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THE INFLUENCE OF HEAT TREATMENT ON STRESS CORROSION OF Al-Zn-Mg ALLOYS

ABSTRACT

The paper presents the results of tests on mechanical properties and corrosion resistance of the new alloy AlZn5Mg2CrZr (experimental industrial production) in various stages of heat treatment and of their comparison with the properties of AlZn5Mg1 alloy which is used in shipbuilding.

INTRODUCTION

Aluminium alloys used in the shipbuilding and in particular the high strength Al-Zn-Mg alloys of 7XXX series can be susceptible to stress corrosion cracking (SCC). SCC is the cause of premature failures in various strategically industries (eg. chemical, nuclear, aeronautical). While SCC is a well- documented [5], [8], [9] that can be easily identified and characterized at a microscopic level by a reduction of mechanical properties during static and dynamic tests. In the numerous studies reported in the literature two basic mechanisms have been proposed as a model of SCC: anodic dissolution and hydrogen embitterment. However, there is currently no consensus on the precise mechanism. Stress cracking is the type of attack in which the tensile stress and a corrosive environment coexist [6]. The tensile stress may be either applied or residual [3].

Aluminium alloys are widely used in the industry, among others in the shipbuilding as ship's hulls and equipment. The use of aluminium alloys for ships construction makes possible to reduce the ship's mass in comparison with that of steel ships by about 50%. In shipbuilding for many years the Al-Mg alloys containing apart from 2 to 6% of magnesium (Mg) small, amounts of manganese (Mn), titanium (Ti), chromium (Cr), zirconium (Zr), and vanadium (V) have been used [1], [4].

In the United States of America , Great Britain, Federal German Republic and in other countries, hulls of small ships and vessels of various types, mainly the alloys of group 5000 of Al-Mg-Mn type are used. At the time the best one are the alloys of the type 5456 (AlMg5) and 5083 (AlMg4,5Mn), with Mg contents 4÷5% and Mn= 0.4÷1%, called „sea alloys" or hydronalions [4].

In the Polish shipbuilding the AlMg5 (PA20) alloy was used for construction of fast ship's hulls and the AlMg3 alloy mainly for ships equipment. At present the hulls are made of AlMg4,5 Mn (PA13) alloy. The AlMg3, AlMg5 and AlMg4,5 Mn alloys in non-hardened state have low mechanical properties (Fig. 1). The improvement of mechanical properties of aluminium, with the simultaneous decrease of plastic properties, may be obtained by strain hardening. In the process of welding of hardened Al-Mg alloys there follows a softening in the region of the heat affected zone (HAZ) up to the state typical for the soft recrystallization annealing.

The ever increasing demand, with the aim of improving the factor $R_{0,2}/\rho$ of the modern construction materials for the hulls of contemporary ships, results in considerable interest in heat hardened alloys (supersaturated and aged) of the series 7XXX of the Al-Zn-Mg and Al-Zn-Mg-Cu alloys, with the ultimate tensile strength R_m>400 MPa .

For example, in Poland for the ship project 620 the AlZn5Mg1tb alloy was used for hulls construction and ship other parts. This alloy has better mechanical properties ($R_{0,2} \geq 260$ MPa, $R_m \geq 340$ MPa) than those of the commonly used in shipbuilding Al-Mg alloys (Fig. 1).

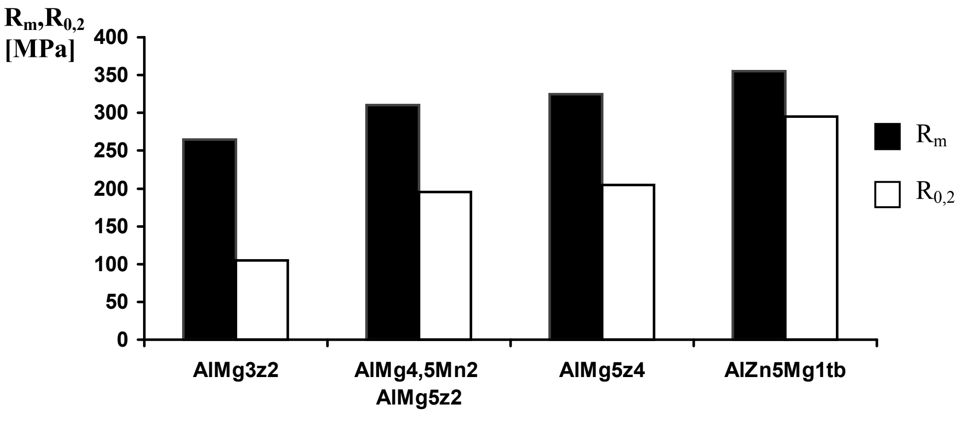


Fig. 1. Mechanical properties of the AlZn5Mg1 and Al-Mg alloys [4]

Introduction of the Al-Zn-Mg alloys containing Zn+Mg>6% has been limited for a long period because of their tendency to stress corrosion and layer corrosion (Fig. 2). In order to increase the stress corrosion resistance, in particular the layer corrosion of the alloys, the content of Mg was limited.

