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RESEARCH ON ANTICORROSION CHARACTERISTICS OF ALZN PSEUDO-ALLOY OBTAINED BY METAL-ARC PROCESS

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Lucrarea analizează rezistenţa la coroziune în medii corozive a straturilor depuse prin metalizarea în arc electric cu două sârme diferite, realizate din Al şi Zn. S-a pornit de la presupunerea că depunerea obţinută este diferită de un aliaj al celor doua elemente chimice, aceasta aflându-se într-o stare de dezechilibru teoretic, datorită diferenţelor fizico-chimice şi mecanice dintre cele două materiale, pentru care a fost denumit „pseudo-aliaj”. In lucrare se încearcă aducerea mai aproape de starea de echilibru a pseudo-aliajului prin aplicarea unor tratamente termice metalizare. In acest scop s-a realizat încălzirea cu flacără la 300 ºC cu răcire în aer şi menţinerea în cuptor la 350 ºC timp de 30 minute cu răcire controlată, evitând depăşirea valorii de începere a transformării eutectice (382 ºC). Criteriile de calitate avute in vedere pentru analiza comportamentului materialului depus au vizat modificările microstructurale si rezistenţa la coroziune. Analizând aspectele microstructurale si estimarea caracteristicilor anticorozive ale depunerilor din pseudo-aliaje AlZn, au rezultat măsuri de îmbunătăţire a proprietăţilor, fiind evidenţiata superioritatea acestor depuneri în raport cu comportarea singulara a zincului sau a aluminiului, cu efecte directe asupra fiabilităţii in aplicaţii practice.

The paper analyzes the corrosion resistance in corrosive environments of some metallization layers obtained by metal-arc process, using two different wires made of Al and Zn. It has been started from the assumption that the deposit obtained is different from an alloy of the two chemicals and that is in a state of theoretical disequilibrium, due to physico-chemical and mechanical differences between the two materials, for which he was called "pseudo-alloy ". The paper is trying to bring closer to steady state by applying to the pseudo-alloy of a heat treatment performed after metallization. To this end was made a heat treatment using a flame to 300 °C followed by cooling in air and maintaining in the oven at 350 ºC for 30 minutes with controlled cooling, avoiding extra heating effect which can start the eutectic reaction (382 °C). The quality criteria considered for the analysis of material behaviour have targeted microstructural changes and corrosion resistance. Analyzing microstructural features and those of corrosion behaviour of deposits made by pseudo-alloys AlZn, has been performed some measures to improve the properties, being

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shown the superiority of these deposits in relation to the singular behaviour of zinc or aluminium, with direct effects on the reliability of practical applications.

Keywords: pseudo alloy, thermal spray coating, corrosion protection, marine corrosion

1. Introduction

Metallic coatings with aluminium and zinc were used as anode coatings for many years to achieve protection of steel structures. Zinc allows an easy metallization and has a better adhesion to the steel substrate. The aluminium coatings have good mechanical properties and good resistance to abrasion in corrosive environment. Zinc is a strong electronegative metal in contact with the carbon steel, which has a potentially more electropositive, and it can provide protection against corrosion by cathodic protection effect. This is known and the carbon steel with zinc coatings is considered for protection in contact with potentially corrosive environments, particularly in marine environments where contact with chlorine is the most actively. The improvement of the corrosion resistance of zinc can be done by alloying with potentially more electropositive elements, the process being defined as noble effect of zinc. A possible measure is adding aluminium, one metal electropositive than zinc, but with a great capacity for passivation in contact with natural atmospheres.

When two different wires are bring simultaneously in a system of metal arch, a pseudo-alloy structure is formed in the coating. Zinc and aluminium wires can be used for metallization to form zinc-aluminium coating pseudo alloy. By bringing a two different wires, Al and Zn, which have different physico-chemical and mechanical properties, deposited layer obtained differs from the pre-alloy, is therefore called pseudo alloy.

