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STUDY OF THE CORROSION RESISTANCE OF SHIP ALUMINIUM ALLOYS

ABSTRACT

This article presents a summary of years of research of corrosion resistance and corrosive-stress marine materials and their joints. Aluminium alloys and marine steels including the austenitic have been the subject of research in terms of resistance of these materials for electrochemical corrosion in sea environment. Under certain conditions austenitic steels and aluminium alloys show low susceptibility to corrosion due to the protective oxide film which form itself spontaneously on their surfaces and which became a part of monitoring corrosion of these materials. Unfortunately, the real conditions of ship structures loads and the impact conditions of the sea environment show the need to search for the new materials or to modify those already used in order to increase their corrosive-stress resistance. The welded joints of the above mentioned materials were the special subject of corrosive research and nowadays their friction stir welding joints.

Modifying the structure of the origin materials by the alloyed elements, changing the parameters of the heat treatment, using the suitable protective paints or selection of the proper adhesives to connect these materials are the methods used in the following research to increase the corrosion resistance of the aluminium alloys. However, monitoring corrosion based on the patent US 2167 23 states a particular point of these research.

Key words:
corrosion resistance, aluminium alloys, ship constructions.

INTRODUCTION

For many years in the Department of Machine Construction at the Mechanical--Electrical Engineering Faculty of The Polish Naval Academy there have been conducted research over the construction materials used not only in the marine industry.

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These research touch the corrosion, impact and ballistic resistance supported by the computer simulation. For more than 40 years, these studies have been conducted in the Basics of Technique Laboratory — LPT (the current name), which is accredited by the PRS and the Minister of Defense in the field of 'security and defense'. Gradually, due to the financial resources, there was occurred the modernization of the technical and engineering facilities and also the research stands that have made it possible to expand the range of the research of the former Institute of Marine Engineering Basics. Particularly, the corrosive studies have become the basis of the mentioned development. There have been modernized and better equipped the standpoints for research of the galvanic corrosion with or without permanent or fatigue load in the sea water and the atmosphere. There also have been introduced the method of Electrochemical Impedance Spectroscopy (EIS) and its dynamic variant (DEIS) with the participation of Gdansk Technical University. In respect to that, here have been done 7 rationalizations applications while some new methods have been describe in the 3 patents.

Construction and operation of ship poses high requirements in the scope of using special engineering materials, which are in compliance with the Ship Construction Requirements. Those requirements concern appropriate level of durability properties, fatigue resistance as well as corrosion and local stresses, which intensify corrosion. In the ship-building industry, selected types of steel are used for the hull and superstructure construction. However, aluminium alloys are used more and more frequently in the ship-building industry. The properties of those alloys, such as a high indicator of relative durability R/ρ, no resistance to cold cracking in low temperatures, amagnetism, good corrosion resistance in a highly aggressive natural environment, which is the sea water and atmosphere, justify using aluminium alloys for construction of high-speed craft operating at a speed up to 50 knots. Ship constructions made of aluminium alloys are three times lighter (ρ_{Al} = 2,7÷2,93 g/cm^3) than those made of hull steel. It allows for increasing carrying capacity, stability and speed of the ship and decreasing its size and the mass of the hull, and finally — increasing power of its drive. In addition, it increases resistance to algae grow and allows for significant savings in the use of anti-corrosive layer, which decreases the number of dockings. Lighter construction of a ship with maintaining of constant stability conditions allows for loading of higher amount of fuel, drinking water, ammunition etc., which increases the autonomy of a ship on the sea, which is currently of high significance in the NATO structure outside of the Baltic Sea.

In addition, high-strength aluminium alloys show positive technical properties, such as good weldability or capability of spontaneous age-hardening of welded joints.

The use of aluminium alloy to construct the big superstructure of 620 design ship during the 80's was a challenge for the Polish ship-building industry. During the conditions of economic and technology difficulties of the shipyard and no qualified crew, a construction was made (of three storeys of L > 40 m length) of the ship superstructure, which showed many important problems during intensive operation. Those problems did not concern only intensive corrosion and corrosion cracking of this superstructure, but also low puncture resistance (ballistic resistance).

For many years the studies have been devoted to operating issues resulted from the use of high-strength aluminium (R_m ~ 500 MPa) in ship-building, which at first were aimed at solving the issue on demand, but then at monitoring and prevention of those negative phenomena.

Chemical and electrochemical corrosion is a common phenomenon, which occurs on surfaces of metallic construction materials in a natural manner and which causes their intensive degradation. The results of this influence on operating properties of materials may be only minimised by using available methods of passive and active anticorrosion prevention.

A SYNTHETIC DESCRIPTION OF ACHIEVEMENTS IN THE SCOPE OF FORECASTING CORROSION OF SHIP STRUCTURES MADE OF ALUMINIUM ALLOYS

The marine environment (the sea water and atmosphere) is the most aggressive natural environment, the concentration of which — mainly of sodium chloride ions in water — gives an electrochemical nature to the influence of corrosion on the surface of the material of an offshore structures (vessels, ports, shipyard infrastructure, drilling platforms and wind farms). The development of material engineering resulted in creation of *technical* groups of alloys (*which are relatively cheap, but which have electronegative potential in relation to the reference electrode*), which apart from good mechanical values also show good resistance to general corrosion thanks to spontaneous creation of a thin protective passive layer on their surfaces. One of these materials are high-strength weldable aluminium alloys of 7xxx series, which are a subject of intensive studies in many research centres throughout the world. High durability properties ($R_{p0,2}$ ~ 320 MPa or R_m ~ 500 MPa), good plasticity properties and controlled welding technology are the reasons why those materials will probably be widely used in the future, not only in the shipbuilding industry. Light weldable structures offer wide possibilities of use to ship constructors when there is a need to obtain a high indicator of the relative durability R/ρ, better stability or increasing autonomous character of vessels, the structures of which are made of those alloys. That is why the Polish Navy used 7020 alloy (described in a Polish standard as PA47tb) in the 80's to construct a big, 40 m high, three-storey superstructure of a ship to fight submarines. However, only 7xxx series alloys without Cu (its permitted content is up to 0,05%) were permitted to be used to build ships to be operated in the sea water environment. First issues related to the use of innovative alloys occurred already during the stage of ship construction, when the lack of accuracy of execution, to be more specific — non-compliance with the technology of straightening of sheets to be welded, resulted in cracking of binders, and in the further stages of operation — in intensive exfoliating corrosion, not only in the HAZ of welded joints, but also in other areas of planking. At the same time, at the Polish Naval Academy, intensive studies under the supervision of prof. K. Cudny were conducted, in which the on-going emerging operating were have been solved. The subject ship has been intensively operated for over 27 years, including operational activities of NATO. Apart from that, it is the real object of the studies, which allows applying the results of laboratory studies on a real structure.

Current studies resulted in the Naval Academy order for production in the Czechowice-Dziedzice foundry of at first samples of and then industrial sheets of a modified alloy, which is described in author's publications as 7020M. The modification was based on a change of the chemical composition and thermal treatment parameters. The total content of Zn + Mg > 7%, was increased, which increased not only the durability but also the effects of dispersion saturation, which on one hand, allows for spontaneous age-hardening of welded joints and on the other, results in intensive exfoliating corrosion. An addition of Cr and Zr as well as limitation of Mn in the host material of the 7020M alloy were not enough to eliminate corrosion and cracks. That is why another stage of the studies was to choose thermal treatment of the new 7020M alloy in order to minimize the corrosive processes — a new construction material.

That is why the tests were commenced tests on protective paints to passively protect this alloy, especially its welded joints. The appropriate choice of the chemical compound used for thermal welding of this alloy to prevent hot welding cracks were described, and there was also conducted research in order to find better joints, e.g. by friction welding — new methods of thermal bonding.

From the theory and practice it seems that corrosion processes in nature are unpreventable, but their destructive influence may be limited by using better technologies, which are a result of deeper understanding of corrosion processes gained by using new measurement and research techniques. Those modern techniques allow us to understand the dynamics of changes of electrochemical parameters of passive layers of construction materials, especially aluminium alloys during the process of their cracking as a result of simultaneous impact of mechanical and electrochemical factors. The cracking of the passive layer results in local corrosion, which by taking the form of pitting, crevice and intergranular corrosion is characterised by high rate of corrosion processes. The created protective layers and methods of their testing become a basis for monitoring of corrosion cracking of the aluminium alloys studies. 'On-line' supervision over corrosion processes, also known as corrosion diagnostics, prevents not only emergencies and expensive stoppages, but above all it increases operational safety of a given construction and of the crew, eliminating the risk of loss of human life or environmental contamination.

