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Corrosion of Al-Mg and Al-Zn-Mg alloys for hull structures

SUMMARY

In the paper results of investigations on corrosion and stress corrosion resistance of Al-Mg and Al-Zn-Mg alloys, applicable for ship structures, in different treatment states and test conditions are reported. Influence of chemical composition, heat treatment, load(stress) and electric potential applied on the mechanical and corrosion properties of the alloys are demonstrated and discussed.

INTRODUCTION

Aluminium alloys are widely used as structural material in many fields of technology . They are also used in shipbuilding for ship hulls, deckhouses etc. For light ship construction alloys of Al-Mg composition have been used till now. For instance AlMg4 (PA11), AlMg5 (PA20), and recently AlMg4,5Mn (PA13) alloys have been applied for ship hull structures. Strength of PA13 alloy is not very high, but the alloy is resistant to general and stress corrosion in sea water.

In the last years properties of Al-Zn-Mg composition alloys have been investigated in many countries. A negative property of this type of alloys is their proneness to stress corrosion cracking in sea water, particularly if total Zn+Mg content exceeds 6%, which called for an effort to find counter-measures for that phenomenon. The investigations to this time are carried out in two basic directions: alloy structure modification by adding alloying elements or structure modification by a suitable heat treatment. Investigations into corrosion cracking mechanism are paralelly carried out.

Heat treatment distinctly influences Al-Zn-Mg alloy structure heterogeneity, and in consequence its corrosion resistance. Many authors attribute the resistance to size of release free zone (SWW) [1], [4]. Generally, the wider the SWW the higher the corrosion cracking resistance. Character of the grain boundary release greatly influences corrosion cracking sensitivity. The continuous phase release deteriorates stress corrosion resistance of an Al alloy [1], [4], [6]. In the last years a hypothesis of hydrogen influence on stress corrosion cracking of Al-Zn-Mg composition alloys grew to particular importance [2], [3].

TESTING METHOD

Tests have been carried out upon the specimens of the diameter d_0=5 mm, cut out of 10 mm thick plate perpendicularly to its rolling direction. Chemical composition of the tested alloys is given in Tab. 1, but in Tab. 2. heat treatment parameters of AlZn5Mg1 and AlZn5Mg2CrZr alloys are specified. AlMg4,5Mn (PA13) alloy has been hot rolled and cristallized (pgr state).

Tab. 1. Chemical composition of AlZn5Mg1, AlZn5Mg2CrZr and AlMg4,5Mn alloys

Alloy symbol	Amount of components [%]									
	Zn	Mg	Mn	Cr	Zr	Ti	Fe	Si	Cu	Al
AlZn5Mg1	4,35	1,25	0,180	0,14	0,04	0,034	0,32	0,16	0,05	the rest
AlZn5Mg2CrZr	5,30	2,13	0,006	0,17	0,19	0,040	0,27	0,15	0,04	the rest
AlMg4,5Mn	0,03	4,30	0,610	0,13	-	0,045	0,31	0,19	0,03	the rest

Tab. 2. Heat treatment parameters of AlZn5Mg1 and AlZn5Mg2CrZr alloys

Item no.	Alloy symbol	Solutioning temperature/time [^{0}C/ h,min]	Cooling after solutioning	Ageing type	State symbol
1	AlZn5Mg1	430/45 min	air	natural - 100 days	ta
2	AlZn5Mg1	430/45 min	water (t=15^{0}C)	20^{0}C/6 days + 90^{0}C/8h + 145^{0}C/16h	tb_{21}
3	AlZn5Mg1	430/45 min	water (t=80^{0}C)	20^{0}C/6 days + 90^{0}C/8h +145^{0}C/16h	tb_{22}
4	AlZn5Mg1	430/45 min	air	20^{0}C/6 days+ 90^{0}C/8h + 145^{0}C/16h	tb_{23}
5	AlZn5Mg2CrZr	450/1,5 h	water (t=80^{0}C)	20^{0}C/6 days + 90^{0}C/15h+150^{0}C/10h	tb_{22}
6	AlZn5Mg2CrZr	450/1,5h	air	20^{0}C/6 days + 95^{0}C/15h + 150^{0}C/10h	tb_{23}
7	AlZn5Mg2CrZr	450/1,5h	air	natural - 100 days	ta

