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INFLUENCE OF HEAT TREATMENT ON CORROSION RESISTANCE OF ZnAl40Ti2Cu ALLOY

The aim of this paper was to determine the effect of heat treatment for the corrosion resistance of the ZnAl40Ti2Cu alloy under "acid rain" conditions. ZnAl40TiCu alloy after supersaturation and after supersaturation and aging was studied. Potentiodynamic studies, potentiostatic studies and studies on structure of the alloy top layer of samples after corrosion tests were carried out. These investigations indicated a significant influence of heat treatment on corrosion resistance of the ZnAl40Ti2Cu alloy. The highest increase in corrosion resistance comparing to the alloy in the as-cast condition may be obtained by supersaturation. A significant influence of the aging temperature and time on corrosion resistance was proved.

Keywords: corrosion, Zn-Al alloys, structure, heat treatment

1. Introduction

Zn-Al alloys are used as an alternative material for bronzes, cast iron and aluminium alloys in bearings, and as a construction material [1-2]. High-aluminium monoeutectoid zinc alloys are characterised by high mechanical, tribologic and attenuating properties. From among all Zn-Al alloys, these alloys are characterised by the highest hardness, tensile strength and wear resistance. On the other hand, insufficient resistance to corrosion and dimensional instability are important disadvantages of Zn-Al-Cu alloys, leading to a limitation of their applications [3-4]. Works by Krajewski [3] indicated that the problem of dimensional instability may be significantly limited by a partial substitution of copper with titanium.

The influence of structural factors on corrosion resistance of metals and their alloys is a rarely contemplated research subject. Analysis of the literature and studies the Author's carried out till now indicate that the structural factors affecting corrosion resistance of metal alloys include, among others [5-7]:

- purity of the alloy, presence of non-metallic inclusions;
- surface roughness;
- grain size;
- crystallographic orientation of the metal surface contacting with the corrosive environment;
- phase composition of the alloy;
- physico-chemical condition of the surface.

Studies on corrosion of zinc and Zn-Al alloys are often carried out in a 3.5% NaCl solution. This medium, although aggressive, does not simulate actual operating conditions of these alloys, but only conditions of operation in a marine environment. The actual operating conditions are much better represented by an "acid rain" solution with pH = 3.5, for which the molar ratio of main components is: H_2SO_4:HNO_3:HCl = 1:0.3:0.17.

2. Scope and methodology of examination

The aim of this paper was to determine the effect of heat treatment for the corrosion resistance of the ZnAl40Ti2Cu alloy. The following alloy was examined: Zn – 40 wt % Al – 2 wt % Ti – 1 wt. % Cu in as-cast condition, after supersaturation at 385°C/24h and after supersaturation at 385°C/24h and aging at temperatures of 175, 150 and 125°C for 1, 10 and 24 h. The scope of the investigations included potentiodynamic studies, potentiostatic studies and studies on structure of the alloy top layer of samples after corrosion tests. In the corrosion tests, a set composed of an electrolyser, a SOLARTRON 1285 potentiostat, and a computer with CorrWare 2 software was used. The values of potentials were reported in relation to the standard hydrogen electrode (SHE). The corrosion tests were carried out in an "acid rain" solution. Measurements of potentiodynamic polarisation curves of the samples were carried out in the range including cathodic and anodic potentials, starting the polarisation from a cathodic potential. The potential change rate was 10 mV/min. In potentiostatic measurements, changes in the current at potentials of the samples more anodic (less negative) by 100 mV than the corrosion potential E_{kor} were recorded. In structural studies, a HITACHI S 3400N scanning electron microscope (SEM) cooperating with an energy-dispersive X-ray spectrometer (EDS) from THERMO NORAN and a SISTEM SIX microanalysis system were used.

