INFLUENCE OF ZINC MICROSTUCTURE ITS RESISTENCE IN AGGRESSIVE ENVIRONMENTS

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The influence of the structural transformations of zinc slightly alloyed with Cu or Cu-Ti on its corrosion resistance has been investigated. The experiments have shown that the plastic deformation of these Zn-Cu and Zn-Cu-Ti alloys has induced a modification of the equilibrium potential. As a consequence several properties have been also modified, namely the adsorption of the SO_4^{2-} and Cl^- ions from the environment, the nature of the interface, the rate and location of the corrosion process. If additional mechanical stresses were added to the structural modifications, a phenomenon of stress corrosion cracking was put in evidence.

A fost studiată influența modificărilor structurale ale zincului slab aliat cu Cu respectiv cu Cu şi Ti asupra rezistenței la coroziune. Lucrările experimentale efectuate au evidențiat faptul că după deformarea plastică a zincului slab aliat potențialul de echilibru înregistrează valori diferite. Acest fapt determină ca adsorbția ionilor SO_4^{2-} respectiv Cl^- din mediile de încercare să dicteze modificări calitative ale interfeței metal/mediu şi ale vitezei şi localizării procesului de coroziune. În condiții de tensionare suplimentară caracteristicile structurale ale materialelor metalice determină susceptibilitatea la fisurare indusă de mediu.

Keywords: zinc; metallic surface, equilibrium potential, adsorbtion capacity; microstructure; reliability

1. Introduction

During plastic deformation the mechanical heterogeneity of metallic zinc increases; between the more deformed areas which involve in their deformation areas less deformed (submitting them to traction) and the areas with reduced deformation which stops the deformation of the first ones (submitting them to compression) it always come out stresses which are kept in the deformed materials even after the forces that produced the deformation have ceased [1-3]. The final result is represented by the appearance of compression stresses in the surface area and of tensile stresses in the center of the deformed metallic product.

The high residual stresses present on the surface of metallic zinc function preferentially as anodes and contribute to the acceleration of the corrosive

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environment penetration in the passive layer, [4,5]. On the other hand, as it resulted from the analyse of the microstructure, the metallic zinc slightly alloyed with Cu or with Cu-Ti is heterogeneous from the crystalline point of view. In order to verify the way by which the crystalline and mechanical heterogeneity influences the partial reactions of the corrosion electrochemical process electrochemical tests have been performed. The qualitative transformations of the metallic surfaces were also examined and attempts were made to verify the susceptibility to stress- corrosion cracking of low alloy Zn-Cu and Zn-Cu-Ti metallic zinc [6].

2. Experimental

The zinc metal materials used in this paper have the chemical composition presented in Table 1.

Table 1

Chemical composition of investigated metallic zinc materials

COD	Element, %									Zn
	Pb	Cd	Fe	Cu	Ti	Sn	Sb	As	Al	
B	0.0018	0.0009	0.005	0.1950	-	0.0007	0.0006	0.0007	<0.0003	REST
C	0.0019	0.008	0.005	0.0923	0.193	0.004	0.0006	0.0007	<0.0003	REST
D	0.0026	0.0016	0.004	0.2180	0.610	0.0020	0.0007	0.0007	<0.0003	REST

Electrochemical measurements were performed by means of a computerized potentiometer PGP 21 Radiometer Copenhagen equipped with aquisition and processing data systems, using the programme VOLTALAB 21.

For the measurements it was used the classical cell without air exhaustion and compartments and the following electrodes:

- The work electrode – electrodes of the investigated metallic material with a surface of $1cm^2$
- Counter electrode – platinum electrode
- Reference electrode – electrode of saturated calomel

For the measurements of the work electrode potential the capillary Luggin–Haber filled with the same electrolyte as the one existent in the polarization cell was used. The solutions were prepared from substances p.a using distilled water. The pH of the electrolyte was measured using a digital pH-meter; the potential scanning speed was 10 mV/sec, and the recording time ≅ 30 minute

The testing conditions for the work electrodes made of metallic zinc materials are presented in Table 2.