Testing against stress corrosion cracking was carried out under constant tensile load in 3.5% NaCl water solution, and anodic and cathodic polarization applied. Corrosion resistance testing was performed in the similar conditions, but free of load. The applied potential values in relation to the stationary potential of a tested alloy were :

+100 mV, +50 mV, -50 mV, -200 mV, -600 mV

The potential values have been measured against the saturated calomel electrode (NEK). Stress corrosion cracking resistance of the tested alloys has been estimated by measuring time-to-fracture of the specimens during their exposure, or by determining mechanical properties (R_m, $R_{0.2}$) of those , which have not fractured during exposure period.

Mechanical properties of the alloys tested during corrosion exposure (free of load) have been determined in accordance with PN-91/H-04319 standard.

Test results

The results of the stress corrosion cracking tests are presented in Tab. 3. Mechanical properties of the specimens, which did not fracture when exposed, are given in Tab. 4.

Tab. 3. Stress corrosion resistance of the tested alloys under $\sigma_o \approx 0,9\ R_{0.2}$ tensile stress in 3,5% NaCl water solution versus applied potential values (in relation to corrosion stationary potential -U_{st})

Alloy symbol (State symbol)	Stress corrosion fracture resistance (endurance) [h]					
	Potential in relation to U_{st} [mV]					
	-600	-200	-50	U_{st}	+50	+100
AlMg4,5Mn	>1000	>1000	>1000	>1000	204	109
AlZn5Mg1 (ta)	75	>1000	>1000	>1000*	42	14
AlZn5Mg1 (tb$_{21}$)	48	>1000	>1000	>1000	530	48
AlZn5Mg1 (tb$_{22}$)	58	>1000	>1000	>1000	940	58
AlZn5Mg1 (tb$_{23}$)	55	>1000	>1000	>1000	940	59
AlZn5 Mg2CrZr (ta)	53	>1000	>1000	>1000*	730	61
AlZn5Mg2CrZr (tb$_{22}$)	38	>1000	>1000	>1000	>1000*	927
AlZn5Mg2CrZr (tb$_{23}$)	39	>1000	>1000	>1000	>1000*	927

**** one out of three tested specimens fractured***

Tab. 4. Mechanical properties of the tested alloys after stress corrosion exposure versus applied potential values (in relation to U_{st})

Alloy symbol (State symbol)	Mechanical properties		Mechanical properties after exposure					
			-200 mV		-50 mV		U_{st}	
	R_m [MPa]	A_{10} [%]	R_m [MPa]	A_{10} [%]	R_m [MPa]	A_{10} [%]	R_m [MPa]	A_{10} [%]
AlMg4,5Mn	298	18,0	295	14,0	295	16,1	298	17,2
AlZn5Mg1 (ta)	384	17,3	341	14,5	338	14,9	301	14,4
AlZn5Mg1 (tb$_{21}$)	398	14,5	349	10,9	356	11,7	353	11,0
AlZn5Mg1 (tb$_{22}$)	373	14,2	355	10,8	355	11,3	358	10,4
AlZn5Mg1 (tb$_{23}$)	354	12,1	345	8,8	348	9,4	350	8,7
AlZn5Mg2CrZr (ta)	397	12,3	317	10,5	315	10,0	309	5,5
AlZn5Mg2CrZr (tb$_{22}$)	445	7,2	439	6,0	444	6,1	438	4,2
AlZn5Mg2CrZr (tb$_{23}$)	366	9,6	399	6,3	345	6,5	347	5,4

The relative decrease of tensile strength and elongation of the tested alloys after corrosion exposure (free of load)is shown in Tab. 5 and 6 in comparison with the properties of the alloys before corrosion exposure. In order to compare the corrosion resistance (free of load) and the stress corrosion resistance of the tested alloys, corrosion exposure time was equal to the stress corrosion endurance of the alloys. Depending on type of an alloy, its heat treatment and applied potential, the exposure time was of the values from less than 20 to 1000 hours (see Tab. 3).