The data presented in the specialty literature show that:

- Pseudo-alloy of metallic aluminium and zinc is more economical and are able to promote corrosion protection of steel structures. The pseudo-alloy coating with zinc and aluminium seems to be able to combine long-term protection provided by aluminium and protection with sacrificial provided by zinc [1];

- Quality of depositions using pseudo-alloys with aluminium and zinc were analyzed to illustrate the performance in the marine environment of thermal spray alloys, of interest being those with 85/15 (% by weight) of zinc and aluminium mixture, by controlling the quantities of each material during heating. Comparative research showed a big difference between the material microstructure and Zn85 Al 15 pseudo-alloy microstructure. The report concludes that the pseudo-alloys offer the best overall protection [2];

- The performance of Al / Zn pseudo-alloy obtained by the arc spray, used for protection against corrosion in marine environment, have shown that the coverage area of 55 Al/45 Zn pseudo-alloy is much better than those of Al 15 Zn85 pre-alloy, obtained with pure metal (with Zn 99.95) [3];

The pseudo-alloy properties are based on electrochemical characteristics of the two individual components and the combined effect of Zn and Al.

Zinc is a metal with strong electronegative potential, with good strength in contact with atmospheric humidity. It gives excellent corrosion resistance of steel substrate which is deposited by cathodic effect. Aluminium is a metal that promote a self- passivation by oxidation of the surface in contact with humid atmosphere, giving protection against corrosion of steel substrate surface, which allow barrier effect [4]. The AlZn pseudo-alloy used as coatings is useful for both Carbons steel structures (improve the operational life), immersed in sea water as well as for those exposed in marine atmosphere (harbour structures). In contact with sea water is very important to protect both parts of the ships structures (non-submerged and submerged), by the cathodic protection. Study of the pseudo-alloy behaviour, obtained by spray arc with two different wires, to different forms of corrosion, was observed compared with pure metals (Al and Zn), on the basis of electrochemical measurements of corrosion in atmospheric conditions in contact with two environments: natural seawater (collected from the Black Sea) and 3% aqueous solution of sodium chloride (NaCl), recommended by the literature [5].

Electrochemical measurements were concerned on several aspects that allow a more accurate assessment of the zinc and aluminium influence on the heat treatment effects applied to the pseudo-alloy, in terms of corrosion, the most important influence having corrosion rate. In this paper had been considered measurement results for:

- Natural passivation capacity, through the evolution in time of corrosion potential (EMC)
- Ability of passivation: re-passivation and polarization, through scrolling potential in the area of (-1000mV, +2000 mV);
- Assessing of corrosion currents by their conversion in the corrosion rate;
- Structural analysis of fingerprints (surface) after electrochemical measurements, as a basis for defining the types of corrosion by the action of chlorine, for pseudo-alloy AlZn [6].

The ensemble of corrosion tests, used to characterize the properties of the coatings made from pseudo-alloy AlZn, with measures to improve these, has shown their superiority in comparison with those of the zinc coatings, with direct effect on reliability in practical use. This pseudo-alloy can be used in the manufacture of sacrificial anodes for cathodic protection controlled. For buildings exposed in marine atmosphere, their use can be made as a measure of direct protection. The research paper shows the importance of using them to ensure cathodic protection of the carbon steels in combination with additional coating, based on organic resins (epoxy, polyurethane), inactive chemicals, which cancels the coverage rate of corrosion action for AlZn. Following the results, it will develop further research regarding the microstructural features, to find the constituents which allow superior resistance to corrosion, and the technological measures that must be taken to obtain these constituents.

2. Samples preparation

Samples were performed by spray arc, using the following wires: Al 99.5%, diameter of Ø1.6 mm; Zn99.9%, diameter of Ø 1.6 mm. Samples were realised by a certified European engineer welder, on a OL37 steel support, having 2 mm thick, and the dimensions of 150x200mm.