Existing studies on corrosion resistance, mainly stress corrosion, conducted at the Naval Academy (the subject studies of author's doctoral thesis) were based on defined standards, which describe the corrosion resistance on the basis of <u>the percentage of decreasing mechanical properties under the influence of a constant load and the marine environment</u>. Those methods and results of the studies could not constitute the methodology for dynamically changing processes of electrochemical corrosion, that is why there were used the latest research and measuring techniques in the studies. It demanded the modernization, and then development of research workstations for studying electrochemical corrosion in potentiostatic and dynamic conditions. Stress corrosion studies covered electrochemical measurements combined with mechanical tests and additional tests such as acoustic emission and microscopic examination. Apart from the SSRT (Slow Strain Rate Test) method, which covered the tensile force strength and the level of elongation in conditions of electrolyte environment influence, there also was conducted electrochemical measurement to obtain evaluation of the risk of cracking of passive layers and also to accelerate this process.

In the studies, there was used the measuring method in potentiostatic conditions and there was monitored the dynamics of changes in the current measured by the process of changes of the protective layer's changes. Those studies allowed me to determine characteristic potential related to the occurrence of the phenomenon of cracking of the passive layers in aluminium alloys. The basic electrochemical methods, which have been used in author's doctoral thesis (determination of protective potential) did not allow for a precise evaluation of the process of cracking of the passive layers in time, such as Electrochemical Impedance Spectroscopy or acoustic emission method. The method of electrochemical noise allows for a constant evaluation of electrochemical parameters, just like the usage of acoustic emission. Unfortunately, Fast Fourier transform used as a method of analysing the results of electrochemical noise measurement results in obtaining average results in a given time.

The development of mathematical methods of analysis allowed for a breakthrough in the electrochemical studies. By using non-stationary, time and frequency methods of analysis of signals for studying various non-linear processes, including linearization and electrochemical noise, it became possible to analyse electrochemical processes of passive layers destruction in conditions of simultaneous influence of an aggressive environment and tensile stresses. The use of a time and frequency analysis also made it possible to analyse impedance measurement in the domain of time, which was later used during pitting corrosion measurement and other dynamic electrochemical processes. This type of measurement methods allow for analysis of the mechanism of an electrochemical process in time, taking into consideration such quick processes as the phenomenon of physical properties changes in passive layers.

During corrosion tests, there was determined not only the level of stresses, which causes the cracking of the passive layer (there was indicated the mechanical properties of thin oxide layers) and initiation of corrosive process (a decrease in electrochemical potential), but also the level of corrosion risk by illustrating the level of oxide layer weakening (an analysis of electrochemical parameters of an equivalent circuit, especially: C — capacity of the layer, R_{ct} — charge transfer resistance). Author took part in potentiodynamic tests (DEIS — the dynamic version of EIS) and the participation in drawing up of conclusions of those studies allowed him to understand better electrochemical corrosion processes, which are a result of a tensile stress.

The innovative use of these methods in the study on the processes of passive layers cracking significantly expended the knowledge in that field. That is why the study of corrosion processes subject to operating load with the use of Electrochemical Impedance Spectroscopy and its dynamic version (DEIS) as well as creep measurement with the use of a fibre-optic cable at stress corrosion with constant tensile load became the basis for acquisition of two patents No. 212604 (author's participation 20%) and No. 216723 (100%).

Combining in the research activity the new research material, operational experience of the real object of tests, the effects of the internships and later cooperation with research centres (the Department of Light Metals at the Institute of Non-ferrous Metals and the Department of Electronic and Mechanical Engineering of the Gdansk University of Technology), as well as modernised laboratory facilities, there was designed and patented the Corrosion Diagnostics System for Ships (OSDK). First implementation studies during operation of the 'Kaszub' ship of the Republic of Poland showed that it is possible to measure and record the value of a local electrochemical potential, the value of which is instantaneous (below the deviation of –10 mV) in relation to the value of stationary potential means that there is a RISK of local corrosion or an INITIATION of corrosive processes long before any side effects of corrosion are visible. In addition, the value of measured electrochemical potential when compared to the results of laboratory tests allows for evaluation of local operating deformation (stress).

By using the physicochemical properties of aluminium alloys (it concerns also austenitic steel of which ships for the Polish Navy are made of), which when combined with oxygen or air create, in a natural way, a thin (up to 20 nm) passive Al_2O_3 oxide layer, the lower parts of the alloy are protected from further oxidation processes. That is why the mechanical and electrochemical properties of this layer allow for monitoring and assessment of corrosion RISK, INITIATION of corrosive processes, and in relation to laboratory tests — the approximate value of deformation/stress. This simple measuring system, correlated with the ship's time, makes it possible (on the basis of event records, the navigational and machine log books and hydraulic and meteorological conditions of sailing) to indicate those activities or phenomenon on the ship that result in the cracking of the passive oxide layer. In addition, this way of on-line monitoring of E_{st} 'on-line' communicated with the alarm system (implementation, for example electrical issues results in an acoustic signal or visual or information sent on the mobile phone of the operator), which allows for immediate reaction of the crew to the risk and undertaking preventive measures (i.e. decreasing the speed in relation to the current meteorological conditions) or makes the crew conscious that tasks undertaken result in the local stress of the structure (e.g. using the on-board armament). The patented OSDK system may prevent all existing negative and expensive experiences in the operation of light offshore structure, and become a system supervising the work of new ship structures in the future (the hull and the structure will be made of austenitic steel).

In the selected publications there were described issues related to operation of ship structures made of aluminium alloys in relation to corrosion resistance:

– studies on properties of the host material (including the new 7020M alloy);
– studies on properties of welded joints, on the choice of adhesives and technology of welding;
– choosing a set of protective paints and parameters of sacrificial (passive) and cathode (active) protection with the determination of electrochemical potentials;

– implementation of the *friction stir welding* method to join aluminium alloys and their testing in the scope of corrosion, including tests in electrochemical conditions, as an alternative to welded joint;
– implementation of modern methods for testing corrosion resistance in the marine environment (EIS and DEIS), using physicochemical properties of aluminium alloys, which create a thin protective layer;
– laboratory tests on corrosion resistance of alloys and their joints (welded an bounded) by indicating the level of risk and initiation of corrosion (the passive layer is weakened at first, and then it breaks) in mechanical and electrochemical studies with the use of AC and DC methods;
– monitoring of the state of electrochemical corrosion risk posed to a ship structure (weakening of the passive layer, which was proved by a decrease in the Est potential to the E_{kor} value below about –10 mV and an increase in the capacity of the layer and a decrease in the resistance of the charge transfer) or indication of initiation of a corrosion process (breaking of the passive layer and a radical decrease in the Est electrochemical potential to below about 200 mV).

TESTS RESULTS

A synthetic description of achievements in the scope of forecasting corrosion resistance of ship structures made of aluminium alloys in operating conditions

The effect of heat treatment on the structure and corrosion resistance of Al-Zn-Mg alloys [10]

Scientific problems solved

The chosen parameters of thermal treatment of high-strength 7020 and 7020M (a new alloy) alloys increased their mechanical properties and corrosion resistance in the marine environment (electrochemical properties under load). Saturation of 7020M alloy at the temperature of 480°C / 1.5 hour, and then cooling it down in hot water of 80°C temperature as well as a two-stage artificial ageing: 95°C / 15 hours + 150°C / 10 hours(designated as tb_{22} according to PN-EN-T651) allowed for acquiring optimal mechanical and corrosion properties of those alloys. It is an alternative for the currently used 7020 alloy and it will probably be used in ship-building in the future.

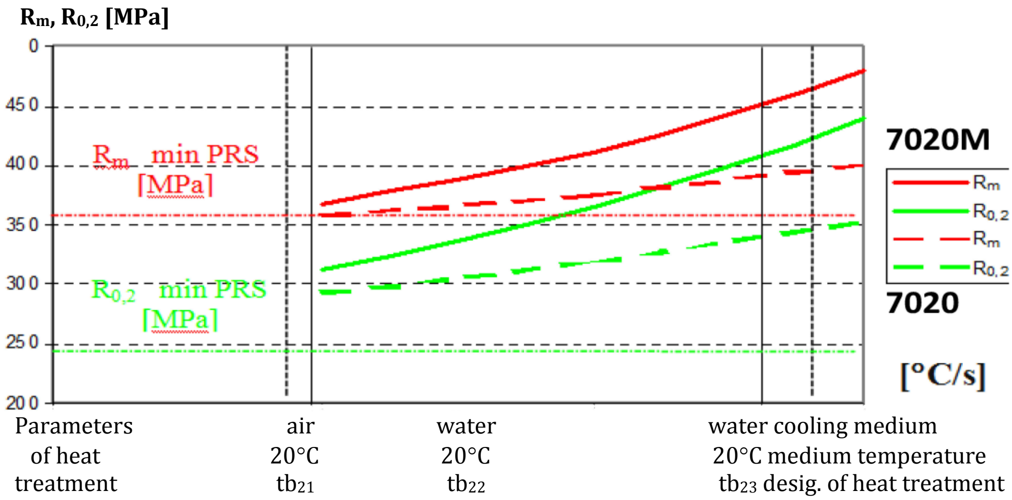


Fig. 1. The influence of the type of thermal treatment on mechanical properties of the 7xxx series alloys [10]

