INFLUENCE OF LEAD ON ZINC RESISTANCE TO ATMOSPHERIC CORROSION

Maria FAUR, Georgeta COSMELEAŢĂ*

Lucrarea prezintă rezultatele cercetărilor proprii efectuate privind determinarea influenţei eterogenităţii chimice a suprafeţei metalice a zincului asupra rezistenţei la corozione atmosferice. Evidenţierea modificărilor ce au avut loc la suprafaţă şi în structura materialului metalic, distribuţia, adâncimea şi forma atacului coroziv precum şi microanaliza limitei de grăunţe şi a suprafeţelor adiacente corodate au condus la stabilirea rolului plumbului, în declanşarea şi evoluţia procesului de coroziiune tip "pitting" în zincul supus coroziiunii 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

* Eng., Prof., Dept. of Science Materials and Physical Metallurgy, University “Politehnica” of Bucharest, Romania
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.

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<th>Chemical composition of the investigated zinc</th>
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<td>Element %</td>
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<td>Pb</td>
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<td>Cd</td>
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<td>Fe</td>
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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).
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).
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. 2. The result of the EDS analysis performed on the surface of the metallic surface of zinc
(a) SEM image of the analyzed metallic surface
(b) The emission spectrum of the radiations
(c) The result of the quantitative analysis
(d) The distribution of the metallic elements: zinc, lead.
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).
This hypothesis is also confirmed by the chemical micro-analysis of porous corrosion products which demonstrates that the activation of corrosion 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).

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/cm² (Fig.7).

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).

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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).

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).
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 emission spectrum of the radiations
(c), (f) The results of the quantitative analyse adjacent area of a pitting corrosion point
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 emission spectrum of the radiations; (c), (f) The results of the quantitative 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:

$$5\text{Zn}^{2+} + 2\text{CO}_2 + 10\text{OH}^- \Leftrightarrow 2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2 + 2\text{H}_2\text{O}$$

(Fig. 3, 4) and on the other side, as zinc basic sulphates, $\text{Zn}_4\text{SO}_4(\text{OH})_6$, 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 $\text{SO}_4^{2-}$ 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/cm² (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 $\text{SO}_4^{2-}$ 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: $2\text{Zn} \rightarrow 2\text{Zn}^{2+} + 4e^-$ and by the cathode reaction: $\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$, 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: $\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$ and $2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \uparrow$. 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 adsorption of $\text{SO}_4^{2-}$ 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 $\text{SO}_4^{2-}$ 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.

REFERENCES