Table 2

The work conditions used for the electrochemical measurements.
The testing environment temperature : 20± 5 ^{0}C

Testing conditions Scanning speed/ intensity if the flow	Testing environment Concentration (M), pH
Drawing the potential curves	
10 mV/min, 10 μA	Na_2SO_4 1M, pH =8,5-9
10 mV/min, 25 μA	Na_2SO_4 1M, pH =8,5-9
10 mV/min, 50 μA	Na_2SO_4 1M, pH =8,5-9
10 mV/min, 10 μA	NaCl 3M, pH =6-7
10 mV/min, 25 μA	NaCl 3M, pH =6-7
10 mV/min, 50 μA	NaCl 3M, pH =6-7
10 mV/min, 10 μA	NaCl 4M, pH =3,5
10 mV/min, 25 μA	NaCl 4M, pH =3,5
10 mV/min, 25 μA	NaCl 4M, pH =3,5
Drawing of the polarization curves	
10 mV/min, ± 250 mV față de E_0	NaCl 4M+HCl, pH =3,0

In order to evaluate the influence of the microstructure of the investigated materials on their suscepebility to stress-corrosion we have created an original method [6]. By applying this method we have contributed to establish the best ratio between the Cu and Ti content in zinc plat products that could diminish the risk of localization of the partial corrosion reactions in favourable environment conditions.

3. Results and discussion

The curves presented in Fig. 3 (CODB) show the fact that in the case of zinc alloyed with 0,19% Cu the structure of the material induces the transformation of zinc potential in a positive sense. The crystalline structure with large crystalline grains induces a great capacity of adsorption of the metallical surface owing to the fact that a crystallographic plane with a large surface a higher oxygen diffusion rate has and a slow zinc dissolving rate.

The orientation changes of the crystal lattice induced by twinning make some crystallographic planes to change in an orientation that has a higher potential. Several consequences result from this fact: the stability of the zinc oxide layer, the increase for the induction period of the Cl^- ions, and along with the increase of their concentrations, the metallic material becomes liable to localized corrosion. The corrosive attack is concentrated in small local cells (cathode-anode), but it can also be localized on extended areas, which could represent crystallographic planes in the structure of the metallic material, Fig. 4 [COD B (c)], Fig. 5 (COD B). Zinc alloying with copper and titanium, leads to an homogenous structure and a reduced adsorbtion capacity of the

metallic surface, this one representing the mean of many small crystallographic surfaces. In the case of zinc alloying with 0,21%Cu and 0,61%Ti the change of the zinc potential in a negative sense was higher than in the case in which the Cu concentration is 0,09%, and the Ti concentration is 0,19%Ti. This fact shows that after the plastic deformation process a decrease of the number of crystallographic interfaces with noble potential is obtained, Fig. 3 (COD C, COD D).

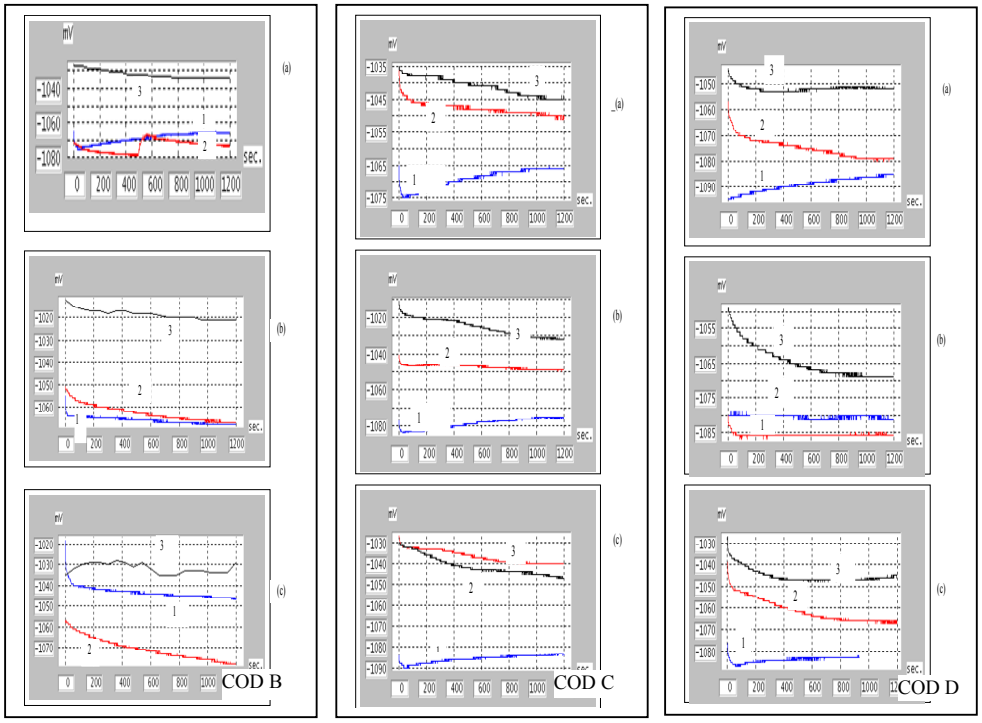

Fig. 3. Potential variation curves in function of time recorded on the tested materials