Tab. 5. Relative decrease of tensile strength of the tested alloys after corrosion exposure (free of load) versus applied potential (in relation to U_{st}). [%]

Alloy symbol (State symbol)	Potential in relation to U_{st} [mV]					
	-600	-200	-50	U_{st}	+50	+100
AlMg4.5Mn	6,0	1,0	0,0	0,0	58,1	57,0
AlZn5Mg1 (ta)	37,5	8,9	8,3	10,9	40,1	41,4
AlZn5Mg1 (tb$_{21}$)	26,1	10,1	9,6	8,5	16,3	15,1
AlZn5Mg1 (tb$_{22}$)	19,3	3,5	3,2	2,4	17,4	20,1
AlZn5Mg1 (tb$_{23}$)	22,9	1,1	1,1	0,6	20,9	32,2
AlZn5Mg2CrZr (ta)	46,3	9,3	9,1	8,6	40,1	41,6
AlZn5Mg2CrZr (tb$_{22}$)	17,7	1,8	1,3	1,1	18,4	20,2
AlZn5Mg2CrZr (tb$_{23}$)	19,0	3,3	3,3	1,9	24,8	26,4

Tab. 6. Relative decrease of elongation of the tested alloys after corrosion exposure versus applied potential (in relation to U_{st}). [%]

Alloy symbol (State symbol)	Potential in relation to U_{st} [mV]					
	-600	-200	-50	U_{st}	+50	+100
AlMg4.5Mn (pgr)	33,3	22,2	11,1	2,8	66,7	73,3
AlZn5Mg1 (ta)	7,5	7,5	6,9	7,5	70,0	82,1
AlZn5Mg1 (tb$_{21}$)	31,0	16,6	10,3	7,6	72,4	86,9
AlZn5Mg1 (tb$_{22}$)	18,3	11,3	7,0	7,0	70,4	88,7
AlZn5Mg1 (tb$_{23}$)	15,5	12,4	6,7	6,7	66,9	85,1
AlZn5Mg2CrZr (ta)	3,3	4,9	3,3	13,0	67,5	68,3
AlZn5Mg2CrZr (tb$_{22}$)	19,4	4,2	4,2	8,3	86,1	97,2
AlZn5Mg2CrZr (tb$_{23}$)	28,1	6,2	5,2	7,3	89,6	97,9

During metallographic tests an intensive layer corrosion of AlZn5Mg1 and AlZn5Mg2CrZr alloys have been demonstrated after exposure with applied anodic potential, as well as traces of micropores and hydrogen microcracks on the specimen surface after corrosion and stress corrosion exposure and applied cathodic potentials (of -200 mV and -600 mV in relation to the stationary potential values).

Fig. 1 to 3 show characteristic macrophotographies of the selected specimens after corrosion and stress corrosion exposure in cathodic and anodic polarization conditions. In Fig. 4, a fragment of AlZn5Mg1 (tb$_{22}$) specimen's surface with a visible hydrogen crack is demonstrated.

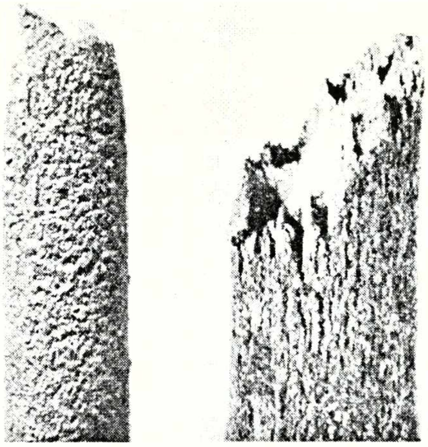

Fig. 1. Macrophotographies of AlZn5Mg1 (tb$_{22}$) specimen after stress corrosion exposure under the applied potential:
a) cathodic: of - 600 mV in relation to U_{st} = -890 mV , exposure time t = 55 h;
b) anodic: of +100 mV in relation to U_{st}, exposure time t = 65 h.

