

Structure and corrosion resistance of aluminium AlMg2.5; AlMg5Mn and AlZn5Mg1 alloys

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Received 22.03.2010; published in revised form 01.07.2010

Properties

ABSTRACT

Purpose: The aim of the work was the evaluation of corrosion resistance and structure of aluminium AlMg2.5; AlMg5Mn and AlZn5Mg1 alloys.

Design/methodology/approach: The corrosion resistance tests of investigated alloys were carried out by means of potentiodynamic method registering anodic polarization curves in 3.5% NaCl solution at room temperature. Registering anodic polarization curves was conducted at the potential rate equal to 1mV/s. As the reference electrode was used saturated calomel electrode (SCE) and the auxiliary electrode was platinum electrode. Mechanical properties were evaluated on the basis of Vickers hardness test. The test was realized with the use of Hauser hardness tester. The observations of the surface morphology after corrosive tests were carried out using Digital Scanning Electron Microscope DSM 940 OPTON.

Findings: The investigations of corrosion resistance of examined aluminium alloys shows that the highest corrosion resistance in 3.5% NaCl solution was observed for AlZn5Mg1 aluminium alloy.

Practical implications: The obtained results can be used for searching the appropriate way of improving the corrosion resistance of analysed alloys because better corrosion resistance, lightweight of aluminium and its alloys makes them as most attractive for the steel replacement in shipbuilding.

Originality/value: The corrosion behaviour in chloride solution of AlMg2.5; AlMg5Mn and AlZn5Mg1 alloys was investigated.

Keywords: Corrosion; Corrosion resistance; Aluminium alloys; Potentiodynamic tests; NaCl solution

Reference to this paper should be given in the following way:

M. Kciuk, A. Kurc, J. Szewczenko, Structure and corrosion resistance of aluminium AlMg2.5; AlMg5Mn and AlZn5Mg1 alloys, Journal of Achievements in Materials and Manufacturing Engineering 41/1-2 (2010) 74-81.

1. Introduction

Steel is a traditional material used over 150 years in the shipbuilding industry because of excellent mechanical properties and low manufacturing costs. Due to the increasing demand for building the larger ships, designers had to search for alternative materials in order to reduce the weight of ships [1].

Aluminium and its alloys were assessed as a possible replacement for steel, due to a high corrosion resistance and a potential of considerable weight saving, as its density is almost three times lower than the density of steel (2.73 g/cm^3 for aluminium vs. 7.85 g/cm^3 for steel) [2].

Finally, the technological progress allowed aluminium alloys to approach the minimum of required mechanical properties in

shipbuilding provided by low carbon steel. Those points had a decisive role in considering aluminium alloys as a promising material for marine applications.

For public transport systems such as high-speed trains, trams, underground and regional trains, aluminium is the market leader in the construction of body shells. As in the automotive industry, energy-saving lightweight materials and design flexibility are the paramount criteria for the constructors, owners and operators of railway systems these days [2-4].

The bus manufactures are also showing increasingly strong interest in aluminium. Driven the same motivation as the rail car and automotive industries, they are looking for new, economic lightweight designs with enable them to build buses with less tooling costs and shorter assembly time than require for traditional designs [5].

Aluminum and its alloys are generally passive and corrosion resistant in aqueous solutions except for pitting corrosion due to some reactive species, such as chloride [6].

Aluminium has a natural corrosion protection from its oxide layer, but if exposed to aggressive environments it may corrode.

From a purely thermodynamical point of view aluminium is active. However, in oxygen containing environment (air, water), aluminium is rapidly covered with a dense oxide layer [7, 8].

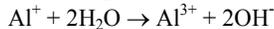
The oxide layer is essentially inert, and prevents corrosion. The thickness of the layer may vary as a function of temperature, environment and alloy elements.

Oxide films formed in air at room temperature are 2-3 nm thick on pure aluminium. Heating to 425°C may give films up to 20 nm [2]. If the oxide film is damaged, e.g. by a scratch, new oxide will immediately form on the bare metal [3]. This way aluminium is given excellent corrosion protection.

The following factors may affect the stability of the aluminium oxide and thereby cause corrosion [9]:

- The oxide is not stable in acidic (pH < 4) or alkaline (pH > 9) environments.
- Aggressive ions (chlorides, fluorides) may attack the oxide locally.
- Certain elements (Ga, Tl, In, Sn, Pb) may become incorporated in the oxide and destabilise it.

Pitting is a highly localized type of corrosion in the presence of aggressive chloride ions. Pits are initiated at weak sites in the oxide by chloride attack and propagate according to the reactions[10, 11]:



while hydrogen evolution and oxygen reduction are the important reduction processes at the intermetallic cathodes, as sketched in Fig. 1.:



As a pit propagates, the environment inside the pit (anode) changes. According to reaction 2 the pH will decrease. To balance the positive charge produced by reaction 1 and 2, chloride ions will migrate into the pit. The resulting HCl formation inside the pit causes accelerated pit propagation.