In order to control the stress and layer corrosion resistance of Al-Zn-Mg alloys, their structure can be modified by adding alloying elements and applied the optimal thermal process [4]. Required resistance to corrosion is achieved by adding Zr, as well as introducing an artificial two-stage ageing after supersaturated. Considerable improvements of the Al-Zn-Mg alloys designated for welded constructions were obtained abroad [4]. Much attention is also focused on the mechanisms of stress corrosion cracking [10].

The results of extensive experiments on Al-Zn-Mg alloys are described in [7]. Selected test results are also discussed in this paper as well as parameters of the new AlZn5Mg2CrZr alloy are presented and compared with those of the AlZn5Mg1 alloy [2], [7].

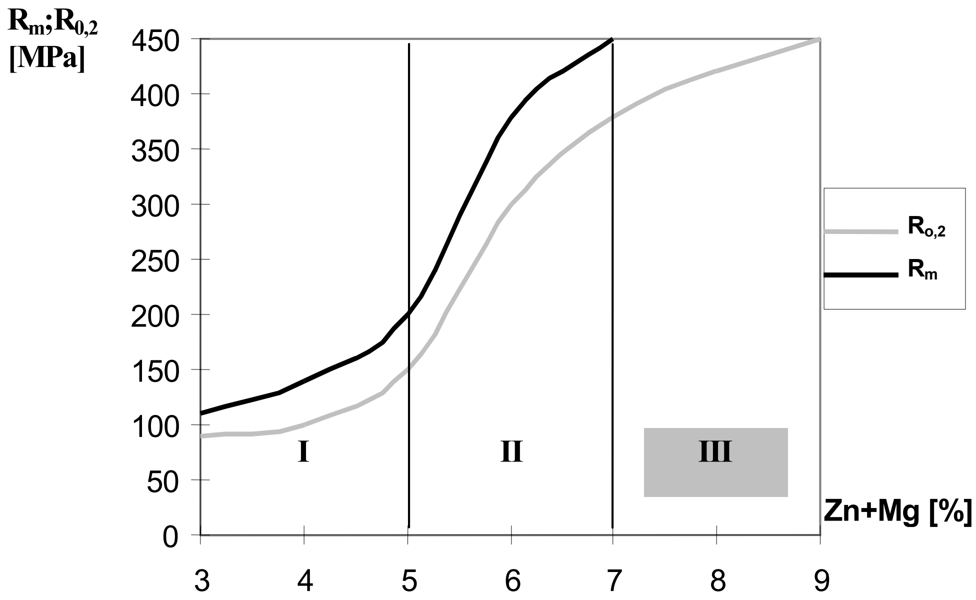


Fig. 2. The influence of content of Zn+Mg on mechanical properties and the tendency to stress corrosion of Al-Zn-Mg alloys containing Zn/Mg=2.5. The range I is not prone to stress corrosion, II may be prone to stress corrosion, III is prone to stress corrosion [4]

Their analysis allowed to choose the appropriate thermal process, which ensures a good resistance to stress corrosion of the AlZn5Mg2CrZr alloy, and increases the knowledge concerning the corrosion cracking of the above mentioned alloys.

THE RESULTS AND THEIR DISCUSSION

CHEMICAL COMPOSITION OF ALLOYS AND PARAMETERS OF THEIR HEAT TREATMENT

The methodology of the research, the shape and dimensions of samples used, satisfied the requirements of the Polish Standards (PS), Polish Register of Shipping (PRS) and the guiding lines of shipbuilding. The samples for the test were manufactured from sheets of new AlZn5Mg2CrZr alloy, from two special melts differing in their chemical composition. Chemical compositions of the AlZn5Mg2CrZr (alloy2) and AlZn5Mg1 (alloy1) alloys are given in Tab. 1.

Tab. 1. Chemical composition of AlZn5Mg2CrZr (alloy2) (report IMN-OML No 4550/91, 36 OML/91) and AlZn5Mg1 (alloy1) (ZN 81/MH-MN-190-06) alloys [6]

No of	chemical composition [%] AlZn5Mg2CrZr										No of batch
melt	Zn	Mg	Cr	Zr	Ti	Fe	Si	Cu	Mn	Ni	Al	and certificate
507	5.13	1.9	0.16	0.15	0.071	0.27	0.15	0.08	0.057	0.006	rest	1086
635	4.81	1.9	0.17	0.12	0.016	0.31	0.21	0.09	0.06	0.006	rest	1085
tb: supersaturation – heating to 480 °C for 50 min, cooling with hot water of min. 70 °C, natural aging 0 – 4 days at 20 °C, two-stage artificial aging 95 °C/8 h+150 °C/8 h											

chemical composition [%] AlZn5Mg1										No of batch
Mg	Mn	Ti	Zn	Cr	Si	Fe	Cu	Zr	Al	and certificate
1.25	0.18	0.034	5.3	0.14	0.16	0.32	0.05	0.04	rest	2945/485/4
tb: supersaturation – heating to 430 °C for 45 min, cooling with water min. 15 °C, natural aging 0 – 6 days at 20 °C, artificial aging 120 °C/96 h										

Basing on the research the parameters of heat treatment were chosen as shown in Tab. 2.