As is known that parameters of metal coverage affect the structure and performance of the spray coating, metallization was carried out with the variation of the parameters, in order to establish the optimal values. The main parameters of metallization taken into account were: current intensity, projection air pressure, flow distance, electric arc voltage. In specialty literature, is show that the characteristics of spray coating are far from those of Zn-Al pre-alloy. In the paper were taken some technological measures to allow the obtaining of some characteristics like to those of pre-alloy, by applying heat treatments. The samples were cut in three pieces from each: one piece was spray coated in order to set the parameters ; other part was sprayed and reheating with a flame crossing at 300°C to achieve the equilibrium diffusion ; last part was placed in an oven at 350 °C with keeping for 30 min, to study diffusion qualities after heat treatment. The temperatures values were chosen so as not exceed the beginning of eutectic transformation (382 ºC) [7].

EDAX analysis was performed on a JEOL type microscope, X-ray dispersive in energy, as quantitative analysis of elemental composition in the microprobe. The results show that porous deposit is formed by melted clusters, having multi-layers and small differences in chemical composition of two sides. It has been shown that on the face in contact with the steel (S2) the percentages of alloying elements are reversed comparatively with the opposite side. The overall parameters confirm that is a pseudo-alloy, composite type Zn50Al50. The resulting data are indicated in Table 1.

Table 1

Microstructural constituents of the atomic features

Compound S1-	Wt % weight	At % atoms	Compound/ S2	Wt % weight	At % atoms
Al	50.63	71.3	Al	46.02	67.37
Zn	49.37	28.7	Zn	53.99	32.63

SEM microscopy analyze was performed on the samples prepared according the metallographic procedure (31 samples). After comparative analysis determinations of the samples, have resulted the follows conclusions: the samples with the best behaviour, were carried out with parameters pressure = 5 at, current intensity = 50 A, projection distance = 170 mm, voltage = 30V. One of these samples has been used for investigations on corrosion resistance.

Multi-layers structures that were exposed more time to diffusion flame, are more compact, and show a beginning of new phases. Multi-layers structures, that were placed in the oven show mixed structures, due to the advanced diffusion processes.

3. Corrosion behaviour of pseudo-alloy Al- Zn

Samples for determining the electrochemical corrosion resistance were carried out by raising the polarization curves and potential variation over time in two solutions, using devices whose block diagram is shown in Figure 1.

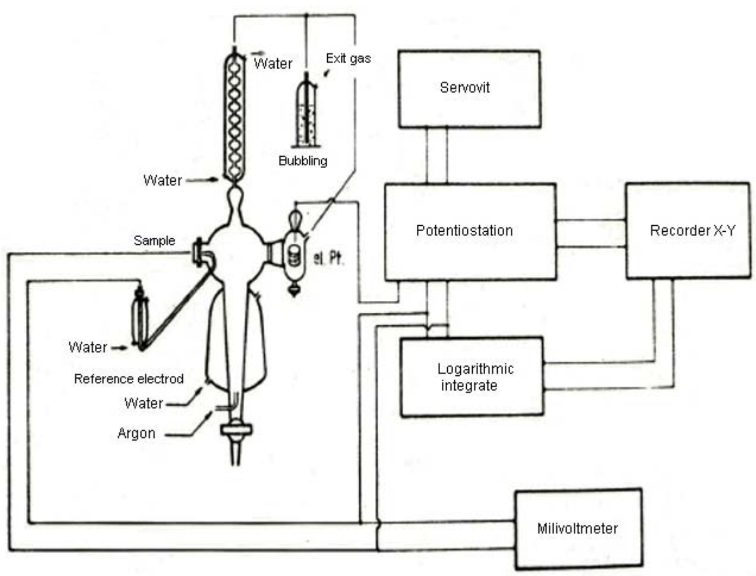

Fig.1 Block diagram of the installation for potentiostatic measurements

Samples used in experimental determinations were realized pseudo-alloy AlZn, without heat treatment (AlZn1); pseudo-alloy AlZn heat-treated at 300 ° C using flame (AlZn 3); pseudo-alloy AlZn heat treated in oven at 350 ° C for 30 minutes (AlZn4); sample of Al 99, 5% and sample of 99.8% Zn. Corrosion tests were achieved by electrochemical measurements using the exposure environment like natural sea water (collected from the Black Sea - MN) and 3% NaCl aqueous solution (specific to assessment of behaviour in marine atmosphere containing chlorine), using the parameters values from Table 2. Measurements were followed by a structural analysis on the footprint of polarization, for determining the type of corrosion and its location.