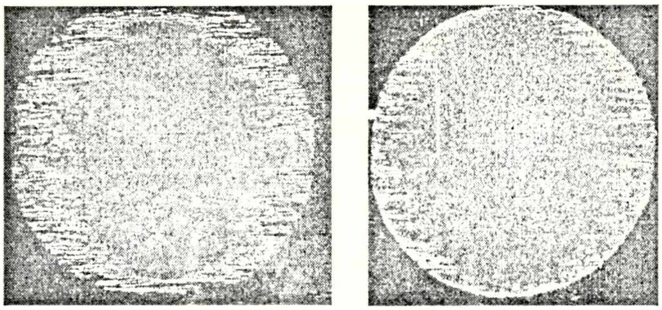

Fig. 2. Macrophotographies of microsection cut perpendicular to specimen axis, after corrosion exposure under the applied anodic potential of + 100 mV in relation to U_{st}:
a) AlZn5Mg2CrZr (ta) alloy specimen, t = 61 h, 10 x enlarged;
b) AlZn5Mg2CrZr (tb_{22}) alloy specimen, t = 900 h, 10 x enlarged.

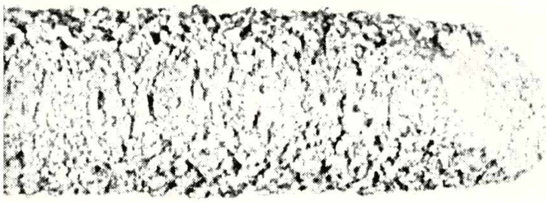

Fig. 3. Macrophotography of AlMg4,5 alloy (pgr) specimen after stress corrosion exposure under the applied anodic potential of + 100 mV, t = 100 h.

Fig. 4. Surface hydrogen crack on AlZn5Mg1 alloy (tb_{22}) alloy specimen after stress corrosion exposure under the applied potential of -200 mV in relation to U_{st}, t =1000 h, 274 x enlarged, SEM.

DISCUSSION

From among all tested alloys, AlMg4,5 (pgr) alloy showed the largest corrosion resistance as well as stress corrosion cracking resistance under stationary potential. The remaining alloys revealed diversified resistance depending on their heat treatment type.

Corrosion resistance tests of AlZn5Mg1 and AlZn5Mg2CrZr alloys under stationary potential (U_{st}) demonstrated some tensile strength decrease in the range of several to 10% for particular alloys after 1000 h exposure (see Tab. 5.).

Different corrosion resistance of the alloys was connected with their different heat treatment. The lowest corrosion resistance was showed by the alloys in ta state, which in tb_{22} and tb_{23} states demonstrated however good corrosion resistance.

The tensile strength decrease after corrosion exposure was caused by electrochemical corrosion. It would be confirmed by traces of layer corrosion, which appeared in AlZn5Mg1 (ta) and tb_{21} alloy and in AlZn5Mg2CrZr (ta) alloy; these were exactly the same as those in which largest decrease of R_m values were observed (Tab. 5). Pure corrosion factor - electrochemical specimen solubilization in the form of layer corrosion - seems to be of importance here.

The second set of results referred to stress corrosion tests under $\sigma_0 \approx 0{,}92\ R_{0,2}$ stress level. Almost all specimens (except one of AlZn5Mg1 (ta) alloy and one of AlZn5Mg2CrZr (ta) alloy (Tab. 3) appeared resistant and did not crack during the standard test lasting 1000 h under stationary potential. However, in most cases the exposure caused degradation of mechanical properties of the materials (Tab. 4). The largest tensile strength decrease was observed in AlZn5Mg1 (ta) and AlZn5Mg2CrZr (ta) alloys. For these states substantial decrease of relative elongation, reaching even 59% for AlZn5Mg2CrZr (ta) alloy, is characteristic.

It can be supposed that the low stress corrosion cracking resistance of Al-Zn-Mg type alloys in ta state was mainly caused by layer corrosion, which together with the applied tensile stress resulted in either cracking of the alloys or degradation of their mechanical properties.