The alloy2 in the naturally hardened state (**ta** state) was obtained by supersaturation heat treatment in temperature of 450 °C for 1.5 h, followed by natural aging.

Tab. 2. The heat treatment parameters of alloy2 and alloy1

No	Alloy symbol	Melt	Parameters of heat treatment of Al-Zn-Mg alloys			State symbol
			supersaturation		aging type	
			temperature and time	cooling after supersaturation		
1	**AlZn5Mg2CrZr** AlZn5Mg1	507	**450 °C/1.5 h** 430 °C/45 min	**air 20 °C**	**natural** 100 days	**ta**
2	**AlZn5Mg2CrZr** AlZn5Mg1	507	**450 °C/1.5 h** 430 °C/45 min	**water 20 °C**	20 °C/6 days + aging: 95 °C/15 h+150 °C/10 h	$\mathbf{tb_{21}}$
3	**AlZn5Mg2CrZr** AlZn5Mg1	507	**450 °C/1.5 h** 430 °C/45 min	**air 20 °C**	20 °C/6 days + aging: 95 °C/15 h+150 °C/10 h	$\mathbf{tb_{23}}$
4	**AlZn5Mg2CrZr** AlZn5Mg1	507	**450 °C/1.5 h** 430 °C/45 min	**water 80 °C**	20 °C/6 days + aging: 95 °C/15 h+150 °C/10 h	$\mathbf{tb_{22}}$

The alloy2 in the artificially hardened state (**tb** state) was obtained by supersaturation heat treatment in temperature of 450 °C for 1.5 h, cooling in the open, and artificial two-stage ageing (95 ^{o}C/15 h + 150 ^{o}C/10 h). For the alloy1 a similar heat treatment was applied as for the alloy2, however the temperature and time of the treatment were different (450 ^{o}C/45 min).

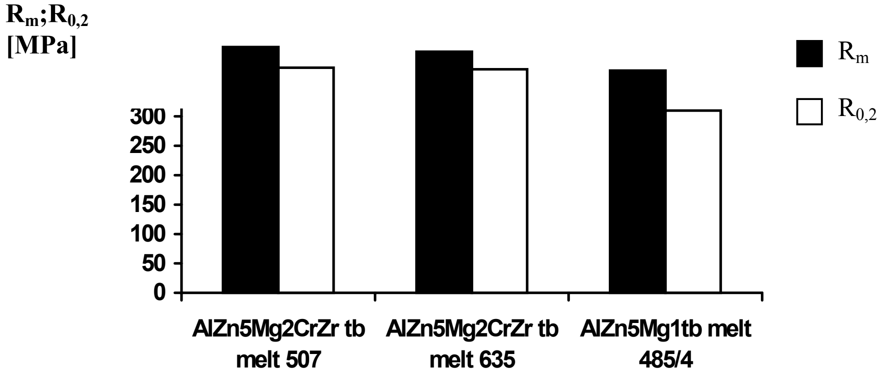
THE INFLUENCE OF CHEMICAL COMPOSITION AND HEAT TREATMENT ON MECHANICAL PROPERTIES OF THE ALZN5MG2CRZR ALLOY (ALLOY2)

The samples of the new alloy2 were made from two melts marked 507 and 635. The melts differed in chemical composition, and were subjected to heat treatment, as in Tab. 2.

The mechanical properties of alloy2 and alloy1 are presented in Fig. 3, from which it may be found that alloy2 exhibits higher R_m and $R_{0,2}$ in the range 20% – 25% in comparison with alloy1, and lower A_5 about 22%.

Basing on the tests results on alloy2 it has been concluded that the sheets 507 and 635 satisfied the requirements of the Polish Ships Register (PRS). They have shown also the highest strength properties among the aluminium alloys used in shipbuilding.

The differences in mechanical properties of the tested Al-Zn-Mg alloys are of course governed by a different chemical composition. Higher mechanical properties has the alloy2 (Fig. 3), due to greater content of Zn and Mg by approx. 0.5%, and higher content of copper (Cu) by approx. 0.01% in comparison with alloy1. Also significant influence on the mechanical properties have the Zr and Ti elements, whose percentage content in the alloy2 is twice as high as in alloy1. The content increase of Zn and Mg as the main elements resulted in better mechanical properties of the alloy2.