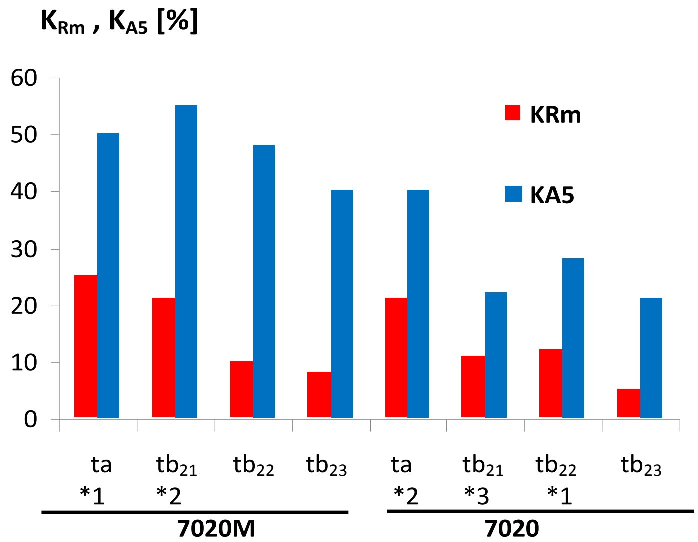


Fig. 2. Mean percentage of reduction of the tensile strength R_m (designated as K_{Rm}) and plasticity A_5 (designated as K_{A5}) of 7020M and 7020 alloys subjected to the heat treatment after exposure to corrosion stress in a 3% water solution of NaCl during the time of 1500 h [10]

**X — number of samples, which underwent cracking prior to elapse of expected time of test — t = 1500 h.*

The rate of cooling done after the saturation has a decisive influence on the mechanical properties and corrosion resistance of the alloys studied. Increasing the rate of cooling after saturation (water of T = 20°C) increases the mechanical properties (fig. 1), but also decreases resistance to corrosion, especially stress corrosion. tb22 thermal treatment parameters (T651) allow for obtaining optimal properties of the alloys (average mechanical properties and plasticity and good corrosion resistance) while using them to construct structures used in the marine environment.

The influence of chemical composition on mechanical properties and resistance to stress corrosion in welded joints from sheets of Al-Zn-Mg alloys [11]

Scientific problems solved

The article describes the influence of the process of welding of high-strength aluminium alloys shielded by inert gas protection on mechanical properties of the host material and the welded joint that was created. The treatment marked as to (T4), which corresponds to the process of welding (heating above the saturation temperature and slow cooling down in ambient temperature), results in the worst mechanical properties among all thermal treatments applied, despite spontaneous age hardening which is characteristic for Al-Zn-Mg alloys (7xxx series). It required an appropriate choice of the welding technology and the chemical composition of binders, other than SPA20 (SAlMg5Ti), which is traditionally used in shipyards to increase corrosion resistance. The corrosion resistance of welded joints of the 7xxx series for SPA20 is illustrated in figure 3a. 7020M alloy obtained better resistance than 7020 alloy which was used to build the ship thanks to its higher content of Zr and Cr and limited content of Mn.

Improvements for the technology of welding high-strength aluminium alloys was presented. The technology covers the choice of welding parameters, compliance with the technology of preparing edges of 7xxx series alloys and the appropriate choice of the chemical composition of the binder (fig. 3b) used for multilayer welding. Technical recommendations requires the use of binder SAlMg5Zn2Zr0,4 which will provide good durability of the weld. Its exterior layers, which get in contact with sea water, should be made using binder SAlMg5Zr0,4. There was proposed avoiding heating of sheets directly before welding, which is frequently done in shipyards, but as a results it is an increased vulnerability of welds to cracks.

In contrast to welding of 5xxx series alloys, when welding 7xxx series alloys, it is inappropriate to use a binder of a chemical composition that is similar to the composition of the host material due to its tendency to get hot welding cracks and its high corrosion vulnerability.

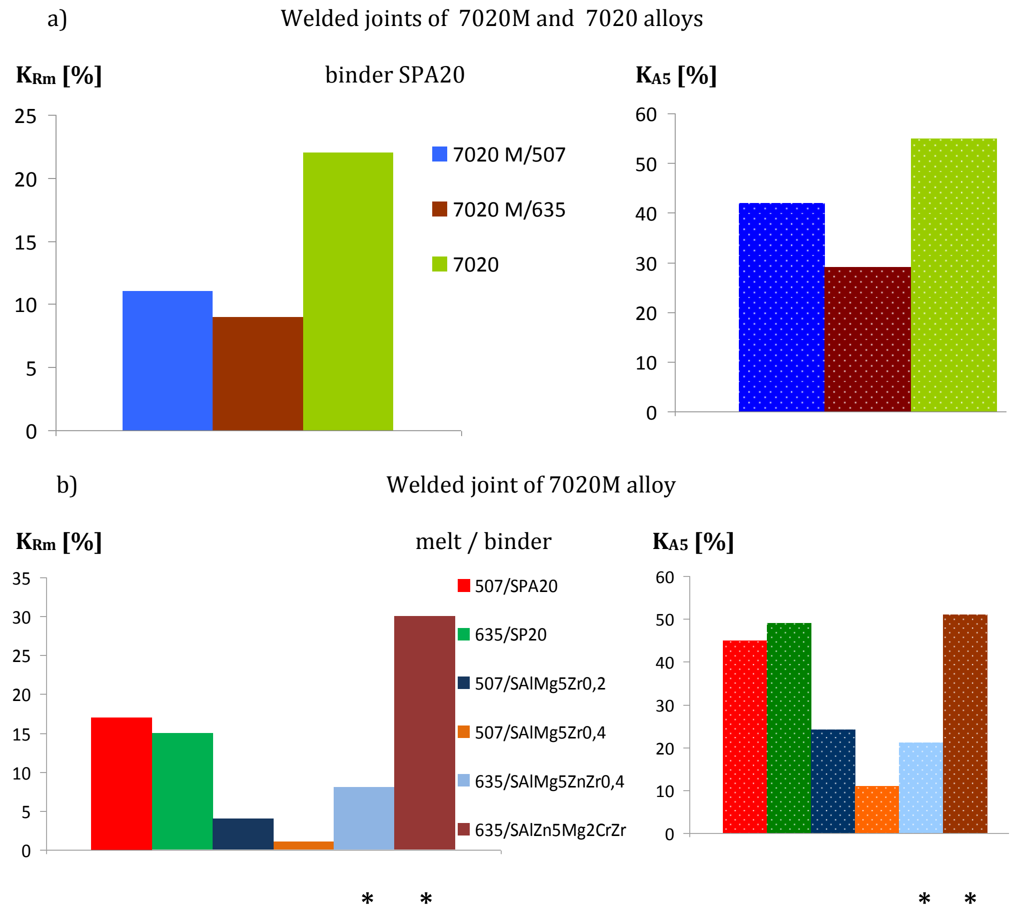


Fig. 3. Mean average decrease in K_{Rm} tensile strength and K_{A5} plasticity after corrosion and stress exposure of a welded joint of 7020M alloy tb (T4) and 7020 alloy tb (T4):
a) 7020M and 7020 alloys, the SPA20 binder, welded with the use of the TIG method, automatically;
b) 7020M alloy for heats 507 and 635 of g = 12 mm joined by: SPA20, SAlMg5Zr0,2, SAlMg5Zr0,4, SAlMg5Zn2Zr0,4, SAlMg5Mg2CrZr binders, using the TIG method, manually [11]

* *3 out of 5 exposed samples cracked.*

In case of multilayer welding (three and more layers) of 7xxx series alloys, due to durability of the welded joints, a binder containing Zn should be used, while external layers of the weld (runs) which get in contact with sea water and air should be welded with a binder containing Zr, and which does not contain Zn.

Welding of the alloys studies using the TIG method automatically minimises the welding time. Thanks to that a welded joint that is created has a narrower heat affected zone (HAZ) than a joint welded manually using the TIG method. HAZ constitutes the weakest link, which is corrosive, that is why the durability is better in case of joints welded automatically, using the TIG method.

Stress corrosion cracking of aluminium alloys intended for ships constructions — transport safety considerations [7]

Scientific problems solved

Stationary potential was determined for the host material of 7xxx series and binders used for its welding at modernised workstations. Stress corrosion for welded joints of 7020 and 7020M alloys created was determined. Chemical compositions of joints in the multilayer welding of 7020M alloy were indicated, introducing improvements to the shipbuilding technology of welding.

The value of E_{st} — electrochemical stationary potential (marked as EPS in the article) of the alloys studied and binders used for different reference electrodes was established — see table 1.

