

DIAGNOSTICS OF CORROSION DEGRADATION OF LIGHT MARINE STRUCTURES

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Summary

Applying diagnostics consisting in evaluation of deformation based on corrosion potential measurements it is possible to extend life time of technical structures and make them safe for people and environment. Development of anticorrosion techniques and staff training is a fundamental requirement for safe exploitation of technical structures made of new 7020M aluminum alloy. Corrosive marine environment enforces engineers and technicians to implement advanced anticorrosion methods to make life on ship much safer. The paper presents results of investigations of ship aluminum alloys subjected to strain test fatigue test and new method diagnostic corrosion.

New aluminum alloy 7020M for selected heat treatment is better than the alloy 7020 utilized so far. Lack of zinc in 5xxx series alloys results in enhanced corrosion resistance as compared to 7xxx series but simultaneously their stress properties are significantly lower. A method of corrosion diagnostic has been proposed aimed at increasing the exploitation safety

Keywords: diagnostic, degradation aluminum alloys, stress corrosion cracking, fatigue corrosion.

DIAGNOSTYKA DEGRADACJI KOROZYJNEJ LEKKICH KONSTRUKCJI OKRĘTOWYCH

Streszczenie

Przez stosowanie diagnostyki oceniającej stan odkształcenia poprzez pomiar potencjału korozyjnego konstrukcji możemy nie tylko przedłużyć żywotność obiektów technicznych ale czynić je bezpiecznymi dla ludzi i środowiska. Metoda pomiaru wartości potencjału korozyjnego odniesiona do wzorca laboratoryjnego możliwa szybko ocenę stanu odkształcenia analizowanego obszaru konstrukcji. Rozwój technik antykorozyjnych i szkolenie specjalistów to podstawowy wymóg dla bezpiecznej eksploatacji obiektów technicznych wykonywanych z coraz to nowszych materiałów inżynierskich. Środowisko morskie o szczególnie agresywnie korozyjnych właściwościach, nakazuje i wymaga od inżynierów i technologów okrętowych wdrażania coraz to zaawansowanych zabezpieczeń przeciwkorozyjnych, które mogą uczynić pracę na morzu znacznie bezpieczniejszą.

W artykule przedstawiono wyniki badań wytrzymałościowych i zmęczeniowych okrętowych stopów aluminium i nowy sposób diagnostyki korozyjnej. Nowy stop 7020M dla określonej obróbki cieplnej jest lepszy od dotychczas stosowanego stopu 7020. Brak Zn w stopach serii 5xxx powoduje że wykazują lepszą odporność korozyjną niż stopy serii 7xxx ale mają znacznie mniejszą właściwości wytrzymałościowe. Przedstawiono sposób diagnozowania procesów korozyjnych mających na celu zwiększenie bezpieczeństwa eksploatacyjnego

Słowa kluczowe: diagnostyka, degradacja stopów aluminium, korozja naprężeniowa, zmęczenie korozje.

INTRODUCTION

The corrosion is inseparable natural process of environmental devastation of the material surface caused by spontaneous chemical and electrochemical processes. The corrosion in sea water and atmosphere is an electrochemical one which is connected with the flow of current and its density influences the intensity (pace) of corrosion. Corrosion problems are related to considerable part of engineer materials applied to the technology. Those materials are usually alloys of at least two chemical elements of large susceptibility to oxygenation. The contact of those materials with air or other corrosive factors causes degradation of their strength properties in result of material decrease.

The anticorrosive system is designed, to assured definite construction durability, to fulfill time of its function, called construction "vitality". Unfortunately, the longer time is, the larger costs are. Data from "Corrosion Costs and Preventive Strategies in the United States Report" verified in 2005 year and published on website www.corrosioncost.com; www.corrosioncost.com shows, that direct expenditures on corrosion in USA at present carry out 276 billion \$ annually (6% national product brutto). Expenditures on corrosion for shipping industry [1] are 1% this sum. It was estimated, that in Poland these expenditures can reach even more than 10% [2].

Corrosion problems of exploiting technical and sea objects appear where the corrosive factor is

found. The increase of tension in construction elements results in the bearing section changes which are caused by corrosive decrease. Those processes appear as a threat to the work safety. The corrosion intensity depends on many factors, mainly on the chemical constitution of the material as well as on the type of the corrosive factor (gaseous or liquid). The final effect of uncontrolled process of corrosion are: failures, the environmental contamination and danger for the human's life and health. The natural sea environment is especially dangerous in respect of corrosion. That is why the type of the sea construction determines the level of safety threat. Devices and elements of supporting structure which proper functioning affects the work safety should be mentioned here. For instance, the corrosive defects of supporting structure elements of drilling platforms, machines, containers, pipe lines ect., may cause the degradation of sea environment. Similar danger is evoked by the corrosion of metal packages which contains hazardous materials such as mustard gas or pearlite. Materials which are mostly used in sea structure constructing are: hull steel, austenitic steel and aluminum alloys. Aluminum alloys are more often used in building enormous dimensions sea constructions due to their relative strength modulus, a magnetism and weldability. In spite of these advantages, aluminum alloys undergo the corrosion processes because of simultaneous influence of exploiting tensions and sea environment. While uncontrolled, this effect may cause failures. This is the reason why in this article specific sea aluminum alloys are characterized in respect of decrease of mechanical properties under the influence of the corrosion and danger of such processes.