Table 2

Electrochemical tests

Test type	**Exposure environment**	**Polarization parameters**	**Potential range**
Mixed potential corrosion Emc	Sea MN 3%NaCl	Expose 30 min la 25°C	Values variation Emc
Slopes Tafel Corrosion speed	Sea MN 3% NaCl	Polarization speed 2mV/s	± 100mV around Emc
Cyclic voltammetry activation/ passivation	Sea MN 3% NaCl	Polarization speed 100mV/s	From -1000 mV to 2000mV, 3 round trip cycles
Pitting corrosion	Sea MN 3% NaCl	Polarization speed 100mV/s	From value Emc to potential for current 500µA/cm^2

3.1 Mixed potential corrosion Emc

Mixed corrosion potential (EMC) is the potential value recorded at the contact surface of metal with the test environment. This potential is a first indication of corrosion behaviour, depending on the state of material (active or passive). Registered values for EMC are presented in Table 2.
In contact with sea water, the values of potential Emc were register around -1000 mV for the pseudo-alloy AlZn samples, with a slight difference depending on the applied heat treatment. These values are similar comparatively to those of unalloyed zinc. For aluminium, the difference is clear, being nobler and having values of Emc at about -600 mV. In the 3% NaCl aqueous solution, evidence shows that the potential for pseudo-alloys AlZn is similar to the recorded in contact with natural sea water.

Their potential is lightly nobler than zinc value, more negative by about 25mV. The Emc value of aluminium is different from those recorded for pseudo-alloys AlZn and Zn, being 25 mV nobler than the one recorded in contact with seawater. In Figures 2a and 2b are shown variations of Emc potential for pseudo-alloy AlZn, for untreated and heat treated samples, in comparison with those of zinc and aluminium in the test environments.

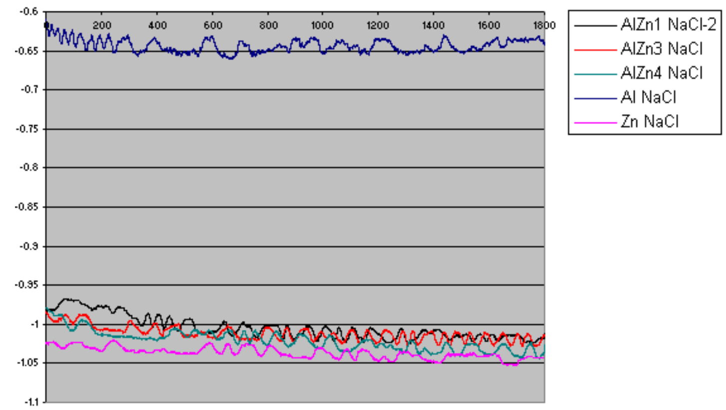

Fig. 2 a Evolution of Emc[V] in relation to time[s] in aqueous solution of NaCl 3%, at 25°C

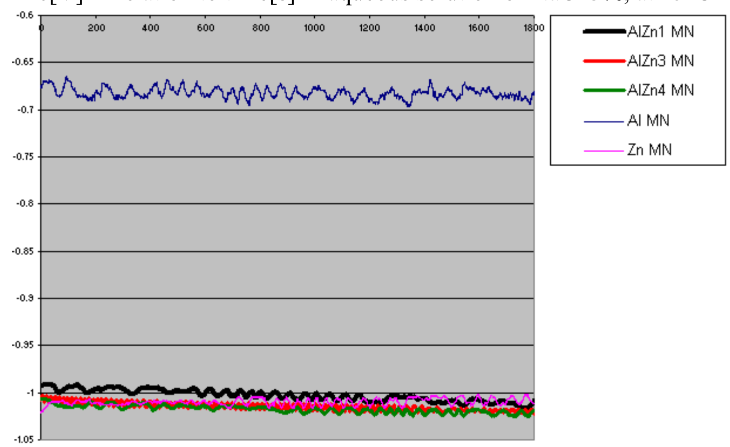

Fig. 2b Evolution of Emc[V] in relation to time[s] in sea water, at 25°C

3.2 Corrosion speeds

Determination of corrosion rates during Tafel linear polarization test (polarization rate of 2mV/s) was achieved in the same medium at 25 °C, in the range of ± 100mV from potential corrosion potential (Emc). The values of corrosion currents, respectively the corrosion rates are presented in Table 3.