When choosing appropriate chemical composition of binders used for welding 7xxx alloys, it is necessary not only to aim to obtain good mechanical values but also to apply the rule that the potential of a binder may not be lower than the potential of the alloy welded. Otherwise, the density of corrosion current will increase, the intensity of corrosion of the weld will also increase (the weld constitutes an anode in the electrochemical corrosion cell) and durability of such joints will be minimal. The saturated calomel electrode (according to the standard) used in the study could not be used in experimental tests on a real object, that is why there was a need to use an alternative electrode. Due to the size and simplicity of its creation — an Ag/AgCl electrode was used, which allowed us to apply the laboratory's measurement system to the operated ship structure. The results of the studies constituted basic data for the Corrosion Diagnostic System for Ships which was created as a methods of monitoring corrosion processes during operation.

Those results were used in practice for active and passive protection (known as combined protection). They constitute a criterion for choosing parameters for cathodic protection and materials for anodic constructions made of the alloys studied and their welded joints.

Table 1. Chosen results of Est tests for the new 7020M alloy and its welded joints [7]

No.	Host material/heat	Sheet thickness [mm]		E_{st} **Electrochemical stationary potential of the alloy**	
				In case of a silver/silver chloride electrode [mV]	In case of a saturated calomel electrode [mV]
1	7020M in **507**	6		−0,824	−0,535
2		12			
3	7020M in **635**	6		−0,855	−0,559
4		12			
No.	**Binder material**	**Binder designation**		**Stationary potential of the alloy**	
				In case of a calomel electrode [mV]	In case of a silver/silver chloride electrode [mV]
1	SAlMg5Ti0,1	SPA20		−0,569	−0,419
2	SAlMg5ZnZr0,2	CZ		−0,812	−0,667
3	SAlMg5Zr0,4	Z		−0,515	−0,398
4	SAlMg5Zn2Zr0,4	SZ		−0,690	−0,488
5	SAlZn5Mg2CrZr	R		−0,855	−0,559
No.	**Welded joint of 7020M alloy with a binder**	**Sheet thickness [mm]**	**Method of welding**	**Stationary potential of the welded joint***	
				In case of a calomel electrode [mV]	In case of a silver/silver chloride electrode [mV]
1	SPA20	12	TIG manually	−0,801	−0,674
2	CZ	12		−0,810	−0,831
3	Z	12		−0,808	−0,681
4	SZ	12		−0,824	−0,830
5	R			−0,835	−0,520

** The differences of measured electrochemical potential included in table 1 for the welded joints, were the effect of weld heat into the heat affect zone (HAZ). Potential measurement was made at 1% and 3% aqueous NaCl solution. Additionally, different joints used for welding (ident. CZ, Z, SZ and R) necessitated the use of such welding parameters, that differentiated HAZ structure, and also its electrochemical potential value.*

Effectiveness of corrosion protection of the welded joints of AlZn5Mg2CrZr naval alloy [6]

Scientific problems solved

Even though the chemical composition of binders used to weld new 7020M (AlZn5Mg2CrZr) alloy (art. 2) was modified (five types of binders were studied) and due to no technical possibilities of heat treatment big aluminium structures in order to increase corrosion resistance of welded joints (the developed thermal treatment marked as tb22 — art. 1), stress corrosion resistance was not satisfying. Due to that reason, in this article passive anti-corrosion methods were used. A technology of anti-corrosive protection was proposed based on using two sets of protective paints for the welded ship structure made of aluminium. In cooperation with the research laboratory of the 'Olivia' centre in Gdansk, paints of modified chemical composition based on epoxy resin were provided to protect welded joints of 7xxx series. This set of protective paints on the basis of epoxy resin constitutes a better anticorrosion protection for the new 7020M alloy than polyvinyl sets used widely in the shipbuilding industry (fig. 4).

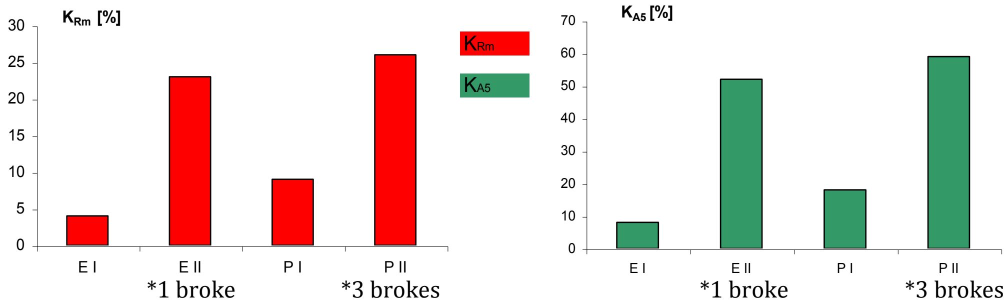


Fig. 4. Mean average decrease in K_{Rm} tensile strength and K_{A5} plasticity after corrosion and stress exposure of welded joints of 7020M alloys made with the use of SPA20 and TIG automatically, protected with a set of epoxy paints /E/ and polyvinyl paints /P/, where: I — $\sigma_0 = 0{,}8R_{0,2}$ during the time of t = 1500 hours, II — $\sigma_0 = 0{,}6R_{0,2}$ during the time of t = 3000 hours [6]

* *X — number of samples which were destroyed before the planned time of the study elapsed.*

Friction welding as a new method of joining aluminium alloys used in marine transport [8]

Scientific problems solved

The results of studies on welded and friction welded joints of 7020 alloys and its modification described as 7020M were presented. Joints of aluminium alloys made with the use of friction welding methods allow for obtaining better mechanical properties and better corrosion resistance in the marine environment in comparison to welded joints made using the TIG method (tab. 2). It is a result of a significant decrease in heat affected zone, which weakens welded joints of aluminium alloys created with the use of friction stir welding (fig. 5). There are no special requirements for preparing the edges of sheets joined by friction welding in contrast to welding (chamfering and cleaning before welding), it facilitates the process and significantly decreases the costs of joining high-strength aluminium alloys used in ships.

Table 2. A compilation of corrosion and stress corrosion resistance properties of welded joints made with the use of the TIG method and friction stir welded alloys of 7xxx series [8]

Alloy/joint	Static mechanical properties $10^{-3}s^{-1}$			Corrosion resistance in			
				marine atmosphere		sea water	
				Corrosion in salt chamber		Stress corrosion t = 1500h at $\sigma_o = 0,8\ R_{0,2}$	
	R_m	$R_{0,2}$	A_5	K_{Rm}	K_{A5}	K_{Rm}	K_{A5}
	MPa	MPa	%	%	%	%	%
Host material							
7020M T6xx	443	397	9,8	4,7	36	9,3	45,7
7020 T6xx	372	317	16	4,4	30	6,4	27,2
TIG welded joint with the use of SPA20 binder							
7020M	380	341	4,8	2,3	9	13,3	16,3
7020	355	304	17	3,8	12	16,3	18,2
Friction Stir Welded Joint — FSW							
7020M	422	398	8,1	1,8	6,3	6,5	8,4
7020	360	280	12	2,4	9,3	7,8	10,3

Joining high-strength aluminium alloys used in ships by friction welding is a promising alternative for arc welding of those alloys shielded by inert gases.

a) b)

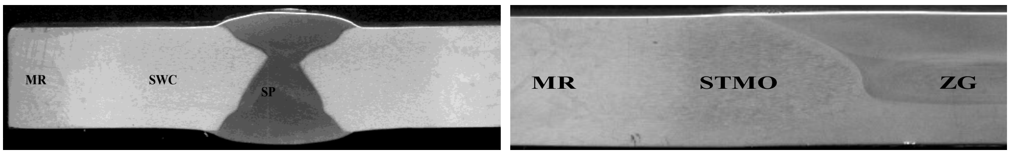


Fig. 5. A cross-section of a welded joint: a) bonded joint; b) 7020 alloy with visible elements of the binder — SP (the weld — ZG), the heat affected zone — SWC (the thermo-mechanical treatment zone — STMO) and the area of the host material — MR (joined) [8]

During the studies of mechanical properties, it was established that cracking of FSW joints takes places outside the STMO zone, so it can be concluded that those joints have similar properties to the host material. At the same time, they show better stress corrosion resistance than welded joint of the aluminium alloys studied.

Influence of friction stir welding on corrosion properties of AW-7020M alloy in seawater [5]

Scientific problems solved

For the tested FSW joints, a balanced model in a form of an equivalent electric circuit was chosen. The results of the EIS test are presented in a form of parameters which characterise the corrosion process as well as in a graphic form in Nyquist diagrams with adjusted theoretical curve (fig. 6) and in detail in table 3.