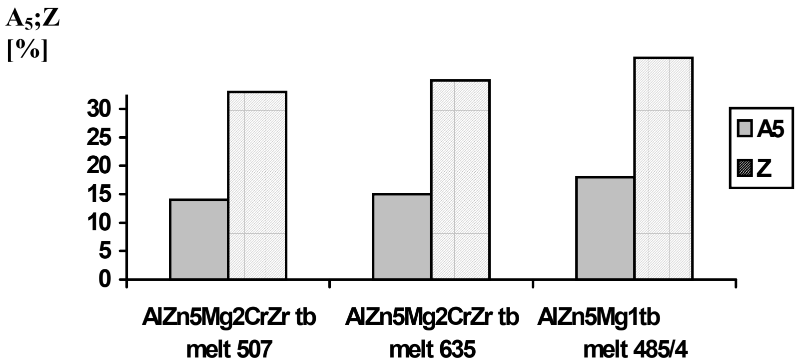


Fig. 3. Mechanical properties (the sheets of g = 12 mm thickness) of alloy2 melts 507,635 and of alloy1

THE INFLUENCE OF HEAT TREATMENT ON MECHANICAL PROPERTIES

The graphic interpretation of the test results is shown in Fig. 4.

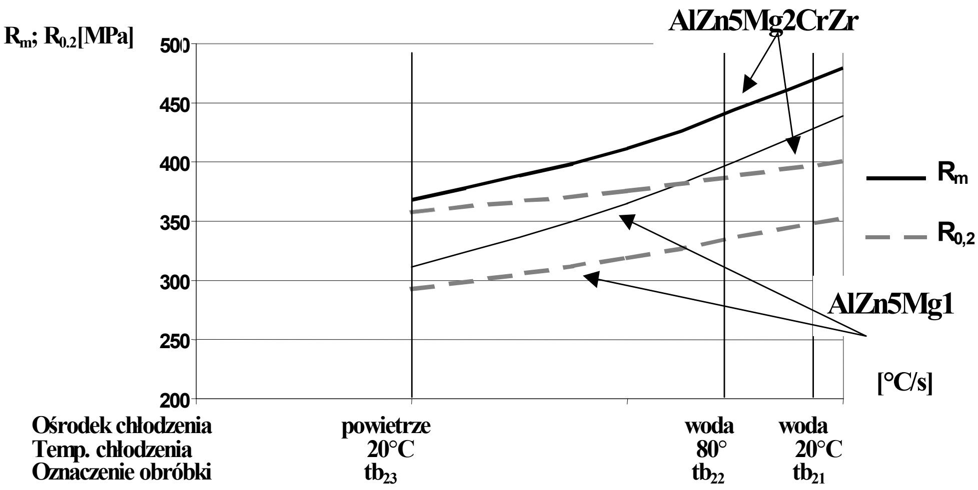


Fig. 4. The influence of the kind of heat treatment on mechanical properties of the Al-Zn-Mg alloys

Zn in the presence of Mg, as well as Cu, significantly improves the mechanical properties, in particular in the alloy2 subjected to heat treatment. The Ti and Zr, doped to the alloy, ensure the small of the grains, by the hindering of grain growth of the during the heat treatment. However, the increase of the content of Mg results in the creation of Mg2Si and Al3Mg2 in alloy2 stronger than in alloy1, which result in hayer hardness of the alloy2.

Fig. 4 indicates that the alloy2 in the **ta** state is characterised by a lower yield point $R_{0,2}$ than the alloy in **tb** state. The artificial ageing, after supersaturation results in the increase of $R_{0,2}$ in comparison with the natural aging. The alloy2 in the state **ta** reached $R_{0,2}$=258 [MPa], and in the state **tb$_{23}$** state- $R_{0,2}$=310 [MPa]. The similar effect of the heat treatment is shown by the alloy1.

In the **tb** state, the increase of cooling rate, after solution heat treatment, results in the improvement of the mechanical properties (R_m, $R_{0,2}$), together with insignificant changes of the plastic properties (A_5, Z). The alloy2 in **tb$_{22}$** state (cooling in hot water after supersaturation) is characterised by R_m=465[MPa]; $R_{0,2}$=418 [MPa], while in the **tb$_{23}$** state (cooling in open air after supersaturation) is $R_{m.}$=381 [MPa]; $R_{0,2}$=310 [MPa].

The alloy2 in the state **tb$_{22}$** shows in comparison with the **tb$_{23}$** state higher strength, but smaller plastic elongation of test samples. The results are, respectively: ΔR_m= +84 MPa; $\Delta R_{0,2}$= +107 MPa; ΔA_5 = -1.7 %. The comparison shows considerable influence of the cooling rate after supersaturation on mechanical properties of the alloy1, but not so strong as the alloy2.

The increase of cooling rate after supersaturation of the 2 and 1 alloys in the **tb** state results in the improvement of mechanical properties. It appeared that the alloy2 attained better mechanical properties than alloy1 (Fig. 4).