Lowest values are recorded for aluminium and the largest values for zinc. The sample of AlZn 1 pseudo-alloy that is untreated by heat, presents the lower corrosion rate, followed by those registered for heat treated samples in the oven (AlZn4). The highest value was evidenced for the AlZn3 sample which was heated with flame. In the figures 3a and 3b are shown records of Tafel slopes for the pseudo-alloy AlZn1.

Table 3

Corrosion speeds in sea water and aqueous solution of NaCl 3%

Material	Thermal treatment	Exposure environment	Emc [mVesc]	icor [µA/cm2]	Vcor [µm /an
Al Zn 1 Al Zn 1	-	Sea MN NaCl 3%	- 1022 - 1090	4.42 1.80	66.12 28.9
Al Zn 3 Al Zn 3	Flame: 300°C Flame: 300°C	Sea MN NaCl 3%	-1032 -1030	7.00 3.84	104.60 57.40
Al Zn 4 Al Zn 4	Furnace: 350°C/30 minutes Furnace: 350°C/30 minutes	Sea MN NaCl 3%	-1022 -1090	5.05 3.23	75.60 48.25
Zn	-	Sea MN NaCl 3%	-1011 -1016	7.10 5.43	106.30 81.28
Al	-	Sea MN NaCl 3%	-635 -627	1.60 1.44	17.47 15.64

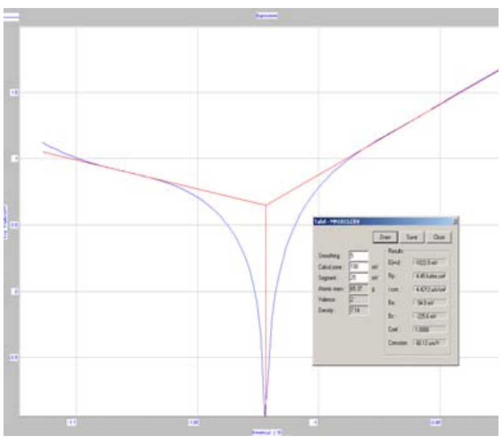
Potential [V]

Fig. 3a Tafel V curve (AlZn1 in NaCl)

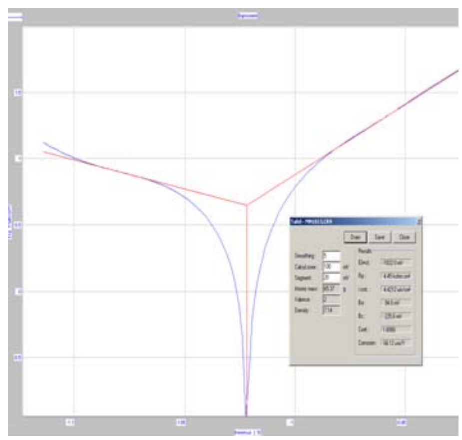
Potential [V]

Fig. 3b Tafel V curve (AlZn1 in sea water (MN))

3.3 Active-passive polarization

Polarization is performed through three consecutive cycles round-trip, for potential values in the range of -1000mV to 2000 mV, for pseudo-alloy AlZn, without passivation tendency. In Table 4 are presents the values of corrosion current value corresponding to potential of activation 2000 mV [8].

The values of corrosion currents are close for the samples untreated and treated in oven, in both environments. For the samples heated with flame, values are higher, especially in contact with sea water. In Figures 4 and 5 are presented curves of polarization (active area) for pseudo-alloy AlZn4, heat treated at temperature of 350 °C for 30minutes.

