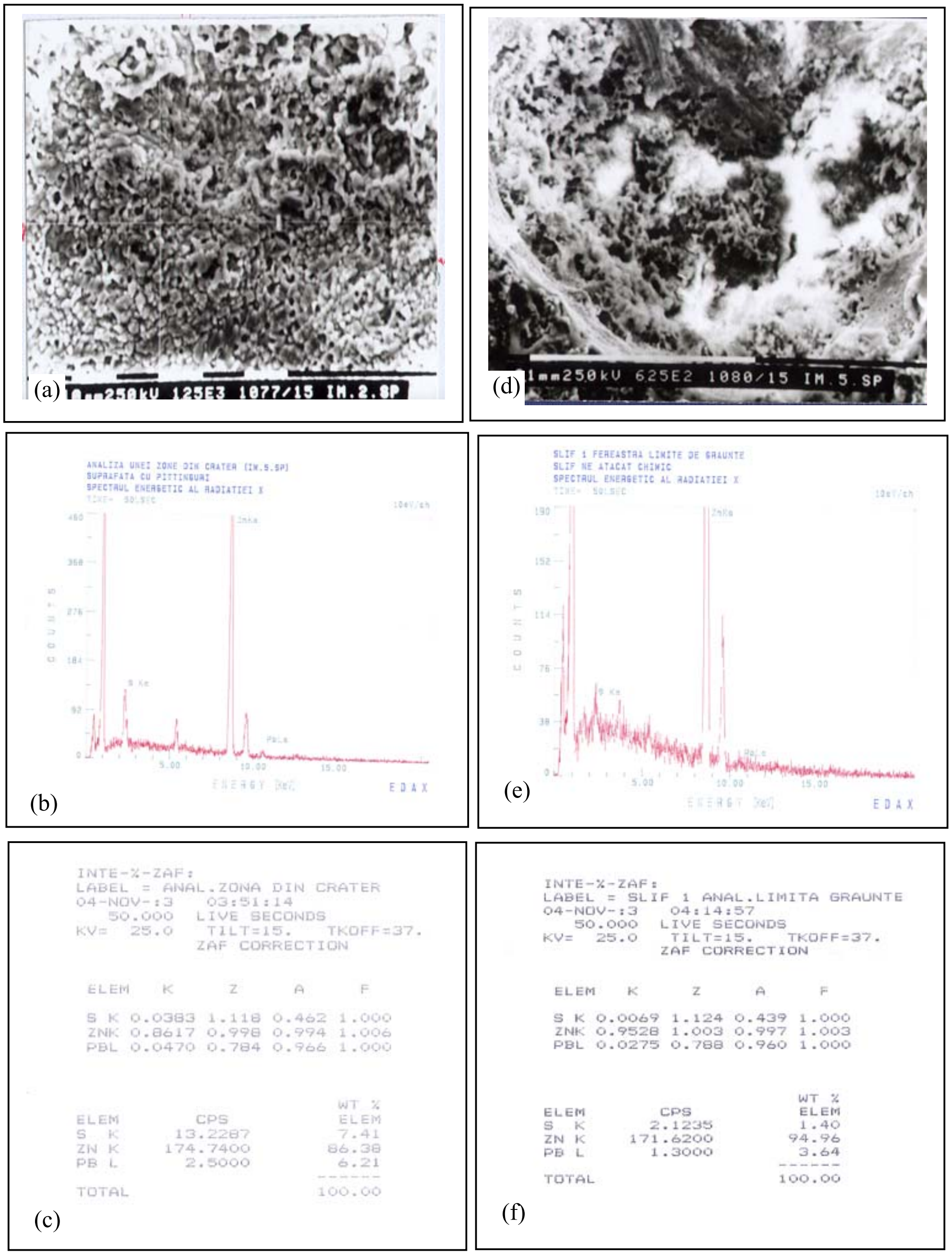
Fig.10. The quantitative results of the EDS analysis performed on the metallic surface
(a), (d) SEM image of the analysed surface;
(b), (e) The emision spectrum of the radiations
(c), (f) The results of the quantitive analyse adjacent area of a *pitting* corrosion point



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             ZAF CORRECTION

 ELEM   K      Z      A      F

 S K 0.0383 1.118 0.462 1.000
 ZNK 0.8617 0.998 0.994 1.006
 PBL 0.0470 0.784 0.966 1.000


                          WT %
ELEM        CPS           ELEM
S  K      13.2287          7.41
ZN K     174.7400         86.38
PB L       2.5000          6.21
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TOTAL                   100.00
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KV=  25.0    TILT=15.    TKOFF=37.
             ZAF CORRECTION