INFLUENCE OF CHEMICAL COMPOSITION ON THE RESISTANCE TO STRESS CORROSION OF THE ALZN5MG2CRZR ALLOY

The investigation of the alloy2 aimed at the ascertaining of its resistance to corrosion in sea water under simultaneous constant tensile load (σ_0). To achieve such an aim, tests on stress corrosion were carried out at σ_0=0.8$R_{0,2}$ in 3% NaCl water solution, and subsequently the influence of corrosion on the change of values R_m, A_5 before and after exposure was determined.

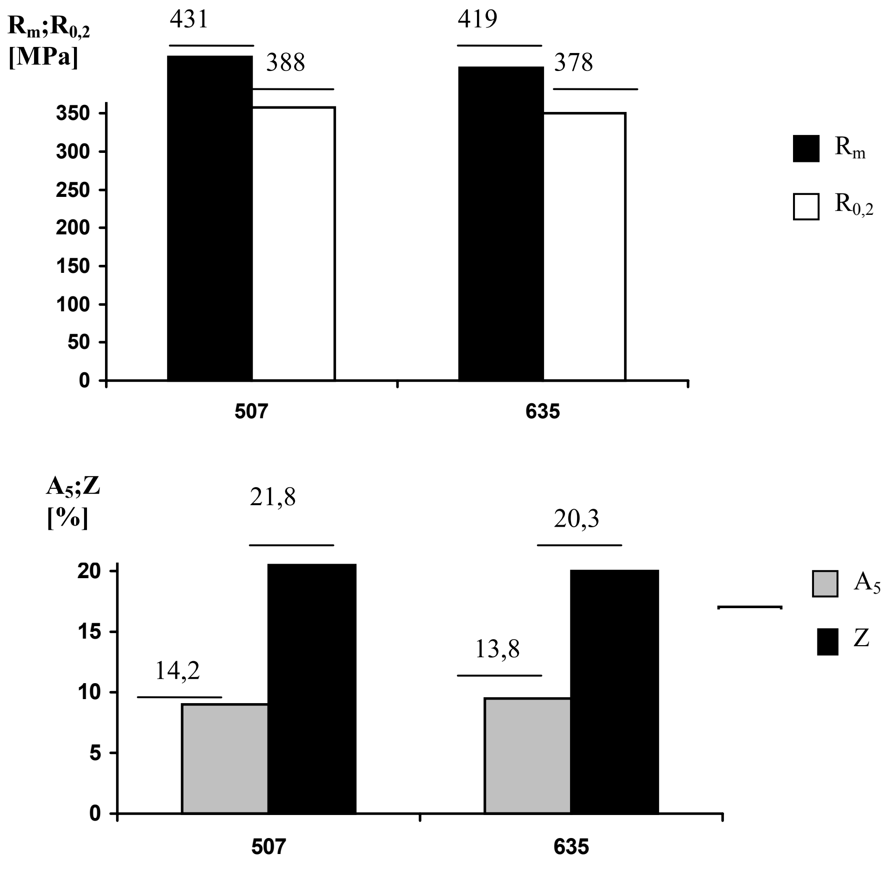


Fig. 5. Mechanical properties of samples of alloy2, before and after exposure to stress corrosion in 3% water solution of NaCl, in the time t=1500 h

None of the samples, made of sheets g=6 mm of alloy2, did break before planned end of corrosion exposure.

In Fig. 5 there are presented the mechanical properties of alloy2 before (horizontal lines) and after (piles) stress and corrosion exposure for 507 and 635 melts. The tests have shown that, as the result of the stress corrosion influence, the $R_{0,2}$ diminishes ($\Delta R_{0,2}$) by c. 6%, R_m diminishes (ΔR_m) by about 5%, and A_5 diminishes (ΔA_5) by 40%.

Similar tests were carried out for the alloy1, which showed that the stress corrosion resistance of alloy2 is relatively higher than that of the alloy1 despite larger content of Zn+Mg (>7%) and Mg (1.9%) in the former.

The increase of resistance to stress corrosion of alloy2 can be explained by the presence of such elements as Cr and Zr. What is not without significance is the process of heat treatment of the original sheets, where the increase of the temperature of solution heat treatment (480 °C) results in preventing the formation of the phase η (Al3Mg2) on the grain boundaries, whose presence stimulates the (especially dangerous) intercrystalline corrosion.

INFLUENCE OF HEAT TREATMENT ON THE STRESS CORROSION CRACKING

The test were to show what is the stress corrosion resistance of the AlZn5Mg2CrZr alloy in different stages of heat treatment. For this research sheets made of the 507 melt were chosen and the following procedures were applied:

- heat treatment of alloy2 due to the parameters given in Tab. 2 was carried out;
- mechanical properties of the tested alloys after heat treatment **ta**, $\mathbf{tb_{21}}$, $\mathbf{tb_{22}}$ and $\mathbf{tb_{23}}$ (Fig. 4) were determined;
- the corrosion exposure was carried out of the tested alloy in the above mentioned heat treatment states, by t=1500 h in 3% NaCl water solution at $\sigma_0=0.8R_{0,2}$;
- tensile testing of the samples was made, in order to determine the mechanical properties, after the exposure to stress corrosion (Fig. 6);
- level of stress corrosion resistance was estimated according to Eqs (2) and (3).