THE SEA ENVIRONMENT AND ALUMINUM ALLOYS

Technical objects which are exploited in the sea environment are constantly affected by corrosive impact and sea atmosphere. Thanks to a large contents of dissolved salts and gases the sea water is characterized by huge corrosion activity. In open seas the salinity is usually about 3,3-3,7%. In inland seas such as Baltic Sea the salinity is changeable and ranges between 0,5-3% [3]. More than 80% of salt contents exist as chlorides. The oxygenated sea water as well as the impact of microorganisms in connection with the stress which occurs during "the normal work" of the construction are the main factors deciding about corrosive degradation of sea construction materials.

The basic way to protect the engineering materials from the corrosion in the sea condition is the active and passive protection as well as the combination of them. The type of used anti-corrosion method depends on the type of sea construction. On the vessel the combination method is used for the hull that is the connection of the cathode (active) method, protection method and the set of protective paints (passive). For superstructures the sets of protective paints are used (passive

protection) and inhibitors are used in closed installations of e.g. the ship cooling.

In the shipbuilding industry 7xxx aluminum alloys series are more often used. They displace commonly used 5xxx alloys series. High-resistant and weldable 7xxx alloys have the best resistance properties among all aluminum alloys used in the shipbuilding. Unfortunately, they are characterized by tendency to stress corrosion in the sea water [4]. Alloys of 5xxx such as 5019(PA20), 5083(PA13) and 5754(PA11) are commonly used in hulls and superstructures building as well as in the equipment of light and fast vessels building. The 5xxx alloys (AlMg6Mn, 7020) as well as 5083 and 7020M (PA47M) are used for stiffening and plating of highly loaded hulls and superstructures which are joined also by welding. It applies especially to fast semi-planing crafts (e.g. motor torpedo boat), hydrofoil boats (e.g. 'Zryw'), catamarans (e.g. tourist crafts Bumerang) and to elements of liquefied gas containers – naturally occurring LNG (Liq. Natural Gas) and as crude oil refining products LPG (Liquefied Petroleum Gas).

For instance, in order to built 3 upper decks, stacks, superstructures, masts and the equipment of the longest, so far, transatlantic ship 'France' (V=66.347 BRT) 1.600 tones of aluminum and its alloys were used. Aluminum alloys are exploited also in various reinforced composites, means of military transport (also bullet-proof means) as well as recreation and rescue equipment, ect. [5]

Despite many advantages aluminum alloys need control and corrosive monitoring connected with the susceptibility on stress and fatigue corrosion in the sea water and atmosphere [6]. In the table 1 mechanical properties of particular ship aluminum alloys are depicted and their resistance to concrete types of corrosion are determined by:

- a) average percentage decrease of mechanical K_{Rm} and plastic K_{A5} properties under the influence of sea atmosphere.
- b) R_m , A_5 ' mechanical properties after corrosive exploiting under constant stretching stress in the sea water
- c) Z_{gok} fatigue-corrosive durability for N= fatigue cycles in the sea water

As a safety parameter, the ship construction engineer assumes the strength and probability of changes of exploiting properties in a result of heat treatment. It determines the usage of 7xxx alloys and corrosive susceptibility is minimalized by the use of protective paints.

ON-SHIP CORROSION DIAGNOSTICS SYSTEM

Utilizing the knowledge on electrochemical corrosion, we can reduce the current loss due to corrosion, without additional investment, by up to 40%. Applying the knowledge of electrochemistry, we can monitor the progress of corrosion processes and response much earlier to accelerated wear by eliminating the damage origin and subsequent degradation of construction material or by using the methods of corrosion protection at right time [7, 8].