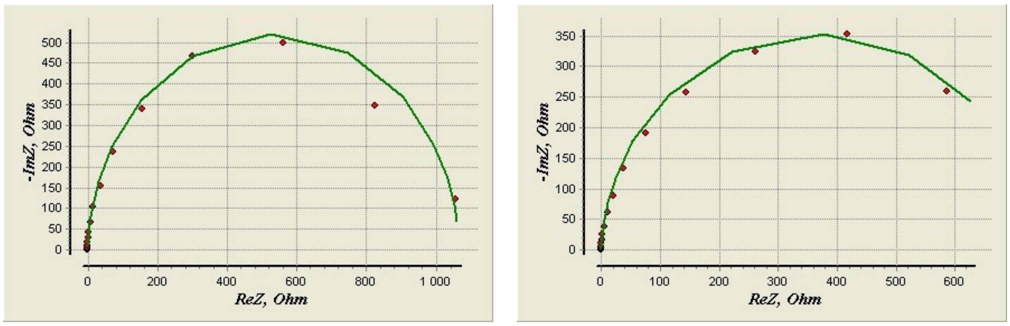


Fig. 6. Impedance spectrum of 7020M alloy (a) and its FSW joint (b) [5]

Table 3. Parameters of the equivalent electric circuit of the corrosive 7020M alloys and joints welded with the use of the FSW method [5]

Sample	R_s [Ω· cm²]	Standard deviation (Sd)	R_{ct} [Ω· cm²]	Standard deviation (Sd)	Z_{CPEdl} [Ω· cm²]			
					Y_{dl}	Sd	n_{dl}	Sd
Host material	0,28	0,07	1241,4	283,5	8,6	3,0	0,99	0,01
FSW	0,45	0,18	614,7	125,4	10,6	4,3	0,98	0,01

R_s — shows the resistance of the electrolyte that constitutes the corrosive environment,
R_{ct} —characterises the resistance of charge transfer over the border of metal/electrolyte phases,
Z_{PEdl} — capacity of the double layer which occurs in the phases studied: Y_{dl} — admittance,
n_{dl} — a component of capacitive impedance.

The analysis of data obtained in impedance spectroscopy studies showed that the sample welded using the FSW method shows lower electrochemical resistance in comparison to the sample of 7020M host material.

A factor that is the most important from the view of electrochemical corrosion — R_{ct} (resistance of charge transfer) achieves values, which are two times higher in case of the material host sample than in case of the FSW welded sample. It means that the host material has significantly higher resistance to stress corrosion in the marine environment.

Other parameters, which describe electrochemical corrosion resistance are at a similar level. An analysis of the component of the n_{dl} exponent of capacitive impedance of the equivalent circuit indicates good pitting corrosion resistance of both the 7020M host material and its joints welded using the FSW method.

Advanced electrochemical studies of those joints on the basis of EIS and DEIS (Dynamic Electrochemical Impedance Spectroscopy) in marine environments of different parameters as well as in a salt spray under operating load were conducted in research project No. 4824/B/T02/2010/38, which was under author's supervision.

The effect of tensile stresses on aluminium passive layer durability [2]

Scientific problems solved

In the pilot studies, EIS and DEIS techniques (research methods) were used to describe the protective properties of the passive oxide layer of 1050 alloy (a technical aluminium alloy) under tensile stress and at a changeable value of anodic polarisation (mechanical and electrochemical studies) in relation to the stationary potential amounting to +50 mV, +100 mV and +150 mV in the anodic direction in relation to Est.

On the basis of registered impedance diagrams (fig. 7a), an equivalent electric circuit was chosen (fig. 7c), the electrical parameters of which describe protective values of the layer. It is the capacity — C and resistance — R of the passive layer that characterise the efficiency of the protective activity of the passive layer under the influence of deformation (as a result of operating stresses). An increase in the capacity — C, and decrease in R and the level of those changes means that the protective capability is decreasing(risk of corrosion) or non-existent (initiation of corrosion). The course of those changes is shown in figure 7b, d.

Figure 7 shows a chosen impedance diagram for 1050 aluminium, which shows that in case of deformation within the range of ε = 0,08–0,09, the layer is weakened (risk of corrosion), and after exceeding ε = 0,1 the layer breaks and corrosive current increases (fig. 8) due to the decrease in R, which is accompanied by an increase in the capacity of the oxide layer, the value of which depends on the level of anodic polarisation (initiation of corrosion). As figure 7b shows, in case of anodic polarisation of +50 mV (marked as □ –0,650 V), the level of the decrease in the total value of R proceeds significantly earlier than for other values of polarisation, which is accompanied also by an increase in corrosion current intensity.

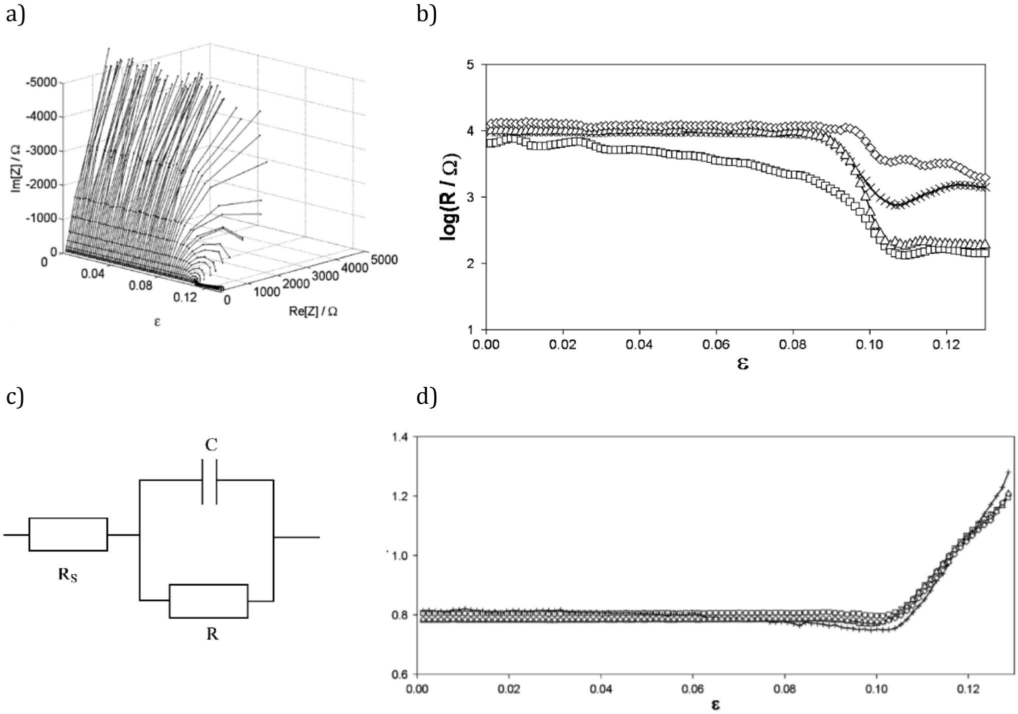


Fig. 7: a) Impedance diagrams for anodic polarisation of 1050 aluminium at E_{st} +50 mV (E_{st} = 700 mV) on the basis of which an equivalent diagram was chosen; b)electrochemical parameters of the equivalent diagram at increasing tensile stress, at polarisation –*E* = □ –0, 650 V, △ –0,700 V, X –0,750V, ◇ –0,807 V [2]

RS — electrolyte resistance, C — capacity of the oxide layer, R — total resistance of the oxide layer and resistance of the charge transfer.

The use of the aforementioned research techniques together with direct current studies allowed for determination of conditions of cracking of the passive layer in relation to the levels of deformation (stress). An evaluation of the influence of anodic polarisation and its value on the conditions of breaking of the oxide layer was conducted. It was concluded that the research techniques used to determine the conditions of breaking of the oxide layer of the aluminium studied are useful. It was unambiguously determined that the level of tensile stress at which the oxide layer cracks does not change with an increase in anodic polarisation. At the same time, it was established that for the value of +50 mV and above of anodic polarisation, there is a corrosive process, which occurs after the passive layer cracks. That suggests that in non-polarised conditions the protective layer would crack as well, but it would not lead to secondary corrosive processes.

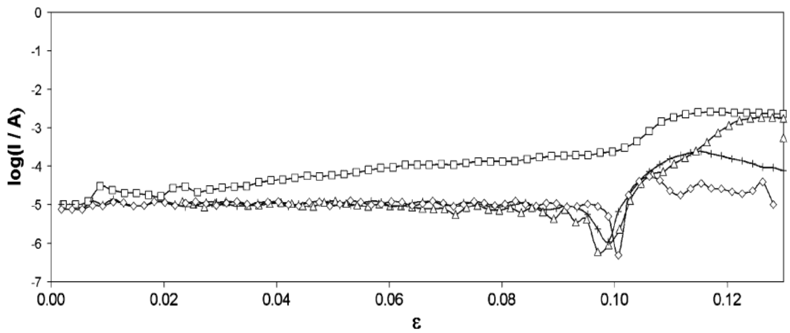


Fig. 8. The profile of the DC corrosive current of 1050 alloy at increasing deformation ε at anodic polarisation of E = □ –0, 650 V, △ –0,700 V, X –0,750 V, ◇ –0,807 V [2]

It was concluded that the level of anodic polarisation does not influence the mechanical properties of the aluminium studied.

For the aluminium studied, the valueε = 0,1 corresponds to stress of σ = 143 MPa, which is close to the limit strength, that is why the cracking of the layer takes place far from the operating field.