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3. Results and discussion

The results of the potentiodynamic studies are presented in Fig. 1 and Table 1. In the case of Zn-Al alloys, no passive range may be distinguished in the potentiodynamic curve, an increase in the potential value most often causes an increase of current density. In this case, corrosion resistance is characterised best by a comparison of the current density values read from the potentiodynamic curve for the same potential values, e.g. for zinc and Zn-Al alloys – for $E = E_{kor}+100$, 300 and 500 mV. The results of the potentiodynamic studies indicate a high corrosion resistance of the alloy subjected only to supersaturation at a temperature of 385°C/24 h. Corrosion resistance of the alloy after supersaturation is higher than that of the alloy in as-cast condition, which is proved by, mainly, lower values of current density (Table 1). Potentiodynamic curves of the alloy after supersaturation and aging run much more high than the potentiodynamic curves of the alloy after supersaturation. Thus probably, the precipitation processes connected with supersaturation of the ZnAl40Ti2Cu alloys lead to a deterioration of corrosion resistance in the "acid rain" environment. In spite of the titanium content no occurrence of a passive range is observed in the potentiodynamic curves (Fig. 1). For the ZnAl40Ti2Cu alloy, supersaturation and aging causes an increase in corrosion resistance irrespective of time and temperature (Fig. 1). It is proved by lower values of corrosion current density and lower values of current density for potentials $E = E_{kor}$ + 100, 300, 500 mV (Table 1). In the case of supersaturation and aging of the ZnAl40Ti2Cu alloy, the highest corrosion resistance may be obtained by aging at 125°C/10 h, while the lowest one is obtained for aging at 125°C/24 h. For lower values of the applied potential ($E = E_{kor}$ + 100 mV), low values of current density are obtained also for aging at 125°C/1 h and 150°C/1 h (Table 2).

Potentiostatic studies allow for verifying of the results of potentiodynamic studies. Both the course of the potentiostatic curve, and the value of current density are important here, particularly at the end of tests, when the latter is already fixed and it does not change significantly in time. Results of potentiostatic tests are presented in Table 2. The results of potentiostatic stud-

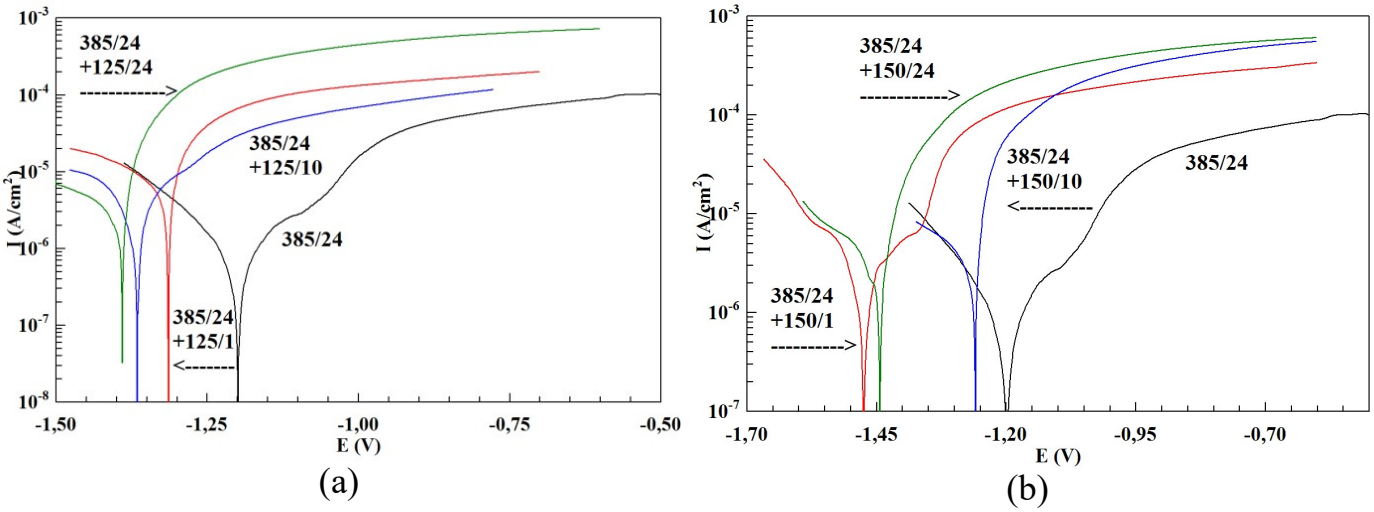


Fig. 1. Potentiodynamic curves of ZnAl40Ti2Cu alloy in „acid rain" after (a) supersaturation and aging 385°C/24 h + 125°C (b) supersaturation and aging 385°C/24 h + 150°C