The same tests were carried out for the alloy1 for comparison.

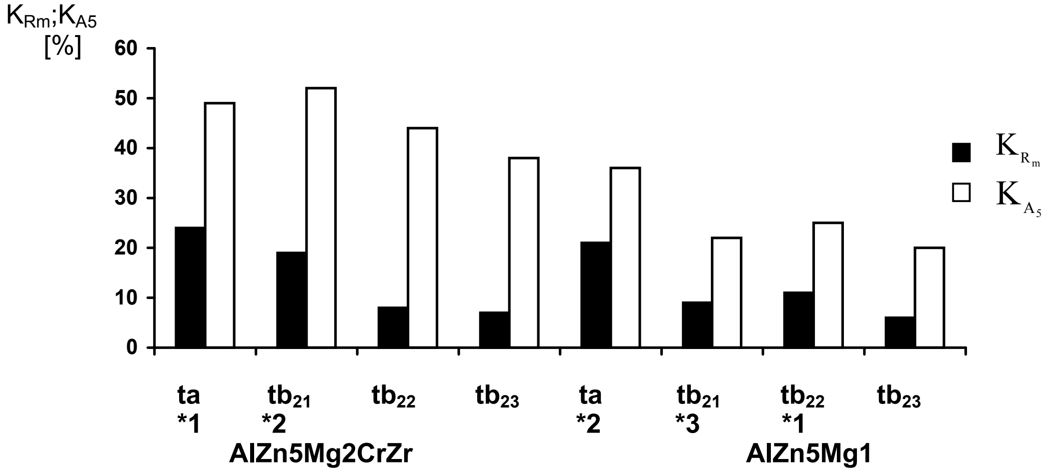


Fig. 6. Mean percentage of reduction of the tensile strength coefficients K_{R_m} and plasticity K_{A_5} of the AlZn5Mg2CrZr alloy and AlZn5Mg1 alloy, subjected to the heat treatment after the corrosion stress exposure in 3% NaCl water solution during 1500 h, where:
*X – number of samples, which were destroyed before 1500h of exposure

$$K_{R_m} = \frac{1}{n} \Sigma \frac{R_{mo} - R_{mk}}{R_{mo}} 100\,\%; \qquad (1)$$

$$K_{A_5} = \frac{1}{n} \Sigma \frac{A_0 - A_k}{A_0} 100\,\%, \qquad (2)$$

where: R_{mo} – ultimate tensile strength before corrosion exposure;
R_{mk} – ultimate tensile strength after corrosion exposure;
n – number of samples;
A_0 – plastic elongation of tested material before corrosion exposure;
A_k – plastic elongation of tested material after corrosion exposure;
K_{R_m} – mean coefficient percentage of the reduction of the ultimate tensile strength after corrosion exposure;
K_{A_5} – mean coefficient percentage of the reduction of the plastic elongation after corrosion exposure, determined on test samples of 5xg gauge length.

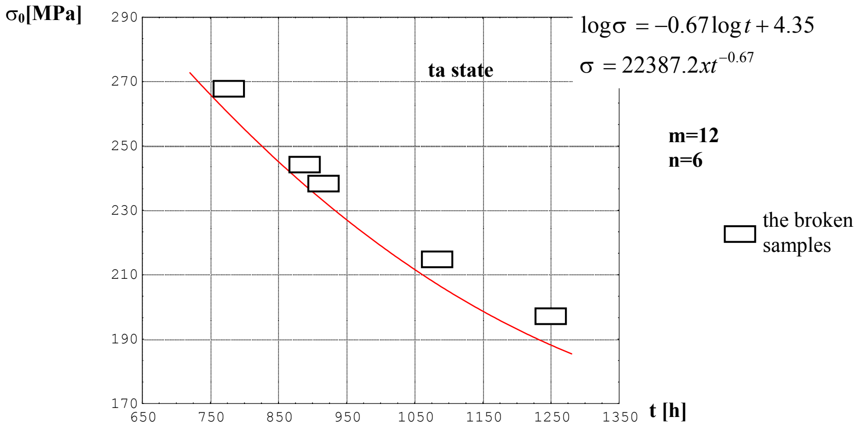
From among 45 samples of Al-Zn-Mg alloys treated thermally either to in the ta state or tb state the best stress corrosion resistance was exhibited by the alloy2 in the **tb$_{22}$** and **tb$_{23}$** states. The same alloy in the ta state and **tb$_{21}$** state was more prone to stress corrosion (increased layer corrosion was observed).

Comparison of mechanical properties of the both tested alloys after stress corrosion exposure allows to conclude that the alloy2 show better resistance to stress corrosion in each state of heat treatment.