Table 4

Values of corrosion current corresponding to potential of +2000 mV

Material	Heat treatment	Exposure medium	Corrosion current [mA/ cm^2]
Al Zn1 Al Zn1	-	Sea water MN NaCl 3%	3 1.6
Al Zn3 Al Zn3	Flame - 300°C Flame - 300°C	Sea water MN NaCl 3%	7.00 2.00
Al Zn4 Al Zn4	Furnace : 350°C/30 minutes Furnace : 350°C/30 minutes	Sea water MN NaCl 3%	4 1.25
Zn	-	sea MN NaCl 3%	5.5 6.00

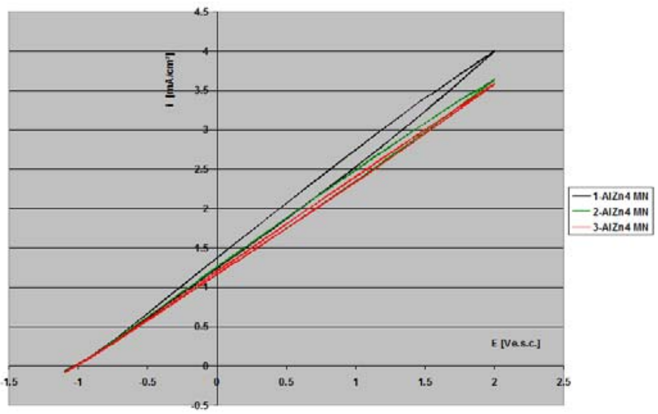

Fig. 4 Curves of cyclical polarization (cycles 1-3, drawn with a speed of 100 mV/s in seawater, temperature 26 ° C) for sample AlZn4

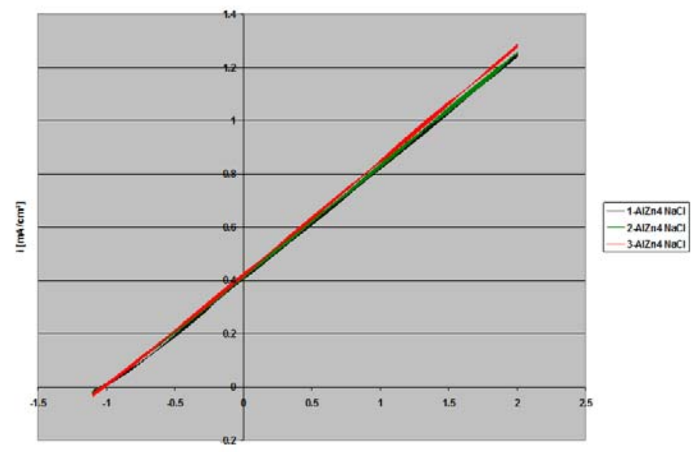

Fig. 5 Curves of cyclical polarization (cycles 1-3, drawn with a speed of 100 mV/s in NaCl 3%, temperature 26 °C) for AlZn4

3.4 Resistance to pitting corrosion

The variation of potential was stopped for ten seconds, to enable to develop pitting corrosion, and then was switched to the reverse polarization. In figure 6, are shown curves of variation of potential round-trip test into the different type of environments, for samples of AlZn4 pseudo-alloy heat treated in oven. In practice a curve that increase going from - to +, overlaps with the return curve, from + to -, in case of contact with sea water (MN) and has an insignificant difference in contact with aqueous solution of sodium chloride NaCl 3%. Intersection of return curve with the direct reverse polarization occurs near the value of Emc.

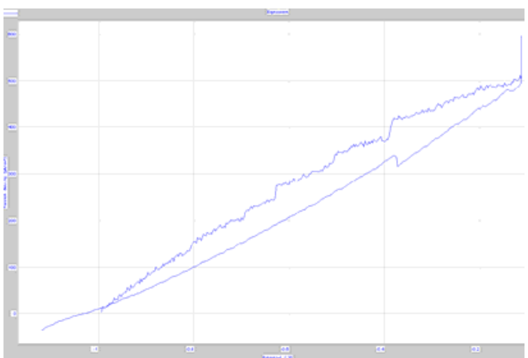
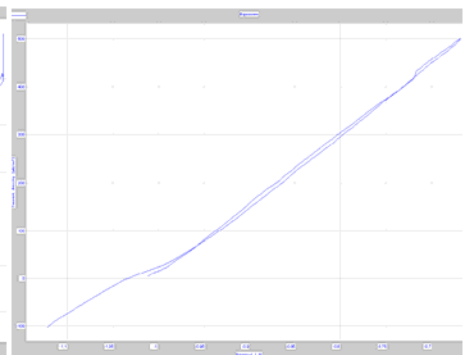