1. NaCl 4 M	pH=3,5	(a)	10 μA
2. NaCl 3M	pH=6,5	(b)	25 μA
3. Na_2SO_4 1 M	pH=8,5	(c)	50 μA

In a acid environment the corrosion products formed on the metallic surface of the zinc samples alloyed with 0,09% cooper – 0,19,% titanium are displayed in a compact and uniform layer, Fig. 4 (COD C, COD D), Fig. 5 (COD C). The aspect of the sample surfaces after removing the corrosion products shows the fact that the corrosion attack is not localized, but generalized. This is especially true on surfaces separated by rows of compounds, and if the compound that forms the main component of the compact layer is $Zn_7(OH)_2Cl_2$, Fig. 6.

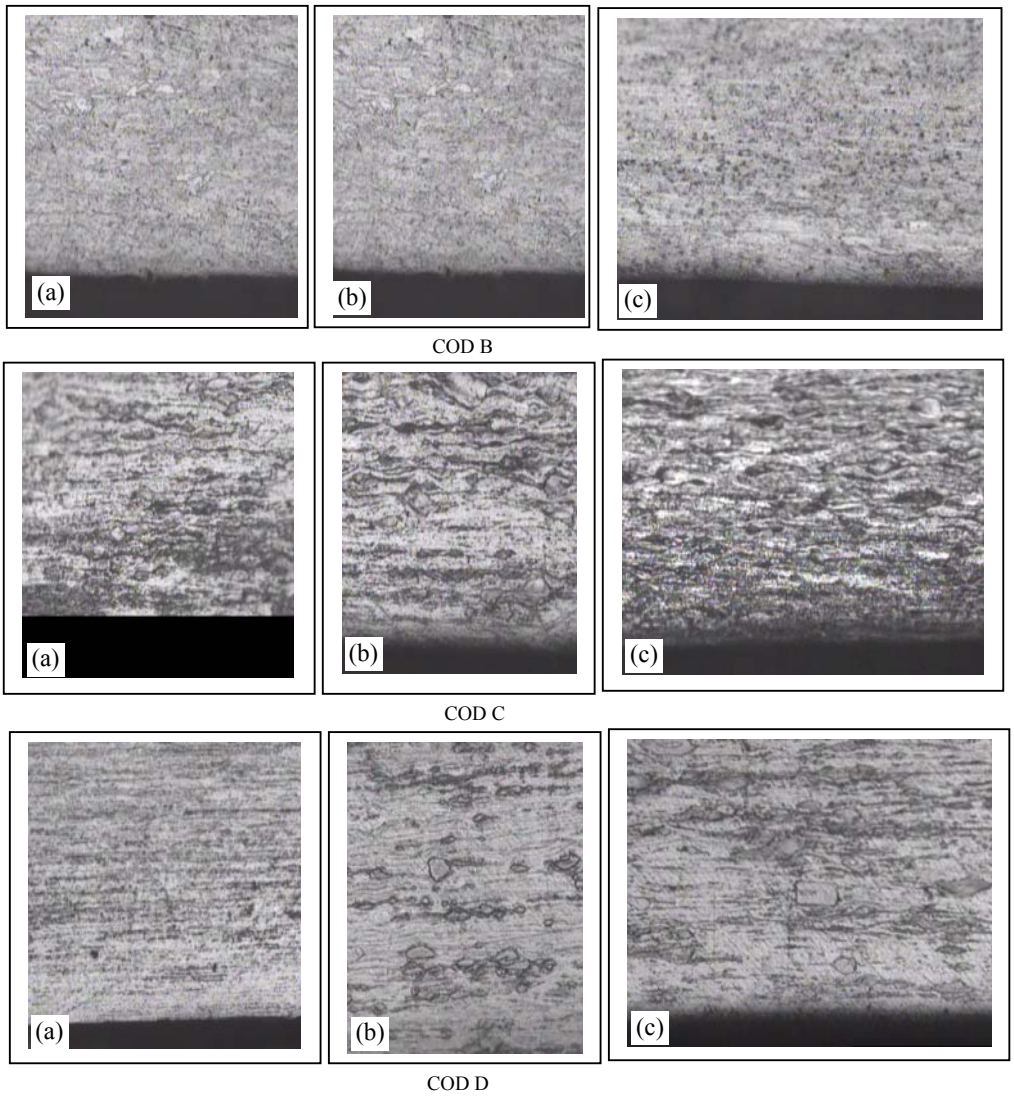

Fig. 4.Optical micrographs on samples after the electrochemical tests, x 200
NaCl 4M, pH = 3,5; flow intensity: (a) 10 μA; (b) 25μA; (c) 50μA

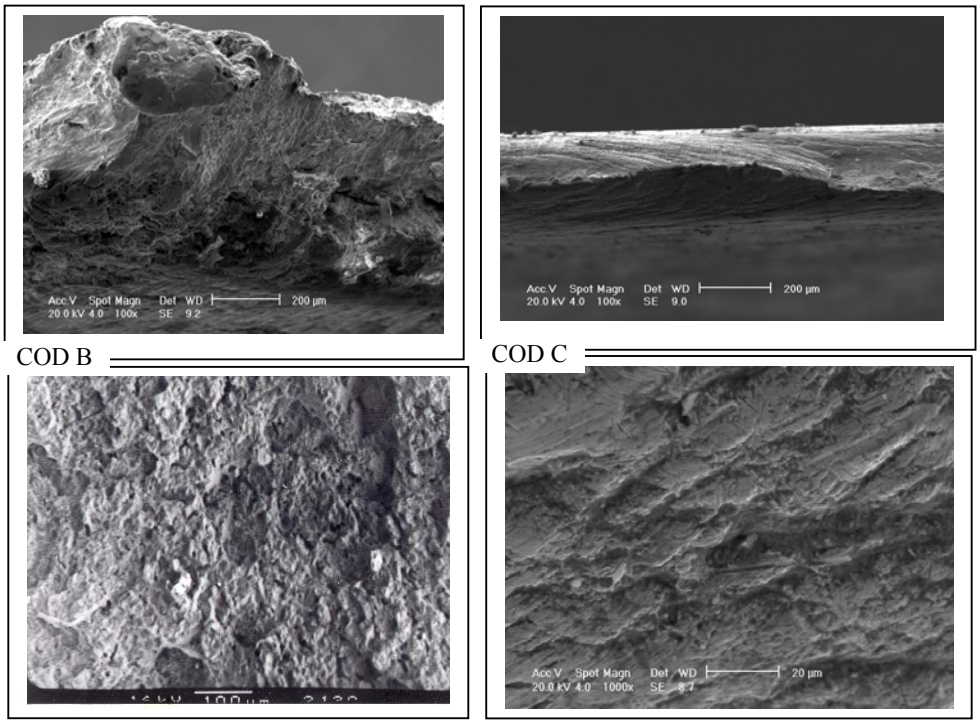

Fig. 5.SEM micrographs on samples after the electrochemical tests (potential/flow density)
(NaCl 4M+HCl, pH =3,0; 10 mV/min, ± 250 mV against de E_0)
(a) – after removing the corrosion products