Combined action of the corrosive surroundings and constant stress resulted in the following decrease of R_m and A_5 in the following states:

- **ta**: ΔR_m= -25%, ΔA_5= -50% (one sample broke before 1000 h);
- **tb$_{21}$**: ΔR_m= -22%, ΔA_5= -54% (two samples broke before the planned time of exposure);
- **tb$_{22}$**: ΔR_m= -10%, ΔA_5= -45%;
- **tb$_{23}$**: ΔR_m= -8%, ΔA_5=40%.

Influence of the stress level on the resistance to stress corrosion of the alloy2 is presented in Fig. 7.



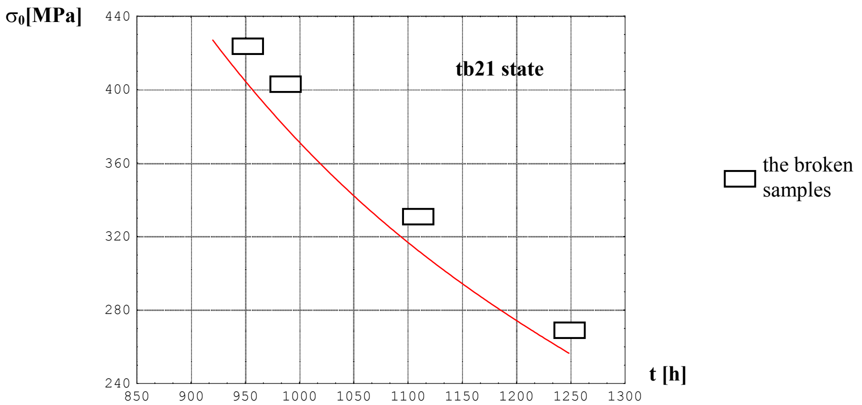


Fig. 7. The stress corrosion resistance of the samples of AlZn5Mg2CrZr alloy in the 3% water NaCl solution, in the heat treatment states **ta** and **tb$_{21}$**, where: m – number of samples, n – number of broken samples

The alloy2 in the **ta** state alloy has shown the lowest resistance to stress corrosion from among 12 tested samples, 6 were destroyed. Similarly, in the $\mathbf{tb_{21}}$ state, the samples of AlZn5Mg2CrZr alloy have shown low resistance to stress corrosion (12 tested samples, and 4 broke in the time shorter than 1500 h). Significant reduction of R_m and A_5 was observed in the **ta** state as a result of the exposure to stress corrosion, at different values of σ_0 (Fig. 8). With the initial load of $\sigma_0=R_{0,2}$ there followed a break of all the tested samples in time shorter than 1500 h.

The horizontal lines in Fig. 8 indicate the mechanical properties of AlZn5Mg2CrZr alloy before exposure to stress corrosion.

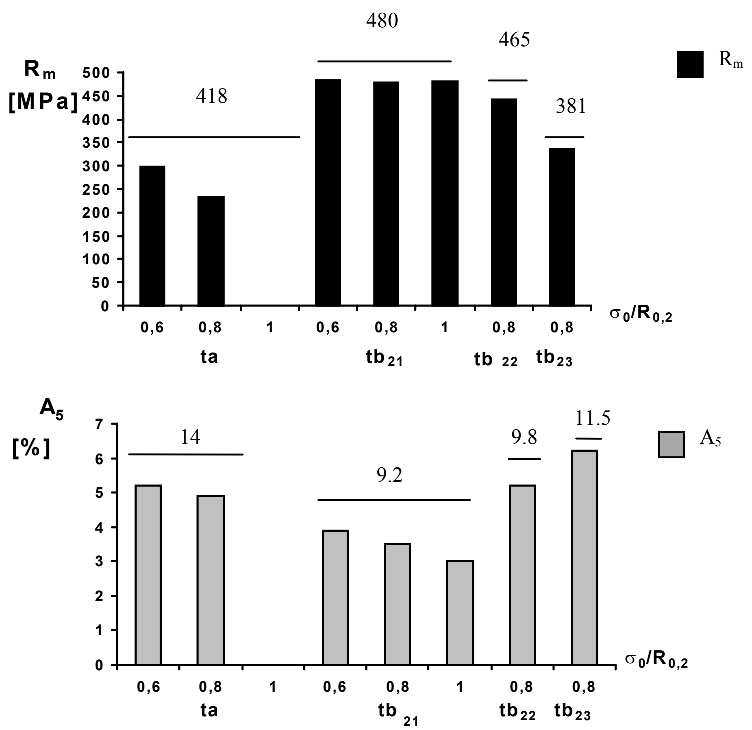


Fig. 8. Mechanical properties of the AlZn5Mg2CrZr alloy (g=12 mm, melt 507) by different heat treatment stages, after the exposure to stress corrosion, in the 3% NaCl water solution in 1000 h, at different levels of initial stress