TABLE 1

Results of potentiodynamic examination of ZnAl40Ti2Cu alloy after heat treatment

	E_{corr} mV	R_p W/cm²	I_{corr} mA/cm²	Current density for potential mA/cm²		
				E_{corr} + 100 mV	E_{corr} + 300 mV	E_{corr} + 500 mV
as-cast	–876	1 654	15,7	165	510	792
385°C/24 h	–1200	32 075	0,8	3	40	74
385°C/24 h + 175°C/1 h	–1506	4 240	6,2	8	162	295
385°C/24 h + 175°C/10 h	–1514	3 856	6,7	10	161	286
385°C/24 h + 175°C/24 h	–1425	4 838	5,4	28	100	155
385°C/24 h + 150°C/1 h	–1475	10 378	2,5	6	129	207
385°C/24 h + 150°C/10 h	–1266	2 655	9,8	92	298	455
385°C/24 h + 150°C/24 h	–1447	4 885	5,3	60	263	420
385°C/24 h + 125°C/1 h	–1317	2 187	11,9	58	128	172
385°C/24 h + 125°C/10 h	–1367	6 903	3,8	14	56	96
385°C/24 h + 125°C/24 h	–1396	3 093	8,4	100	350	535

TABLE 2

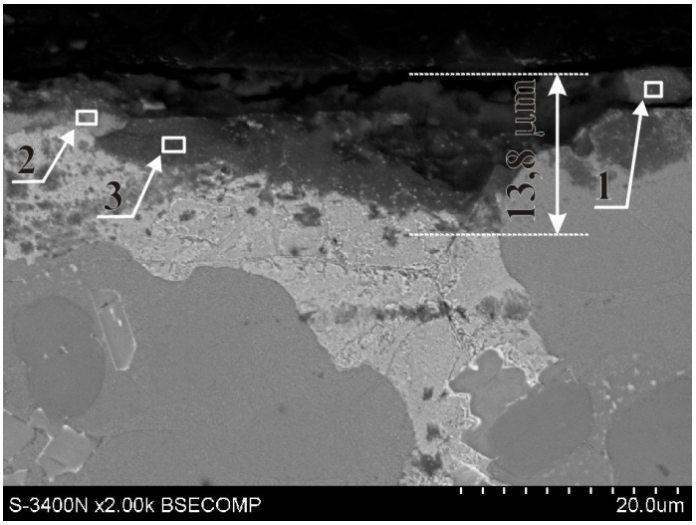
Results of potentiostatic examinations of ZnAl40Ti2Cu alloy after heat treatment

Heat treatment	Current density after time [mA/cm^2]															
	3 h	**6 h**	**9 h**	**12 h**	**15 h**	**18 h**	**21 h**	**24 h**	**27 h**	**30 h**	**33 h**	**36 h**	**39 h**	**42 h**	**45 h**	**46 h**
as-cast	32	46	52	51	47	39	30	34	32	32	32	33	33	32	31	30
supersaturation	1,5	1,4	1,7	1,8	2,0	2,0	1,8	1,8	1,8	2,0	2,3	2,3	2,2	2,0	2,0	2,0
125°C/1 h	19	15	15	11	6,0	1,0	1,2	4,3	7,2	5,8	3,8	2,0	0,8	0,5	0,7	0,6
125°C/10 h	15	18	18	16	15	13	10	12	14	15	14	13	13	14	14	14
125°C/24 h	44	30	21	25	28	30	34	32	27	27	26	24	23	22	22	22
150°C/1 h	16,2	5,5	0,7	2,5	3,5	4,4	6,0	7,0	5,7	5,9	6,9	7,7	9,6	6,0	5,8	5,0
150°C/10 h	21	14	13	17	22	25	27	29	29	29	29	27	27	25	24	24
150°C/24 h	17,7	11,5	-8,2	-8,3	11	17	19	20	22	22	23	24	25	26	26	26
175°C/1 h	11,5	8,5	5,5	2,3	2,0	3,0	4,0	5,0	5,0	6,0	6,0	6,0	5,6	7,0	7,0	7,0
175°C/10 h	38	40	43	43	43	40	36	31	27	23	19	17	17	15	15	15
175°C/24 h	35	24	9,3	4,5	4,6	15	24	28	36	34	30	28	27	28	28	28

ies of the ZnAl40Ti2Cu alloy after supersaturation and aging confirm the results of potentiodynamic studies. Irrespective of the heat treatment variant used, the alloy subjected to heat treatment is characterised by a better corrosion resistance than the ZnAl40Ti2Cu alloy in as-cast condition. The results of potentiostatic studies confirmed a high corrosion resistance of the alloy after supersaturation. Among the samples subjected to supersaturation and aging, the highest corrosion resistance characterises the samples after supersaturation and aging at 385°C/24 h + 125°C/1 h (Table 2). The results of potentiostatic studies indicate also that both increasing the aging duration, and increasing the aging temperature cause a decrease in corrosion resistance. Irrespective of the aging temperature, the highest corrosion resistance characterises the alloy after aging for 1 hour; increasing the aging duration causes, irrespective of the aging temperature, a decrease in corrosion resistance. The largest decrease in corrosion resistance is observed when the aging duration is increased from 1 to 10 h.