 ELEM   K      Z      A      F

 S K 0.0069 1.124 0.439 1.000
 ZNK 0.9528 1.003 0.997 1.003
 PBL 0.0275 0.788 0.960 1.000


                          WT %
ELEM        CPS           ELEM
S  K       2.1235          1.40
ZN K     171.6200         94.96
PB L       1.3000          3.64
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TOTAL                   100.00
```

Fig.11. The quantitative results of the EDS analysis performed on the metallic surface
(a), (d) SEM image of the analysed surface;
(b), (e) The emision spectrum of the radiations;
(c), (f) The results of the quantitive analyse inside a *pitting* corrosion point (c); on the boundary between crystals (f)

2. Discussion

Our experimental results have indicated a severe chemical segregation of lead in the Zn-Pb-Cd alloy used as a structural material in the range 1-6% Pb that extends over a length 229µm (Fig.1, 2).

The action of atmosphere on Pb containing zinc determines the corrosion products to form as carbonates, on one side, in accordance to the reaction: $5Zn^{++} + 2CO_2 + 10(OH)^- \Leftrightarrow 2ZnCO_3 \cdot 3Zn(OH)_2 + 2H_2O$ (Fig. 3, 4) and on the other side, as zinc basic sulphates, $Zn_4SO_4(OH)_6$, arranged in brittle and porous layers with variable thickness (Fig. 5, 6).

Having in mind the existence of a composition variation of lead on the metallic surface, it is easy to admit the ion $S0_4^{2-}$ absorption in zones with higher lead concentration, Fig. 10c (Pb 13,91%), Fig. 10f (Pb 3,09%). The initiation of corrosion points is associated with active cells formation (anode-cathode), the lead being more noble than zinc. The corrosion points are non-uniformly distributed and present an average density of 37 -75 points/cm^2 (Fig.7). The presence of an acid environment in corrosion points determines a higher zinc solution rate at the beginning. This fact involves attraction of other SO_4^{2-} ions and the local generation of an environment even more acid (Fig. 11f) (Pb 3,64% - S 1,40%). In these conditions the corrosive attack process is developing between the anodic zone from *pitting* bottom and the cathode zone of its cavity (Fig.11c) (Pb 6,21% - 7,41%S).

At the beginning the corrosion process on the zinc metallic surface exposed to the atmosphere, is developing following a mechanism illustrated by the reaction of anodic oxidation: $2Zn \rightarrow 2Zn^{++} + 4e^-$ and by the cathode reaction: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, in a system similar to the operation of an electro-chemical cell, where the zones with higher lead concentration act as active zones from an energetic point of view and thermodynamically unbalanced.

In the conditions of a high acid pH, the corrosion process is amplified, and in the same time with zinc ionization also the simultaneously generation of reactions takes place: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ and $2H^+ + 2e^- \rightarrow H_2 \uparrow$. Because zinc is a metallic material able to be passivated, the emphasized pitting corrosion, being a typically electro-chemical process, is governed by the laws of electro-chemical cell operating. The ratio between the small anodic surface represented by *pitting* and the large cathode represented by the remaining metallic surface in passive state, determines the development of an attack in depth (85µm, 225µm and 325µm). Due to the fact that the zinc metallic material is exposed in atmosphere, there is enough oxygen that acts like an anodic inhibitor.

The aggressiveness of this type of corrosive attack is determined by the fact that the location of the process is close to the intergranular zones and on the boundaries between the crystals; this fact involves high depth of corrosion attack having as a final result the breaking of metallic material and putting it off of work (Fig. 9).

Conclusions

1. In contrast to the general opinion, we have proved that in the context of the inclusion state of zinc used as a structural material , the lead in concentration of 1,08% is not inoffensive as far as the resistance to the atmospheric corrosion is concerned and therefore it is not a factor of thermodynamic stability;
2. The metallic zinc surface exposed to the atmospheric action is heterogeneous from the chemical point of view, situation that favors the differentiate adsorbtion of $SO^{2}_{4}{}^{-}$ oxianions resulting in the formation of active anode-cathode cells and in starting the localized corrosion process of *pitting;*
3. The presence of an acid environment in the corrosion points determines the attraction of other SO_4^{2-} ions, the production of a more acid environment, and, therefore, the corrosion process would take place in depth, between the anodic area at the bottom of the pitting and the cathodic area inside the cavity;
4. The preferential disposal of lead nearby the intergranular areas and at the grain boundaries determine the aggressivity of this kind of corrosion process, which, in time, evolve up in the perforation of the metallic material.

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