Table 1. Mechanical properties and corrosion resistance of particular ship aluminum alloys in heat treatment which are the most resistant to corrosion in the sea environment

Alloys in the state	Static mechanical properties for $10^{-3}s^{-1}$			Corrosion resistance									
				in the sea atmosphere		in the sea water							
				corrosion in the salt spray chamber		stress corrosion for $t=1500h$ and stretching stress $\sigma_0=0,8 R_{0,2}$			rotary-flexural fatigue corrosion for $f=50Hz$ and N fatigue cycles				
	R_m	$R_{0,2}$	A_5	K_{Rm}	K_{A5}	R_m'	$R_{0,2}'$	A_5'	Powietrze		3%NaCl		
MPa	MPa	%	%	%	MPa	MPa	%	N=10 ⁵	N=10 ⁶	N=10 ⁵	N=10 ⁶		
									Z_{go} MPa	Z_{go} MPa	Z_{gok} MPa	Z_{gok} MPa	
7020M T_{622}^{*1}	443	397	9,8	4,7	36	426	377	2,9	236	175	224	134	
7020 T_{622}^{*1}	372	317	16	4,4	30	339	305	8	233	180	226	160	
5086 H111	358	180	23	3,5	23	340	196	15	167	140	155	90	
5083 0	295	151	20	3	10	285	146	13	185	155	152	118	

*1 heat treatment of 7xxx alloys - T_{622} – super saturation and time - $450^{\circ}C/1.5h$ ($430^{\circ}C/45'$), cooling in the heat water $80^{\circ}C$ and ageing type: $20^{\circ}C/6$ days + artificial ageing: $95^{\circ}C/15h+150^{\circ}C/10h$ [7].

*2 heat treatment of 5xxx alloys 0(H111- annealing recrystallize $350^{\circ}C$ with speed heating and cooling $50^{\circ}C/h$ [8]

The results of corrosion researches given in the table 1 show that the corrosive resistance of aluminum alloys of 5xxx set (hydronalium) is higher than the resistance of 7xxx alloys. However, strength properties of 7xxx are better than strength properties of hydronalium.

The development of techniques for monitoring and combating corrosion can only minimize the effects of its degradation character and contribute to the improvement of the service. This is achieved through learning of the mechanisms of corrosion. Corrosion protection is prevention of natural destruction process resulting in the extension of life cycle i.e. from creation to destruction of the material. Such is the perception of the problems of corrosion and corrosion protection [8 9].

OCDS – On-ship Corrosion Diagnostics System applies to the recording, collection and signaling of corrosion risk of structural elements. Based on the registration of the stationary potential, electrochemical (E_{st}) of the selected area of structure, not only marine one, one can give a close approximation, using the monograms (tabulated results of laboratory mechanical and electrochemical tests based on electrochemical impedance spectroscopy and its dynamic mode) of the initiation of corrosion processes and the state of deformation (strain) of structures for a given material. Fig.1a. shows the E_{st} registration system in selected areas of ship superstructure shown in Fig.1b.

This system is developed for metallic materials, which have a natural (or artificial) tendency to form on its surface, dense, well adherent, passive oxide film. For aluminum alloys, bi-layer film of oxide is amorphous boehmite and porous hydrargilite This layer is formed as a result of the alloy surface contact with oxygen from air or water. Corrosion of materials in the marine environment is electrochemical corrosion, which is accompanied by a current, which value depends mainly on the value of E_{st} potential, dependent on the level of stress. This insulating layer of oxide must have the appropriate mechanical and physical properties.

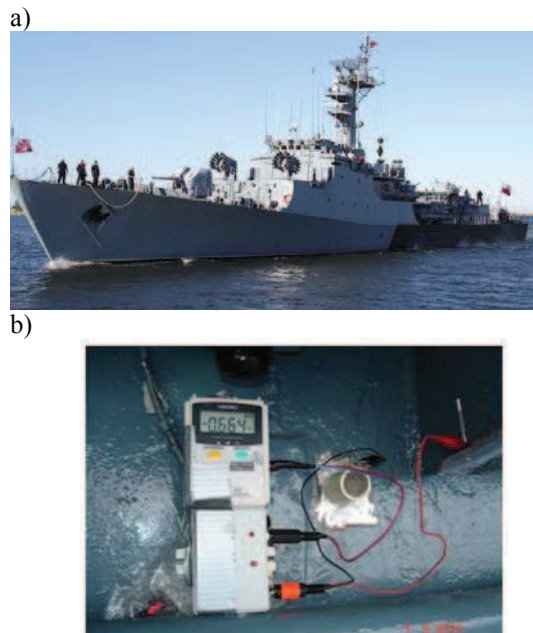


Fig.1. OCDS installed in selected areas (cracked) of aluminum (alloy 7020) superstructure of the design ship 620: a) 40-foot 3-Deck superstructure being a test object tested with the b) following set-up: Data Logger (voltage record with its own memory and power supply), separator and the mini electrochemical cell with electrolyte, which was attached to the crack of the base metal and welded joints [Patent no. P.394421 of 2011]