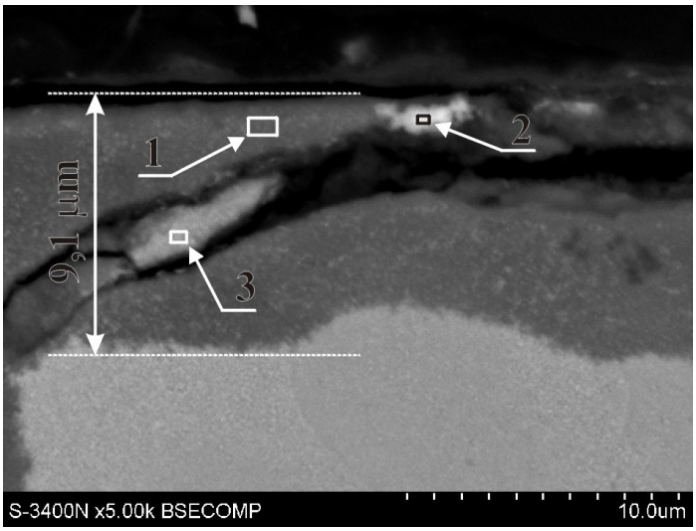
Investigations of the surface condition and the structure of the top layer of the samples after corrosion enable to define, among others, the corrosion character (e.g. pitting corrosion, uniform corrosion) and the changes caused by the corrosive environment in the top layer of the alloy, being in a direct contact with the corrosive environment (e.g. dezincification of the alloy). After corrosion in "acid rain," the dezincificated layer of the ZnAl40Ti2Cu alloy subjected to heat treatment is characterised by a low thickness. Frequently, characteristic "islands" may be observed – spots in which a decreased zinc content is found (Figs. 2-6). In the case of the alloy aged at a higher temperature (175°C), occurrence of large open pits is most often observed, within which a significantly increased aluminium content is found (Fig. 2).

In the case of the alloy aged at a temperature of 150°C for a shorter duration (1 h), the dezincification zone is very shallow, and cracks occur within it. Therefore, an analysis of chemical composition in the microareas is rendered more difficult (size of some precipitations is smaller than the size of the excitation area – pt. 2, Fig. 3). In the vicinity of the cracks, occurrence of precipitations with a high copper content may be observed, visible as bright areas in the scanning electron microscope (pt. 2,



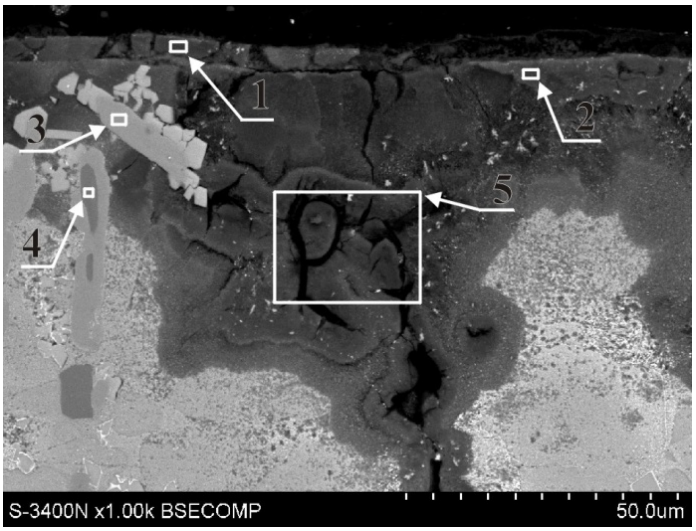
	Zn % at.	Al % at.	Cu % at.	S % at.
pt 1	21,6	73,6	2,4	2,4
pt 2	23,7	68,9	3,5	3,9
pt 3	23,3	68,2	2,7	5,8

Fig. 2. Structure of surface layer of ZnAl40Ti2Cu after supersaturation and aging 385°C/24 h + 175°C/1 h after corrosion tests in „acid rain"