Passive layer cracking studies performed on A95056 aluminium alloy by means of dynamic electrochemical impedance spectroscopy and acoustic emission [1]

Scientific problems solved

Electrochemical techniques were introduced to mechanical properties and corrosion resistance tests. The process of cracking of the passive layer of the 5056 alloy in variable conditions of tensile stresses and anodic polarisation was measured with the use of the DEIS technique and acoustic emission (AE) as a comparative method. In the laboratory conditions, operation of an aluminium structure (a sample) subjected to loads (tensile lodes) at changeable parameters of active protection (anodic polarisation) were simulated by determining corrosion process parameters with the use of high-tech EIS measurement methods.

Electrochemical and mechanical causes of initiation of corrosion under load were established. A threshold (critical) tensile value (σ ≈ 150 MPa) was indicated, at which the process of cracking of the passive layers (the beginning of corrosion) was registered in relation to the aluminium alloy studied (fig. 9a). The process studied was accompanied by a significant increase in the acoustic activity (acoustic pressure A_0/A, fig. 9g).

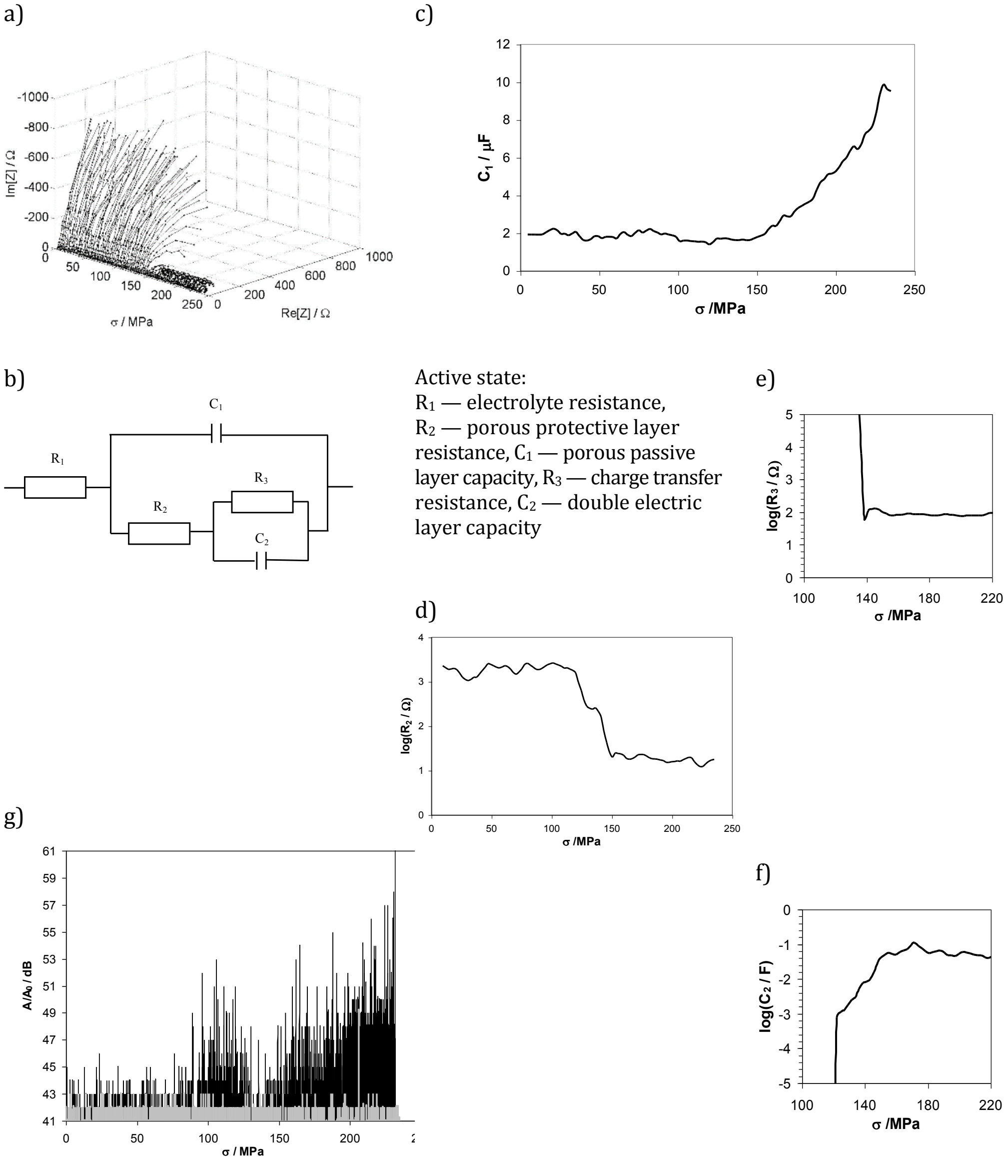


Fig. 9. An overview of mechanical and electrochemical parameters and acoustic emission of thin Al_2O_3 passive oxide layer of 5056 alloy used in ship-building [1]

On the basis of Z impedance of the passive layer (fig. 9a), for the determined value of E_{st} electrochemical potential (the basic registered diagnostic parameter) and for various states of σ stress, electrical parameters of the chosen equivalent circuit were measured. The increasing capacity of the passive layer (fig. 9c) at decreasing R_2 resistance (fig. 9d) with simultaneous decrease in the charge transfer resistance R_2 (fig. 9e) and increasing corrosion current show the state of corrosion risk for a defined stress state σ (deformation ε).Those phenomena are accompanied by an increase in the electronegative direction of electrochemical potential to the E_{kor} value of about –10 mV. Another stage at increasing stress is cracking of amorphous interior Al_2O_3 layer and a radical increase in the potential in the electronegative direction up to the E_{kor} value of about –200 mV.

Those laboratory tests constitute a basis for corrosion monitoring of a structure, during which registration of the E_{st} value 'on-line' in reference to the aforementioned parameters, allows the crew to be informed about the risk of corrosion or initiation of corrosion (depending on the state of the oxide layer and its protective performance).

After we confirmed the usefulness of AC and DC electrochemical techniques used to determine corrosion resistance of aluminium by monitoring passive characteristic of the oxide layer, we conducted studies on alloy of 5xxx series (5056) used for shipbuilding. In addition to mechanical and electrochemical studies and in order to verify and confirm cracking of the protective layer, acoustic emission (AE) tests were used. It was evaluated, which of the techniques used is better for capturing the moment of cracking of the passive layer. The tests showed that AE shows earlier symptoms, even before electrochemical symptoms occur, which is shown by an increase in corrosion current being a result of a decrease in resistance, which was determined by the DC method (fig. 10a). Changes of parameters of the passive layer at the moment of cracking of the layer are more visible when measured by DEIS than by the DC method. However, a higher signal of cracking comes from the DEIS method, the DC increases at a higher stress because the initiation of corrosion effects, such as a change of capacity resistance, occurs at lower stresses as the process is related to the passive layer. It means that DEIS is a better technique of monitoring properties of the passive protective layer than DC because it allows for earlier capturing of that moment (fig. 10b).

a) b)

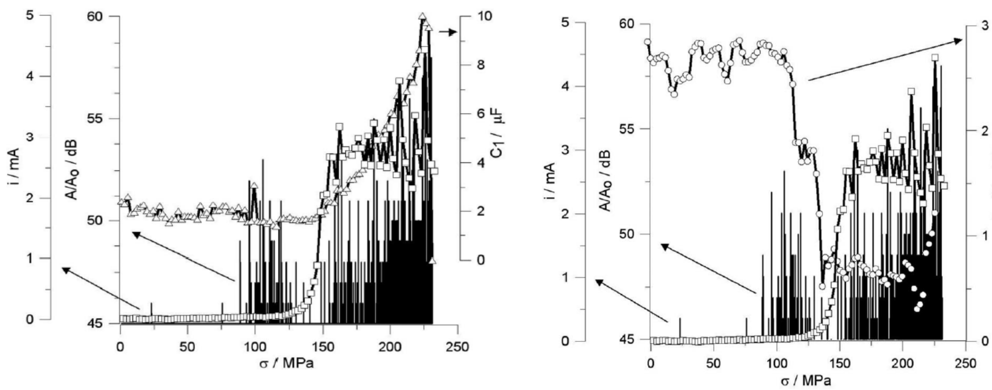


Fig. 10. Mechanical and electrochemical parameters of the oxide layer of 5056 alloy for anodic potential of E_{st} = –700 mV measured with the use of: a) DEIS (with C_1), b) DC (with R_2), where: A/A_0 — an acoustic event [dB], △ — capacity of the oxide layer C_1 [µF], ○ — resistance of the oxide layer R_2 [Ω], □ — intensity of corrosive current and [mA] [1]

Comparative electrochemical analysis of the passive layer cracking process on aluminium alloys performed by means of DC and AC techniques [3]

Scientific problems solved

The process of cracking of the passive layer of 1050, 5052, 5056 and 7020 aluminium alloys in variable conditions of tensile stresses and anodic polarisation was studied with the use of the DC technique, the alternating current technique (EIS) in its dynamic version (DEIS) and the acoustic emission(AE) technique as a comparative method. The conducted studies showed an advantage of the AC technique and acoustic emission over the classical DC method. The exact level of stress indicated by AC and DC methods did not exceed 10%, but it was higher for the high-strength 7020 alloy than for 5xxx series alloy. Figure 11 shows registered levels of deformation (stress) of the passive layer using DC and DEIS methods. The AE technique confirmed the moment of cracking for alloys studied that the DEIS method indicated. In operation of ship structures made of 7xxx alloys, monitoring of properties of the passive oxide layer with the use of AC methods should be used as its cracking occurs in the scope of elastic deflections. In case of 5xxx series alloys and technical alloy of aluminium, cracking of passive layers occurs in the scope of plasticity (apart from the operating scope), that is why monitoring is necessary.