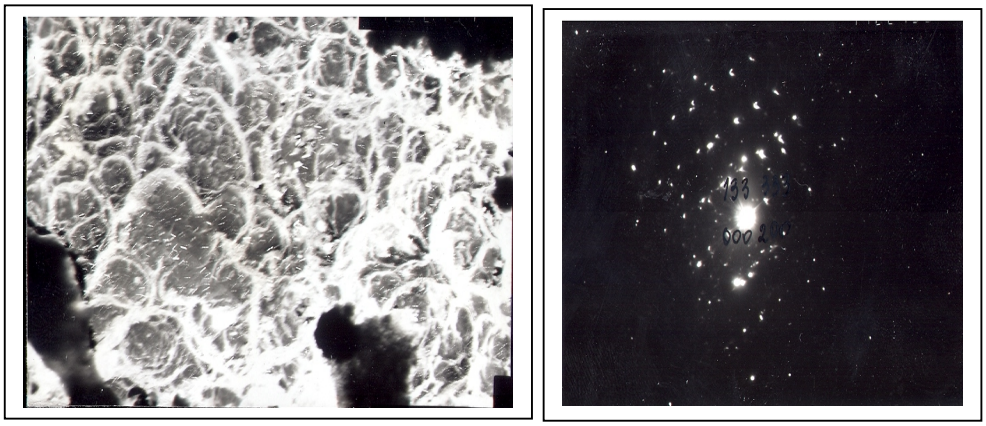

Fig. 6 SEM micrographs in bright field of the layer of corrosion products formed on the surface of the metallic material COD C, x 3000; electronic image on particles extracted which identifies the compound: $6Zn(OH_2)ZnCl_2$ (orthorhombic system)

Under the combined action stress-environment [6], the samples taken from the zinc metallic material alloyed with 0,19%Cu were fractured after 56 hours. The microstructure presented in the Fig. 7 shows that under the action of a additional stress (74,9 N/mm^2) the layer of corrosion products formed on the metallic surface were severaly cracked creating in this way the paths by which the electrolyte reached the metallic surface. The electrolyte was adsorbed on the active areas of the metallic surface (tension areas) releasing electrons for the cathodes reaction of the corrosion process. As a consequence increase of the local acidity in the tension conditions activated the corrosion process on crystallographic planes with a more electropositive potential than the one of zinc. The cracks seen in the metallic material present a character mostly transcrystalline and are stopped in their growth by a unfavourable orientation of some crystallographic planes already existing in the structure of the metallic material.

Fig. 7. Optical micrograph (Material COD B) after trying to determine the resistance to stress-corrosion cracking, x 200; (Na_2SO_4 2M , pH =4-5; the value of the applied tension: 74,9 N/mm^2; the period of time until the sample teared: 56 hours)

Alloying zinc with copper and titanium changes the behaviour of these metallical materials under the combined action stress-aggressive environment. The microstructure of the selected sample from the proximity of the crack area (Fig. 8) doesn't show the presence of the cracks in the structure of the zinc alloyed with 0,09%Cu and 0,19%Ti. This demonstrates that this metallic material is not liable to stress-corrosion cracking, under the conditions of the experiment. This fact is due mainly to the structural homogeneity that creates an equilibrium of the stresses on the metallic surface and between the crystallographic surfaces with different orientations and electrochemical potentials. Even more, the presence of the compound $TiZn_{15,}$ uniformly distributed in rows in zinc limited the increase of the dimensions of the crystalline grains to the spaces between the rows, providing

in this way a mean dimension of the zinc crystalles characterized by a mean adsorbtion capacity of the oxianion SO_4^{2-}, which doesn't allow the local increase of acidity. On the other hand, the presence of the compound $TiZn_{15,}$ uniformly distributed in longitudinal direction stops the development of cracks in the metal.

Fig. 8. Optical micrograph (Material COD C) after the attempt to determine the resistance to stress-corrosion cracking, x 200; (Na_2SO_4 2M , pH =4-5; the value of the applied tension: 85,75 N/mm^2; the time period until the sample was torn: 72 hours)

The elongation of the zinc alloyed samples with 0,21%Cu and 0,61%Ti, during the testing, demonstrates the existence of an unbalance between the existing crystallographic planes in the structure of the metallic material; applied creating new shifting surfaces, Fig. 9.