Fig. 6 Pitt AlZn4 (NaCl) Pitt AlZn4 (sea water-MN)

Measurements have shown, both for pseudo-alloy AlZn without heat treatment and with heat treatment, the presence of an active area, without reach the corrosion and re-passivation. It wasn't shown any influence due to aluminium presence, as an alloying element. In conclusion, the electrochemical measurements do not indicate corrosion occurring like points or crevasse.

3.5. Structural analysis of corrosion

Analysis of susceptibility to various types of corrosion for pseudo-alloys AlZn was performed after the electrochemical polarization, in range of potential varying from 1000mV up to 2000 mV, was made on structures attacked with chemical and highlighted the differences compared to zinc and aluminium.

The corrosive attack performed analysis indicates the following:

- Corrosive attack is generally doubled by a limited attack on the sediments located to grain boundary; Stress-corrosion cracking is shown for the samples untreated by heat (AlZn1), figure 7;

- Susceptibility to corrosion in caverns (corrosion specific for welded points and overlapping areas), accompanied by intergranular attack, figure 7 (pseudo-alloy AlZn1), figure 8 (pseudo-alloy AlZn3, heat treated with flame at 300 °C) and figure 9 (pseudo-alloy AlZn 4 heat treated in oven at temperature of 350^{o}C for 30 minutes; A very pronounced corrosion in caverns for zinc (figure 10); For aluminium, some isolated structure shows mainly attack on certain areas of the grain boundaries (figure 11).

Whatever heat treatment applied the resistance against corrosion of pseudo-alloys AlZn is diminished in relation to zinc.