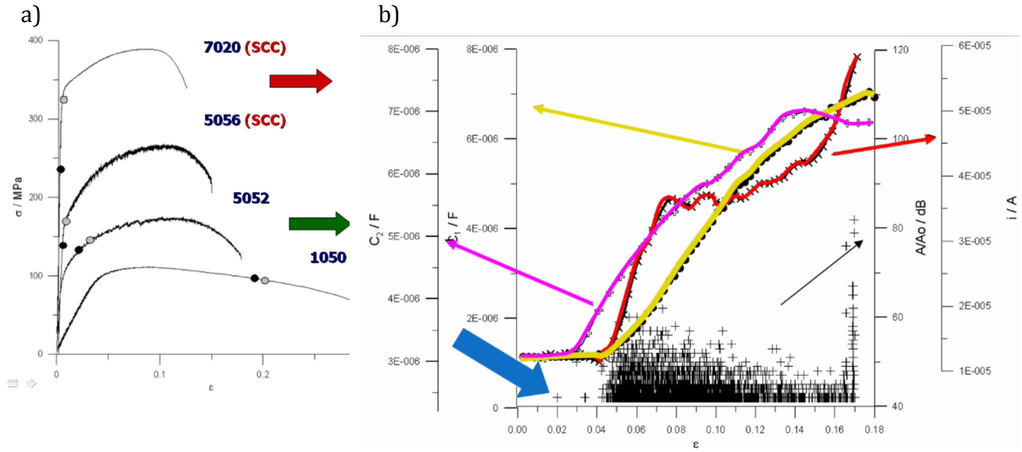


Fig. 11. Diagrams: a) static tensile load of aluminium alloys studied with determination of levels of cracking of the oxide layer with the use of • DC and • DEIS methods; b) a chart presenting an amplitude of acoustic emission, C_1 and C_2 parameters of the impedance spectrum (for the equivalent circuit — fig. 10b), direct current in the deflection function, registered during measurements of the polarisation potential E = –0.460 V of the chosen 5052 alloy, × — direct current, • — C_2 capacity, ✠ — C_1 capacity, + — acoustic events [3]

The higher the resistance of aluminium alloys (higher content of Mg and Zn), the more the level of stress of cracking of the oxide layer decreases to the upper limits of elasticity for 5xxx series alloys. For 7020 alloy, cracking of the protective layer takes place in the operating (resilience) scope which was proved by studies conducted on the superstructure of ship 620. In order to prevent any breakdowns of this kind of construction made of those alloys, corrosion monitoring should be used.

On the basis of studies conducted, the following conclusions can be made:

1. Under a static tensile load of the aluminium alloys studied in the electrolyte environment, a phenomenon of cracking of the passive layer occurs.
2. Detection of this phenomenon may be achieved on the basis of an acoustic emission activity analysis, an analysis of each parameter of the equivalent electric circuit with the use of DEIS method and classical methods, such as potentiostatic measurement.
3. The obtained critical value of stress, at which cracking of the passive layer is observed, varies depending on the fact if the analysis was made on the basis of AC or DC tests.
4. A detailed analysis indicates that the critical value of deformation obtained from DC tests is misleading as it was determined on the basis of an analysis of already occurring corrosive process of aluminium, and not on the basis of evaluation of electrical parameters of the passive layer (EIS studies).

5. A discrepancy between critical values of deformations may lead to significant errors when it comes to the evaluation of stability of the passive layer of aluminium alloys affected by an electrochemical and a mechanical factor.
6. The biggest discrepancies in the results obtained by both methods occur when cracking of the layer occurs in the region of elastic deflections.
7. The content of alloying elements has an influence on the conditions of cracking of passive layers. When magnesium content is high and when there is zinc in the structure of the alloy, cracking of the passive layer (on the basis of DEIS tests) occurs in the zone below the resilience limit, which is of high practical meaning in forecasting of corrosion cracking of aluminium alloys.

On the basis of the studies conducted, it may be concluded that a more detailed explanation of the process of cracking of passive layers of aluminium alloys under the influence of tensile forces must be sought in the structure of alloys studied.

Damage and corrosion diagnostics of welded light alloys ship constructions [4]

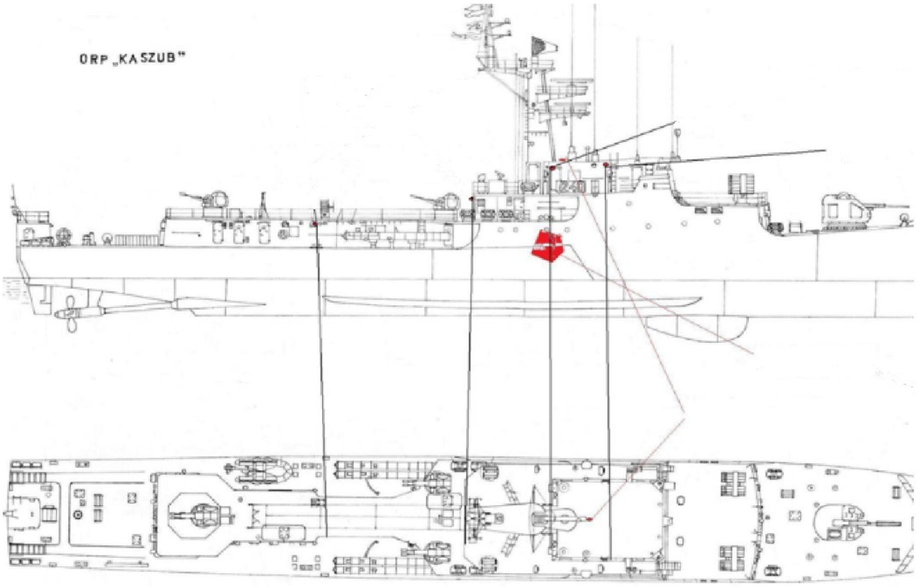
Scientific problems solved

Using patent No. 216723 (W. Jurczak's authorship), recording of electrochemical potential and deformations on chosen areas of each board of superstructure (4 areas — fig. 12a) during a stay on the sea (fig. 13) was conducted. A simplified laboratory measuring system (with Ag/AgCl electrode), which was previously used, was used to determine the potential and characteristic stress level, which cause cracking of the passive layer on a real object (fig. 12b). In the same picture adhesions of tensometers (preceded by indication of the direction of the biggest deflections with the use of a tensometric rosette), which allow for recording of deformations correlated in time with potential measurement, are shown. Those operating tests were conducted for alloy 7020, from which the superstructure of ship 620 is made of.

Oscillations of the corrosive potential in relation to the stationary potential indicated to and confirmed the cracking of the layer of that alloy in the operating (resilience) scope. The timely correlation of electrochemical potential records with deflection recorded and log book entries (machine, navigation and event log books) allow for determination of reasons of cracking of the protective oxide layer, as a result of which degrading corrosive processes are initiated.