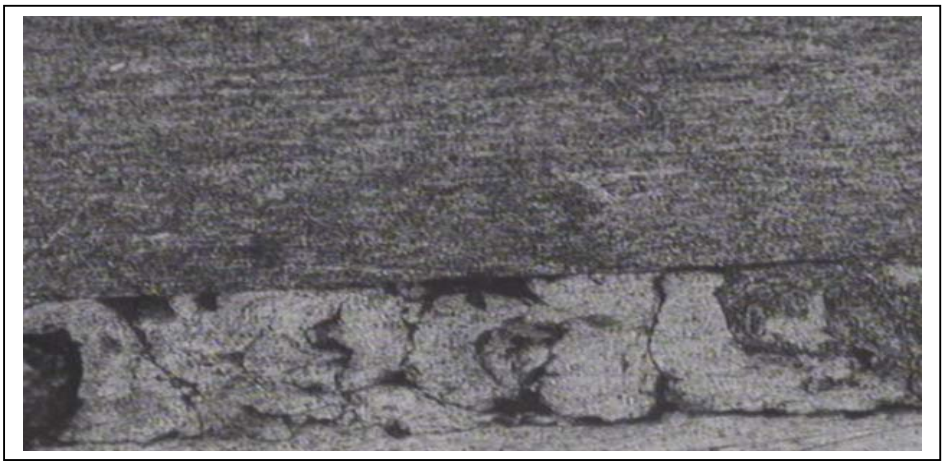

Fig. 9. Optical micrograph (Material COD D) after the attempt to determine the resistance to stress-corrosion cracking, x 200; (Na_2SO_4 2M , pH =4-5; the value of the applied tension: 105 N/mm^2; modification of elongation of zinc alloyed sample by ≅ 20% after 2 hours)

The microstructure analyse of the tested sample of zinc alloyed with 0,21%Cu and 0,61%Ti (Fig. 9) shows that during the tests, the applied stress lead to a large crack of the corosion products layer formed on the metallic surface as a result of the action of the testing enviroment, the corrosion process being activated in some areas, possibly non homogeneous from the stress point of view. The increase of the titanium content dissolved in zinc at this level of titanium concentration leads to an increase of the flow limit of the metallic material. By displaying the compound in the form of rows and mostly in the form of plates of different dimensions produces, in the cold rolling process, inadequate orientation of the crystalline gains and their decreased dimension over an admitted limit. In these conditions, by applying a stress of 105 N/mm^2, the value of the yield point of the metallic material is exceeded, and if we consider that in case of zinc the value of the tangential stress depends a lot on the alloying elements contained in zinc, the ratio between cooper and titanium concentrations in the zinc material studied was not proper one.

4. Conclusions

1. The crystalline structure with large crystalline grains of the alloy Zn-Cu determines an important adsorbtion capacity of the metallic surface as a result of an increase of the oxygen diffusion rate and a slow dissolving zinc rate. The orientations changes of the crystal lattice as a result of the twinning deformation leads to crystallographic planes oriented differently and to the shift of the equilibrium potential in a positive sense. The following consequences results: the stability of the zinc oxide layer, the increase of the induction period of the Cl^- ions and the increase of their concentration. The metallic material becomes liable to localized corrosion; the corrosive attack is concentrated in small local cells but it also may be present in extended areas. The affinity of the metallic surface towards the oxianione SO_4^{2-} is very high; the stressed areas and those with a more electropositive potential represent the active centres of the metallic surface, and the presence of the acid environment determines the porosity of the basic zinc hydroxide. The metallic zinc alloyed with 0,19%Cu is liable to stress-corrosion cracking.

2. The fine crystalline structure of zinc alloyed with 0,21%Cu and 0,61%Ti compared with the one of the zinc alloyed with 0,09%Cu and 0,19%Ti determines a greater adsorbtion capacity of the metallical surface, representing the mean of more small crystallographic surfaces. By alloying the zinc with copper and titanium the shift of the potential in a negative sense is higher; so in this case, the unbalance between the crystallographic surfaces with different electrochemical potentials is in favour of the negative ones. In order to obtain an adsorbtion capacity of the metallical surface with a mean value a proper ratio between the

concentrations of the alloying elements, copper -titanium, contained in zinc is required. The ternary zinc alloy with 0,09% Cu and 0,19% Ti is not liable to stress-corrosion cracking. This fact that demonstrates the existence of an equilibrium of the strsses on the metallic surface and of an equilibrium between the crystallographic surfaces with different orientations and different electrochemical potentials.

REFERENCES

[1]. *E. Cazimirovici,* Theoretical fundamentals of plastic deformation (in Romanian) BREN Publ. House, Bucharest, 2002
[2]. *B. Tihonov ,* Zinc rolling (in Russian), Moscow 1963
[3]. *M. Philippe,* Modeling of texture evolution for materials of hexagonal symetry-aplication to zinc alloys, Metallurgica **vol. 42**, 1994
[4]. *T. Badea,* Science and engineering of corrosion (in Romanian), Academy Publ. House, Bucharest, 2002
[5]. *S. Zamfir*, Corrosion of metallic materials (in Romanian) Teaching Publ. House, Bucharest, 1994
[6]. *M. Faur, G. Coşmeleată*, Zinc and zinc alloys: a method to evaluate the stress corrosion cracking, Patent proposed