Artificial ageing after solutioning improved stress corrosion cracking resistance of the tested Al-Zn-Mg alloys. In the artifical ageing state tb the stress corrosion cracking resistance increases as cooling speed after solutioning decreases.

Good corrosion and stress corrosion resistance for the tested Al-Zn-Mg alloys was obtained by applying low cooling speed after solutioning and two-stage artificial ageing. For AlZn5Mg1 alloy the best results were obtained when hot water as cooling agent and two-stage artificial ageing were applied, i.e., tb_{22} state. This type of heat treatment allowed to obtain the following mechanical properties:

$$R_m = 373\ \text{MPa},\ R_{0,2} = 317\ \text{MPa},\ A_{10} = 14\ \%.$$

For AlZn5Mg2CrZr alloy, having applied the similar heat treatment tb_{22} , the following was obtained:

$$R_m = 446\ \text{MPa},\ R_{0,2} = 398\ \text{MPa},\ A_{10} = 7{,}2\ \%$$

and good corrosion and stress corrosion resistance under stationary corrosion potential.

Electrochemical polarization directed to anode resulted in relatively fast cracking of all tested alloys. Time-to-crack was diversified depending on type of an alloy and its heat treatment.

The increase of stress corrosion cracking proneness of AlZn5Mg1 and AlZn5Mg2CrZr alloys under anodic polarization was surely caused by the accelerated electrochemical corrosion. It was confirmed by metallographic investigations of these alloys in various heat treatment states and exposure to corrosion and stress corrosion under anodic polarization. Macro and microscopic investigations revealed distinct traces of layer corrosion (see Fig. 1b and 2). The mechanism of AlZn5Mg1 and AlZn5MgCrZr alloy deterioration under anodic polarization consisted then mainly in an accelerated dissolving of alloys along grain boundaries situated parallel to plate rolling plane.

The shortest time-to-crack under anodic polarization was shown by AlZn5Mg1 and AlZn5Mg2CrZr alloys in ta states (Tab. 3.), which were characterized by low layer corrosion resistance even under stationary potential. The alloys in tb_{22} or tb_{23} state were resistant against layer corrosion under stationary potential and showed higher stress corrosion resistance under anodic polarization (Tab. 3).

Fig. 2. demonstrates how strong is heat treatment influence on corrosion resistance where AlZn5Mg2CrZr (tb_{22}) alloy, in spite of being longer exposed, showed higher layer corrosion resistance in comparison with the alloy in ta heat treatment state.

Comparative investigation of AlMg4,5Mn (pgr) alloy under anodic polarization yielded a different character of cracks in the alloy when compared with the tested Al-Zn-Mg alloys. The alloy revealed low corrosion (see Tab. 5 and 6) and stress corrosion resistance (Tab. 3) under anodic potential. The alloy yielded uniform corrosion (Fig. 3) without any sign of layer corrosion. The alloy structure was characterized by uniform Al_3Mg_2 distribution in grains, without distinct clusters at their boundaries.

The cathodic polarization from about -50 mV to -200 mV in relation to stationary potential stopped layer corrosion in AlZn5Mg and AlZn5Mg2CrZr alloys in ta state. For AlZn5Mg2CrZr alloy in ta, tb_{22} and tb_{23} states a greater relative elongation was obtained after corrosion exposure under cathodic polarization (-50 mV and -200 mV) than that after exposure under stationary potential (see Tab. 6.). The investigations showed that protective potential was then placed, depending on an alloy type and its heat treatment, within -50 mV and -200 mV in relation to stationary potential with current density from 40 to 70 mA/m².

Under cathodic polarization of - 200 mV in relation to stationary potential of the tested alloys hydrogen micropores or microcracks were observed on specimens' surface (see Fig. 4.). The cathodic polarization rise to ΔU = -600 mV caused a drastic increase in number of hydrogen microcracks and micropores, which contributed to alloy cracking when exposed to stress corrosion or also to mechanical properties degradation after corrosion exposure.