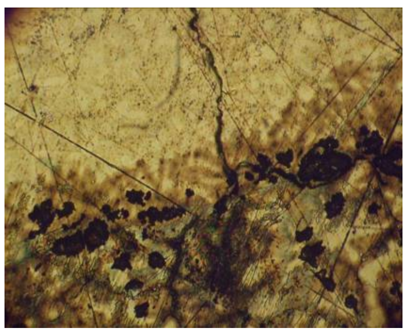
Fig. 7 Pseudo-alloy AlZn1

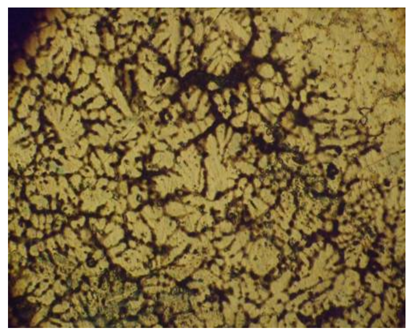
Fig. 8 Pseudo-alloy AlZn3

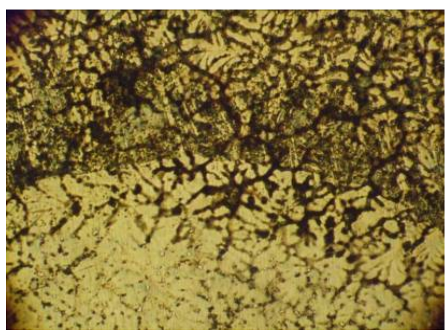
Fig. 9 Pseudo-alloy AlZn4

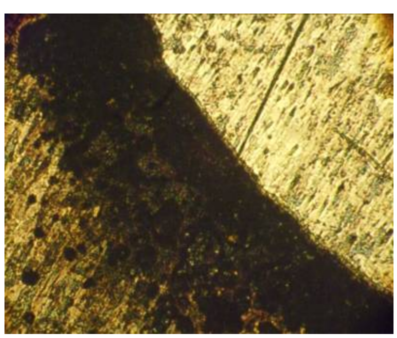
Fig. 10 Zn sample

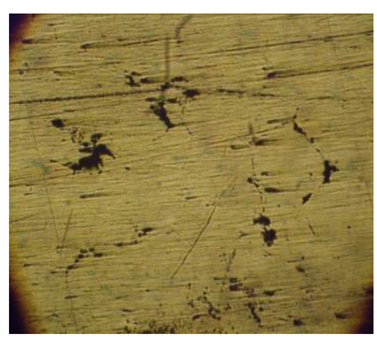
Fig. 11 Al sample

5 Conclusions - interpretation of corrosion resistance

Since the chlorine present in marine environments allow very corrosives effects, the possibility to improve the resistance to corrosion of the metallic surfaces exposes in these environments is important. The results obtained allow the following conclusions:

- The electrochemical measurements allow a more accurate assessment of the zinc influence in the aluminium alloy, from point of view of corrosion rate.
- The electrochemical measurement data indicate that for pseudo-alloy AlZn, in first approximation, zinc corrosion resistance is clearly differentiated from those of aluminium, in contact with the test environments, which prove that they retain the capacity to provide cathodic protection in contact with steel.
- Values for mixed corrosion potential (initial potential Emc) is around of -1000 mV, for both zinc and for pseudo-alloys AlZn, while potential value for aluminium is about 350mV, due to the electropositive nature.
- If the potential is slightly negative, the interaction with the corrosive environment indicating a certain corrosive effect (sea water and 3% NaCl solution). The curves of potential polarization in the range from -1000mV to + 2000 mV, using cyclic voltammetry (3 cycles round-trip) shows the existence of an interaction with the corrosive environment, without touching the passive state, considered the most favourable situation in terms of corrosion behaviour.
- Current values corresponding to corrosion potential of 2000 mV, reveals that for the aluminium alloys and zinc alloys the heat treatments have a positive influence to decrease the process of interaction with the corrosive environments. This decrease is in the following order: Zn-pseudo-alloy AlZ 3 (heat treated with flame at temperature of 300 °C), then pseudo-alloy AlZn4 (heat treated in oven at temperature of 350 °C for 30minutes) and then pseudo-alloy AlZn1 (without any heat treatment).
- Evaluation of corrosion rates, basis on Tafel polarization, show that their values are relatively small for pseudo-alloys AlZn. By alloying between aluminium and zinc and applying of some heat treatments, for pseudo-alloy AlZn has been obtained a real decrease of corrosion rates, following the same hierarchy as that indicated above.
- The values of corrosion rates provide the overall look on corrosion behaviour in contact with the corrosive environments considered.
- Polarization tests, performed starting from values close to potential Emc, at the electric current density value of 500 $\mu A/cm^2$, with reversed polarity until around Emc, showed no activation of a localized corrosion, both in the coatings with pseudo-alloys AlZn and alloyed zinc, used for comparison. The results highlight the fact that measurements upon the coatings realised by

pseudo-alloys AlZn that are in contact with the test environments are active in terms of passivity and resistant to corrosion pitting. The missing of pitting corrosion effects was proved by examining the structural appearance of fingerprints on the surface, resulting from electrochemical polarization tests. The appearance of fingerprints indicate a lack of corrosion in spots, but emphasizes the action of chlorine on some structural compounds present in intergranular spaces [9];

- Another important consideration highlight is the susceptibility to corrosion in crevices, which starts in welded areas and overlapping surfaces. The intensity of structural attack, revealed by comparative analysis, highlights the positive role of the alloying of aluminium with zinc, and heat treatments applied to AlZn coatings, to reduce corrosion effects.

It should be noted that to avoid structural corrosion, in particular the "caverns" type, is very important to take some measures related material (using combinations of zinc with aluminium, thermal treatments) to be correlated with structural measures of objectives which apply to surface coatings AlZn (avoiding overlapping areas, or providing additional protection operations with organic resin materials immune to corrosion type epoxy, polyurethane.)

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