Passive state, protection (meaning there are no corrosion processes) ensures the continuity and integrity of amorphous boehmite adhesion to the substrate alloy. Insulating properties of the brittle layer prevent the flow of corrosion current (state 0) at fixed values of E_{st} according to the diagram shown in Fig.2a. Properties of the passive layer and of porous hydrargilite giving information on the risks of corrosion in the laboratory conditions are determined by EIS, and are described by the electrochemical parameters of the oxide layer

determined based on the equivalent circuit shown in

a)

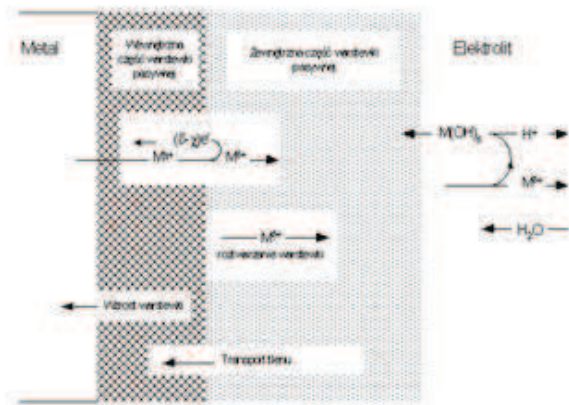
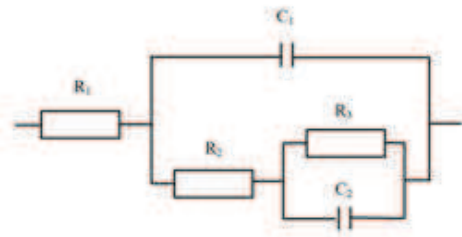


Fig.2b.

b)



Equivalent circuit for aluminum passive layer:
 R_1 – electrolyte resistance,
 C_1 – capacitance of the passive layer,
 R_2 – coupled resistance of the passive layer and the charge transfer reaction,
 R_3 – adsorption resistance,
 C_2 – negative capacitance.

Fig.2. Electrochemical parameters of passive oxide film naturally or artificially (polarization in acid) formed on the surface of the alloy determined by EIS or DEIS: a) schematic diagram of the flow of corrosion current b) equivalent circuit of passive oxide layer

Intact (without load) passive oxide film as the dielectric isolates the aluminum substrate from oxygen and the flow of corrosion current (transition of metal cation Me^+ to the electrolyte - which is sea water or the atmosphere - Cl^- anion to the metal surface) and its further oxidation

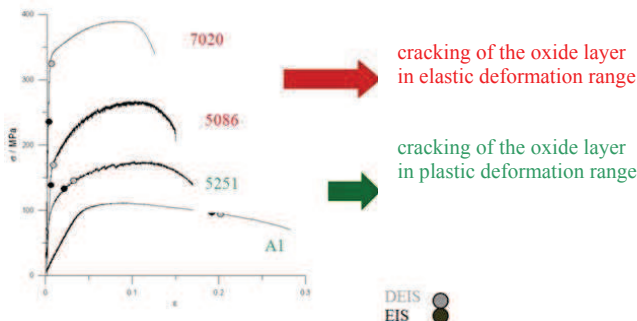


Fig.3. Mechanical properties of ships aluminum alloys, inclusive of their level of stress cracking of the oxide layer as determined by the DEIS and EIS (owner of DEIS method is Gdansk University of Technology, Chemical Faculty) compared to the properties of pure aluminum [9,10]

Fig.3. shows the results of electrochemical studies of slow strain rate test of ship aluminum alloys. Stress level at which the oxide film rupture occurs and the process of corrosion initiates were determined.

If the rupture takes place in the elastic range (operating range), the "lifetime" of the structure is shorter. As it can be seen the problem concerns high-strength alloys (7020), which means that the aforementioned superstructure should be monitored in terms of stress level and additionally protected with coating systems.

CONCLUSIONS

1. Modification with Cr and Zn of the alloy 7020 for $Zn+Mg>7\%$ (7020M) resulted in an increase in stress properties and comparable corrosion resistance.
2. Better corrosion resistance is revealed by 5xxx series alloys as compared to 7xxx alloys, but they possess inferior stress properties.
3. Corrosion resistance of 7xxx series alloy can be improved using selected heat treatment T622 (artificially aged after saturation), in which cooling after saturation was accomplished in hot water ($80^\circ C$).
4. For investigated alloys the additional anticorrosion protection measures have to be applied.

SUMMARY

It is possible not only to increase the life of technical object but also to keep humans and environment safe throughout proper corrosion protection and monitoring corrosion processes. The development of anti-corrosion techniques and training of specialists are the basic requirements in safe exploiting of technical objects made of latest engineering materials. The sea environment has particularly aggressive corrosion properties. The sea imposes and requires implementing modern anti-corrosion protection from engineers and ship technologists which may make the work on a sea much safer.

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