In the ta state, the mechanical properties were lowered by ΔR_m = -50% and ΔA_5= -65%, in relation to the mechanical properties before the exposure to stress corrosion at σ_0=0.8 $R_{0,2}$. The differences in the mechanical properties, before and after stress corrosion exposure, become smaller with decreasing initial load, i.e. the resistance to stress corrosion of the AlZn5Mg2CrZr alloy in ta and $\mathbf{tb_{21}}$ state is better when the tensile load is smaller. In the $\mathbf{tb_{21}}$ state the samples possess better resistance to stress corrosion, than in the ta state. At the same time, lower A_5 (ΔA_5= -68%) and insignificantly lower ΔR_m (ΔR_m= -4%) were determined. The plastic properties in the $\mathbf{tb_{21}}$ state are sensitive to the change of the initial load. The increase of the load from σ_0=0.6 to 1.0 $R_{0,2}$ results in lowering of the plastic qualities from ΔA_5= -59% to -73% in relation to the plastic qualities before the exposure to stress corrosion.

In the $\mathbf{tb_{22}}$ and $\mathbf{tb_{23}}$ states, the resistance to stress corrosion is somewhat similar, but the best results were obtained by the AlZn5Mg2CrZr alloy after heat treatment $\mathbf{tb_{22}}$. The cooling in hot water ($\mathbf{tb_{22}}$) after supersaturation results in the improvement of stress corrosion resistance in relation to cold water cooling ($\mathbf{tb_{21}}$). For the tb23 state, the lowering of the cooling rate after supersaturation (air cooling), similarly as for the $\mathbf{tb_{22}}$ and $\mathbf{tb_{23}}$ states, improved the resistance of the AlZn5Mg2CrZr alloy to the stress corrosion.

CONCLUSIONS

1. The mechanical properties of Al-Zn-Mg alloys depend on the parameters of heat treatment.
2. As a result of the tests carried out, one can conclude that the AlZn5Mg2CrZr alloy, in **tb** state, has better resistance to stress corrosion than in **ta** state.
3. The analysis of results of the carried out tests of mechanical properties and corrosion resistance of the AlZn5Mg2CrZr alloy, in comparison with those of the AlZn5Mg1 alloy, show higher wear and corrosion resistance.

BIBLIOGRAPHY

[1] Bugłacki H., *Wpływ obróbki cieplnej oraz składu chemicznego spoiw na własności mechaniczne i korozję naprężeniową stopu AlZn5Mg1 w spawanych konstrukcjach okrętowych*, rozprawa doktorska, Politechnika Gdańska, Gdańsk 1981.

[2] Chrzanowski J., Zieliński A., Łabanowski J., Warmuzek D., *Effect of the retrogression and reaging (RRA) heat treatment on mechanical properties of the AlZn5Mg1 alloy,* Environmental degradation of engineering materials porc. of „EDEM-99", Jurata 1999, September, 20 – 21, pp. 157 – 162.

[3] *Corrosion and Corrosion Protection Handbook*, editor P. A. Schweitzer, 2nd ed., Marcel Dekker, New York 1988.

[4] Cudny K., *Technologia konstrukcji okrętowych ze stopów aluminium*, Wydawnictwo Politechniki Gdańskiej, Gdańsk 1996.

[5] Desjaridin D., Oltrain R., *Corrosion souse contrainte of Metals*, NACE, Huston, TX, 1990, p. 21

[6] Fontana M. G., *Corrosion Engineering*, 3rd ed., McGraw-Hill, New York 1988.

[7] Jurczak W., *Wpływ składu chemicznego i obróbki cieplnej na własności mechaniczne i odporność korozyjną stopów układu Al-Zn-Mg przeznaczonych na spawane konstrukcje okrętowe*, rozprawa doktorska, Politechnika Gdańska, Gdańsk 1998.

[8] Magnin T., [in.], *Strength of materials*, editors Oikawa and others, The Japan Institute of Metals, 1994, p. 25.

[9] Parking R. N., [in.], S. M. Bruemmer, E. I Meletis, R. H. Jonem, *Fundamental aspect of stress corrosion cracking,* TMS, Warrendle, PA, 1992, p. 3.

[10] Pickens J. R., Venables D., Green J. A. S, *Improved SCC resistance of Al-Zn-Mg alloys by control of Mg content in the bulk metal and in the oxide film,* Hydrogen Effects in Metals, editors J. M. Bernstein, A. W. Thompson, TMS, AIME, Warrendall, 1981.

STRESZCZENIE

W artykule przedstawiono wyniki badań własności mechanicznych i odporności na korozję naprężeniową nowego stopu AlZn5Mg2CrZr (próbny wytop przemysłowy) w różnych stanach obróbki cieplnej i porównano z własnościami stopu AlZn5Mg1 zastosowanego w budownictwie okrętowym.

Recenzent prof. dr hab. inż. Witold Precht