The designed system of signalling (acoustic, visual or text messages) is started at the moment when the value of recorded potential exceeds –200 mV below the stationary potential and informs the crew about corrosion initiation (long before its destructive effects are visible), and allows for indication of causes of this state of affairs, that is hydro-meteorological conditions, the speed of the ship or tasks performed on the ship, e.g. artillery shooting.

a)



b)

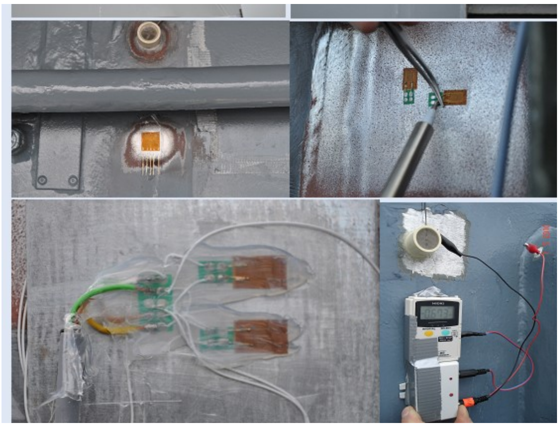


Fig. 12. Localisation of chosen measurement areas on the superstructure of ship 620 (a) on which the system of potential measuring was installed (Data Logger) and cRIO deformation with NI 9107 module (b) [4]

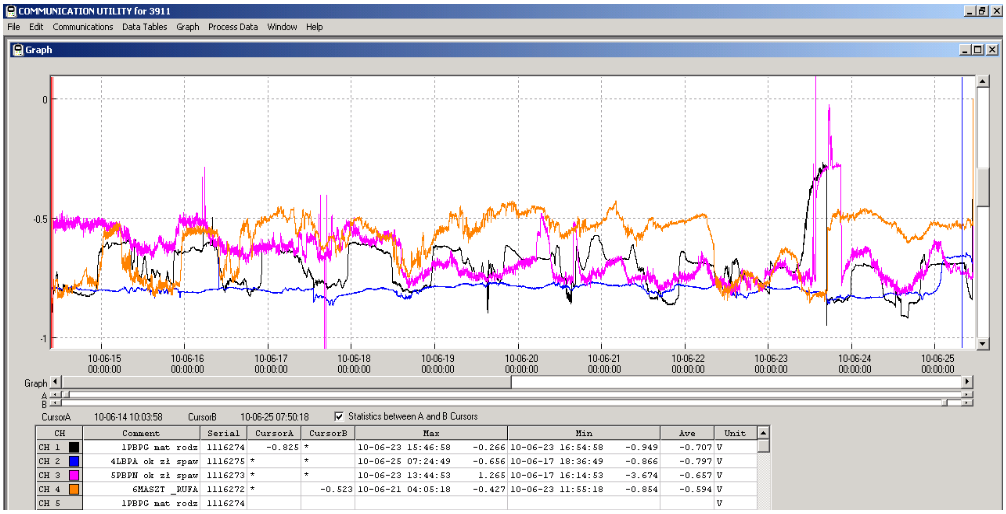


Fig. 13. Diagrams of recorded electrochemical stationary potential measured on areas 1–4 of the superstructure of ship 620, starboard (PBP): main board (G), navigation board (N-mast), artillery (A), signal (S) for 10 days of the ship's stay on the sea with a stop in a port [4]

Changes of potential and deformations registered in this way are subject to an exhaustive evaluation with a simultaneous analysis of event records, which allow for indication of factors causing cracking of protective layers on chosen area of the superstructure. Those results of studies, which have not been published yet, are shown in a report on research project No. 4824/B/T02/2010/38,which is under author's supervision.

Simulating the Impact of exposure to corrosive medium on cracking initiation in AW7020M alloy specimens [9]

Scientific problems solved

Influence of operation of ship 620's superstructure of many years on degradation of durability properties of 7020 alloys, from which it was made of was determined. Samples of 7020 alloy were collected from the hull of the superstructure and Young's modulus was indicated (in various directions in relation to the direction of rolling). Afterwards, they were compared to properties of this alloy, which was not exposed to corrosion. The same test was conducted for an alternative, new alloy — 7020M. Load was stimulated in conditions of static tensile test of the normalised samples of the alloys studies, on which the minimal depth of corrosion pits were marked, which have influence on their durability. The assessed evaluation of the depth of corrosion pits indicated in the studies allows for indication of those corrosive damages to operators that must be immediately regenerated (for example by hardfacing) to prevent local cracks of the structure's hull.

SUMMARY

A practical effect of many-years studies was development and implementation of the Corrosion Diagnostics System for Ships (OSDK), which provides a possibility of detecting corrosion risk and initiation of corrosive processes. When it is combined with the results of laboratory tests, it determinates local stresses in exploited structure. Using the electronic system, those adverse phenomena may be signalled to the crew in a form of an alarm signal (an acoustic or visual signal) informing about initiation of corrosion processes in the structure, and thereby about an increase of stresses in the ship structure. The OSDK method is based on collection and registration of data and signalisation of corrosive risk concerning elements of a ship's structure during various conditions of operation (the state of the sea, the speed of the ship) and tasks performed. On the basis of registration of the value of stationary electrochemical potential (E_{st}) of a chosen element of the structure (not only the naval structure), it is possible to determinate initiation of corrosive processes with close approximation as well as the state of structure deformation (stress). The method was approved by the Patent Office and author was awarded with the PL 216723-B1 (100%) patent. It was later implemented to the operation practice.

In this research area, under author's supervision there done three statutory works, one project of the National Centre of Research and Development. Author was also engaged in three projects implemented by other universities. The results of those studies were presented in 58 publications and at 37 polish and international conferences. It needs to be added that two patents were acquired and (as a co-author with majority participation) six improvement proposals were given.

REFERENCES

[1] Darowicki K., Orlikowski J., Aratunow A., Jurczak W., *Passive layer cracking studies performed on A95056 aluminium alloy by means of dynamic electrochemical impedance spectroscopy and acoustic emission*, 'Electrochemical and Solid-State Letters', 2005, Vol. 8, B55–B59.

[2] Darowicki K., Orlikowski J., Aratunow A., Jurczak W., *The effect of tensile stresses on aluminium passive layer durability*, 'Electrochimica Acta', 2006, Vol. 51, pp. 6091–6096.

[3] Darowicki K., Orlikowski J., Zieliński A., Jurczak W., *Comparative electrochemical analysis of the passive layer cracking process on aluminium alloys performed by means of DC and AC techniques*, 'Journal of the Electrochemical Society', 2007, Vol. 154 (2), C74–C80.

[4] Jurczak W., *Damage and Corrosion Diagnostics of Welded Light Alloys Ship Constructions*, 'Solid State Phenomena', 2013, Vol. 196, pp. 20–27.

[5] Jurczak W., Dudzik K., *Influence of friction stir welding on corrosion properties of AW-7020M alloy in seawater*, 'Advances in Science Materials', 2015, Vol. 1, pp. 7–13.

[6] Jurczak W., *Effectiveness of corrosion protection of the welded joints of AlZn5Mg2CrZr naval alloy*, 'Polish Journal of Environmental Studies', 2007, Vol. 16, 3c, pp. 43–51.

[7] Jurczak W., Grządziela A., *Pękanie korozyjno-naprężeniowe stopów aluminium przeznaczone na konstrukcje okrętowe*, 'Logistyka', 2010, No. 6 [*Stress corrosion cracking of aluminium alloys intended for ships constructions — transport safety considerations* — available in Polish].

[8] Jurczak W., *Spajanie tarciowe jako nowa metoda łączenia stopów aluminium stosowanych w transporcie morskim*, 'Technika Transportu Szynowego', 2013, No. 10, pp. 2370–2379 [*Friction welding as a new method of joining aluminium alloys used in marine transport* — available in Polish].

[9] Jurczak W., Szturomski B., *Simulating the Impact of Exposure to Corrosive Medium on Cracking Initiation in AW7020M Alloy Specimens*, 'Solid State Phenomena', 2014, Vol. 210, pp. 130–135.

[10] Jurczak W., *The effect of heat treatment on the structure and corrosion resistance of Al-Zn-Mg alloys*, 'Polish Maritime Research', 2008, No. 4, pp. 66–71.

[11] Jurczak W., *The influence of chemical composition on mechanical properties and resistance to stress corrosion in welded joints from sheets of Al-Zn-Mg alloys*, 'Marine Technology Transactions. Technika Morska', 2000, Vol. 11, pp. 105–115.

ODPORNOŚĆ KOROZYJNA ALUMINIOWYCH KONSTRUKCJI OKRĘTOWYCH

STRESZCZENIE

W artykule przedstawiono podsumowania wieloletnich badań odporności korozyjnej i korozyjno-naprężeniowej materiałów okrętowych i ich połączeń. Stopy aluminium i stale okrętowe, w tym austenityczne, były podmiotem badań w aspekcie odporności tych materiałów na korozję elektrochemiczną w warunkach morskich. Stale austenityczne i stopy aluminium w określonych warunkach wykazują małą podatność na korozję ze względu na samorzutne tworzenie się na ich powierzchni ochronnej warstewki tlenkowej, która stała się elementem monitorowania korozyjnego tych materiałów. Niestety, rzeczywiste warunki obciążeń konstrukcji okrętowych i oddziaływanie warunków środowiska morskiego pokazuje potrzebę poszukiwania nowych materiałów lub modyfikacji już stosowanych celem zwiększenia ich odporności korozyjno-naprężeniowej. Szczególnym obiektem badań korozyjnych były połączenia spawane powyższych materiałów, a obecnie ich połączenia spajane tarciowo.

Modyfikacja struktury pierwotnych materiałów pierwiastkami stopowymi, zmiana parametrów obróbki cieplnej czy stosowanie odpowiedniej farby ochronnej oraz dobór spoiwa do łączenia tych materiałów to metody wykorzystywane w przedstawionych badaniach celem podwyższenia odporności korozyjnej stopów aluminium. Szczególnym elementem badawczym jest monitoring korozyjny oparty na patencie PL 216723.

Słowa kluczowe:

odporność na korozję, stopy aluminium, konstrukcje morskie.