The highest stress corrosion resistance under the cathodic polarization of -600 mV in relation to U_{st} was shown by AlMg4,5Mn (pgr) alloy. None of three tested specimens cracked in t = 1000 h exposure time (see Tab. 3.).

CONCLUSIONS

- AlZn5Mg1 and AlZnMg2CrZr alloys, naturally age hardened (ta), demonstrated low layer corrosion resistance. Artificial two-stage ageing after solutioning improved layer corrosion resistance and stress corrosion cracking resistance of the alloys.

- AlZn5Mg2CrZr (tb_{22}) alloy yielded good mechanical properties as well as good corrosion and stress corrosion cracking resistance under stationary potential and applied low cathodic polarization, due to its higher Mg content at Zn+Mg 7% level, added Zr, lower Mn content and application of an appropriate heat treatment.

- The tested Al-Zn-Mg alloys were cracking dependent on electrochemical polarization conditions, mainly due to electrochemical solubilization of the alloys along boundaries of their grains placed parallel to plate rolling surface, under anodic polarization, as well as due to creation of hydrogen pores and cracks under high cathodic polarization.

- AlMg4,5Mn alloy in pgr state was characterized by very good corrosion and stress corrosion cracking resistance under stationary corrosion potential and applied cathodic polarization; it had, however, low tensile strength in comparison with the AlZn5Mg1 (tb_{22}) and in particular the AlZn5Mg2CrZr (tb_{22}) alloy.

NOMENCLATURE

R_m - tensile strength
$R_{0,2}$ - yield point determined at 0,2 % offset
A_{10} - elongation of test specimen determined on $10xd_0$ gauge length
σ_0 - stress applied in stress corrosion tests
U_{st} - corrosion stationary potential

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Appraised by Konstanty Cudny, Prof., D.Sc., M.E.

Miscellanea

Jubilee Faculty of 1995

Tradition of the education of shipbuilding engineers at the Technical University of Gdańsk reaches back to the beginning of XXth century. The Shipbuilding Faculty established in 1904 has been always a hallmark of the university.

Poles also studied at this university in the period between the world wars, and it is from them that a group of engineers - pioneers of the Polish shipbuilding industry and education was formed.

It has been 50 years since the takeover of the University by Polish authorities; and this is why the Shipbuilding Faculty has celebrated also its jubilee.

About 150 students entered the first post-war year of education in shipbuilding, but in the 1970s, i.e. during the most dynamic development period of Polish shipbuilding industry, the number of the Faculty students reached 900 persons. In the past 50 years about 3500 engineers graduated from the Faculty. They work not only in Polish shipbuilding and shipping industries but also abroad.

The Jubilee Faculty which was in 1990 renamed „ Faculty of Ocean Engineering and Shipbuilding Technology", having suferred temporarily a drop in number of students down to 300, educates recently again over 800 students in M.Sc. and B.Sc. courses carried out by the following chairs:

- Chair of Ship Automation and Turbine Propulsion,
- Chair of Ship Hydromechanics,
- Chair of Marine Materials Engineering,
- Chair of Ship Structural Mechanics and Hull Structures,
- Chair of Ship Power Plants,
- Chair of Underwater Technology,
- Chair of Ship and Off-shore Units' Equipment,
- Chair of Ship and Off-shore Units' Technology,
  as well as:
- Ship and Off-shore Units' Design Department and
- Information Techniques Department.

Teaching and research staff of the Faculty consists of 5 professors, 7 contracting professors, 5 assistant professors and 39 lecturers, tutors and scientific research engineers.

A ceremonial open session of the Faculty Council was held on 27 May this year in which many Faculty's graduates of various yearly lists were present. The attached photo taken during this ceremony shows some prominent participants of it (from left): assist.prof. Jerzy Jamroż (Vice-Dean of the Faculty), prof. Józef Lisowski (Rector of Merchant Marine Academy in Gdynia), prof. Jerzy Doerffer, prof. Edmund Wittbrodt(Rector of the Technical University of Gdańsk), prof. Zygfryd Domachowski (Dean of the Faculty) and mr. Janusz Ziółkowski,M.Sc,(Vice-Dean of the Faculty).