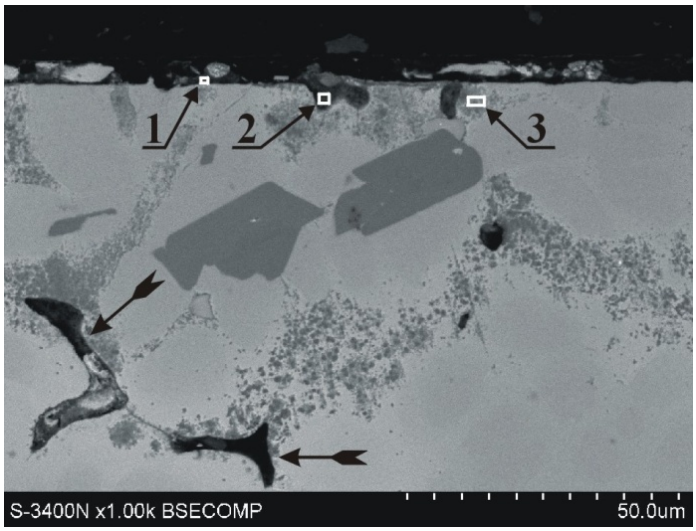
	Zn % at.	Al % at.	Cu % at.	S % at.	inne % at.
pt 1	26,0	73,3	–	–	Cl: 0,7
pt 2	7,5	13,9	75,8	2,0	Cl: 0,4 Mg: 0,4
pt 3	43,2	56,3	–	0,5	–

Fig. 3. Structure of surface layer of ZnAl40Ti2Cu after supersaturation and aging 385°C/24 h + 150°C/1 h after corrosion tests in „acid rain"



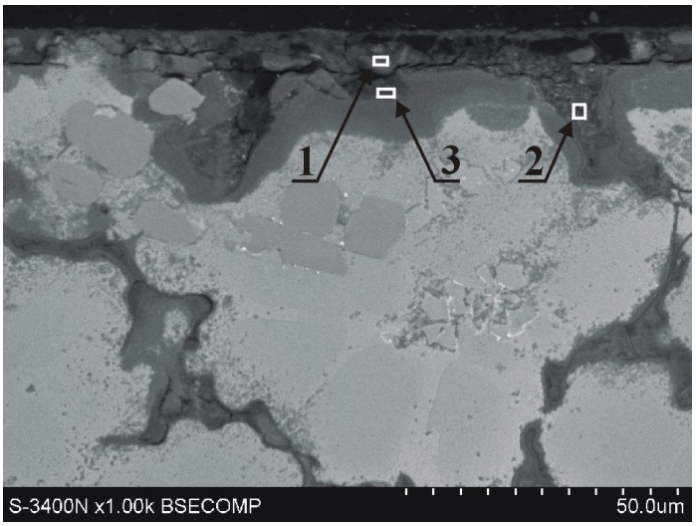
	Zn % at.	Al % at.	Cu % at.	Ti % at.	S % at.
pt 1	18,9	70,8	3,4	–	6,9
pt 2	16,1	78,9	–	–	5,0
pt 3	20,8	49,6	–	29,6	–
pt 4	6,6	59,3	–	34,1	–
pt 5	19,9	67,4	5,5	–	7,2

Fig. 4. Structure of surface layer of ZnAl40Ti2Cu after supersaturation and aging 385°C/24 h + 150°C/10 h after corrosion tests in „acid rain"



	Zn % at.	Al % at.	Cu % at.	Mg % at.	S % at.	Cl % at.
pt 1	36,4	60,3	–	1,5	1,3	0,5
pt 2	24.0	73,3	–	1,3	1,4	–
pt 3	37.6	60,8	1.6	–	–	–

Fig. 5. Structure of surface layer of ZnAl40Ti2Cu after supersaturation and aging 385°C/24 h+ 125°C/1 h after corrosion tests in „acid rain" (pits marked)



	Zn % at.	Al % at.	Cu % at.	Mg % at.	S % at.	Cl % at.
pt 1	34,7	39,4	4,1	3,3	11,3	7,2
pt 2	25,0	65,2	6,5	–	2,6	0,7
pt 3	29,3	59,7	–	1,2	7,8	2,0

Fig. 6. Structure of surface layer of ZnAl40Ti2Cu after supersaturation and aging 385°C/24 h+125°C/24 h after corrosion tests in „acid rain"

Fig. 3). On the other hand, areas with zinc content increased in relation to the rest of the dezincificated zone may be observed within the cracks (pts. 3 and 1, Fig. 3). For the alloy aged longer at a temperature of 150°C, occurrence of large and branched pits is characteristic (Fig. 3). A significantly increased aluminium content remains not only near the surface being in direct contact with the corrosive environment (pts. 1 and 2, Fig. 4), but also within the pits (pt. 5, Fig. 4). Both in the vicinity of the layer, and within it, occurrence of precipitations of titanium-rich phases may be observed (pts. 3 and 4, Fig. 4). However, the pits do not run through precipitations of these phases, but stop on them or pass round them (Fig. 4).

In the structure of the ZnAl40Ti2Cu alloy after corrosion in an "acid rain," occurrence of voids located more deeply, partially filled with corrosion products, may be observed apart from the pits running "from the surface." As no porosity has been found in the alloys in as-cast condition, it should be assumed that they are also pits. In this case, the pits probably assume a form of branched threads, with the zinc-rich phase being the preferred place of their formation. Occurrence of these characteristic branched pits may be observed mainly for the alloys aged at a temperature of 125°C/1 h (Fig. 5). In the case of alloys aged for a longer time at a temperature of 125°C, pits are observed. The top part of the dezincificated layer is rich in S and Cl originating from the corrosive environment, and it is cracked (pt. 1, Fig. 6). Therefore, is constituted probably by the corrosion products: sulfides and chlorides. Formation of the corrosion products causes cracking of this part of the dezincificated layer. Significantly increased aluminium and copper contents are observed below it, however the contents of S and Cl originating from the corrosive environment are lower (pts. 2 and 3, Fig. 6). A characteristic morphology feature of the dezincificated layer of the ZnAl40Ti2Cu alloy subjected to aging at 125°C/24 h consists in the course of the dezincificated layer. Most often, the dezincificated layer "passes round" the precipitations of titanium-rich phases, the zinc-rich phases being the preferred place of its formation (Fig. 6).

The studies carried out proved a significant influence of heat treatment on corrosion resistance of the ZnAl40Ti2Cu alloy in the "acid rain" environment. The highest resistance may be obtained for the alloy after supersaturation. Probably, the high corrosion resistance is a consequence of a structural homogenisation in the result of supersaturation. Aging causes a decrease in corrosion resistance comparing to the alloy after supersaturation. Precipitation processes which occur during aging affect the corrosion resistance of the alloy unfavourably. Increasing of the aging duration and aging temperature may have an unfavourable influence for corrosion resistance of the ZnAl40Ti2Cu alloy. It may be connected with precipitation of Cu-rich phases in the structure. Copper participates in the solution hardening process of Zn-Al alloys, forming dipoles. Therefore, their presence may affect corrosion resistance of the alloy significantly, improving corrosion resistance of the alloy after supersaturation. The precipitation of Cu-rich phases reduces this effect, which probably influences the corrosion resistance unfavourably.

The studies carried out have indicated also that courses of the pits within the alloys depend on the phases occurring in the structure. The pits may "pass round" some phases. In the case of the studied alloy, these phases were Ti- and Al-rich phases, probably intermetallic phases. It is connected, most of all, with a higher bond energy and a higher packing density of the structure (a higher coordination number) in relation to other phases present in the structure. Due to both these factors, it is much harder to remove an atom from an intermetallic phase than from other phases. It results in the observed non-typical course of the pits. One characteristic property of the alloy top layer after corrosion consists in the presence of a dezincificated zone, within which a higher alloying elements content is observed. Yet the layer thickness is the lower, the higher the corrosion resistance of a given sample. This may explain the initial increase in current density during potentiostatic studies (connected with the dezincification) and the later decrease in current density (top layer is richer in Al and Cu, thus the corrosion resistance increases).

4. Conclusions

The presented results allow for enunciating of the following conclusions:

– Heat treatment of the ZnAl40Ti2Cu alloy causes an increase in corrosion resistance, the highest corrosion resistance is characterised by a stop after supersaturation.
– Corrosion of the ZnAl40Ti2Cu alloy has a local character; Zn-rich dendrites constituting the preferred corrosion spots.
– On a cross-section of the ZnAl40Ti2Cu alloy, a dezincificated layer may be observed, with a thickness depending on the corrosion resistance of the alloy and being the higher, the lower the corrosion resistance of the alloy.
– Within the layer, a significantly increased content of alloying elements (aluminium and copper) may be observed. The increase in the alloying elements content is responsible for the decrease in the corrosion rate, observed during potentiostatic studies.
– The presence of precipitation of intermetallic phases in the structure of the ZnAl40Ti2Cu alloy probably affects an improvement of their corrosion resistance in the "acid rain" environment.

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