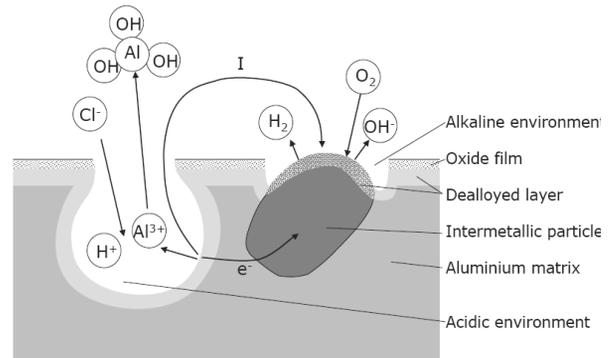


Fig. 1. Generalised illustration of pitting corrosion on aluminium alloys [9]

The reduction reaction will cause local alkalisation around cathodic particles. As previously mentioned aluminium oxide is not stable in such environment, and aluminium around the particles will dissolve (alkaline pits). The active aluminium component of the particles will also dissolve selectively, thereby enriching the particle surface with Fe and increasing its cathodic activity. Etching of the aluminium matrix around the particles may detach the particles from the surface, which may re-passivate the alkaline pits. This may also reduce the driving force for the acidic pits causing re-passivation of some in the long run.

2. Materials and methods

The aim of the work was the evaluation of corrosion resistance of aluminium AlMg2.5; AlMg5Mn and AlZn5Mg1 alloys in selected corrosion environment.

The research was conducted on samples of size 20x15x3 mm made of the analysed alloys. The chemical composition of the investigated alloys is presented in Table 1.

Metallographic examinations of the structure were made on Leica light microscope with magnification from 500 to 1000x.

Examinations of the surface morphology after corrosive tests were conducted using Digital Scanning Electron Microscope DSM 940, with 12nm of resolving power and 20 kV accelerating voltage containing EDAX energy dispersion X-ray spectrometer, supplied by OPTON Company. Mechanical properties included Vickers hardness tests made on HAUSER tester according to the standard PN- EN ISO 6507-1:2007 [12].

The corrosion resistance tests of samples were carried out by means of potentiodynamic method (registering anodic polarization curves). The measurements were conducted in 3% solution of NaCl at room temperature. The research was realized by means of the system used for electrochemical research VoltaLab 2.1.

As the reference electrode the saturated calomel electrode (SCE) was applied, the auxiliary electrode was platinum electrode. The measurement of corrosion potential was realized in time of 120 min. Registering of anodic polarization curves was conducted at the potential rate equal to 1 mV/s.

In order to calculate the corrosion current, the Stern- Geary equation was used (5) [13, 14]:

$$R_p = \frac{b_k \cdot b_a}{2,3 \cdot i_{cor} (b_a + b_k)} \quad (5)$$

where: b_k - the slope coefficient of the cathodic Tafel line, b_a - the slope coefficient of the anodic Tafel line, i_{cor} - the corrosion current density [mA/cm²], R_p - the polarization resistance [Ω cm²].

3. Results and discussion

The structures of investigated alloy in initial state were analysed within the confines of metallographic investigations. Examinations were carried out on lateral microsections.

In the structure of AlMg2.5 it was found evenly distributed precipitations with diversified size in solution matrix α .

The size of precipitations is contained in the range 1 do 5 μ m (Figs. 2 a and b).

The precipitations in the AlMg5Mn and AlZn5Mg1 alloys occurred in the banding system in solution matrix α and they have microhardness about 82 HV50 (Fig. 3).

In the no etched microsections the precipitations have light colors and after etching of the AlZn5Mg1 alloy the precipitations etched on dark or grey-blue color (Fig. 4). The microhardness of light etched precipitations is about 117 HV20.

According to equilibrium system in the material can be probably presented such phases as: solid solution α , phase Al₈Mg₅ (β) (weakly visible in no etched state) and Al₃Fe phase. Mg solute atoms tend to precipitate out as an equilibrium β -phase (Al₈Mg₅) along the grain boundaries or randomly distributed in the structure.

This process occurs slowly even at room temperature, and could be significantly accelerated at high temperatures. Since the corrosion potential of β -phase (-1.24V), is more negative than the potential of Al-matrix (-0.87V), dissolution of anodic β -phase particles would occur in an appropriate solution, such as seawater.

The susceptibility of Al-Mg alloys to different forms of corrosion (intergranular, stress corrosion and exfoliation) depends not only on the presence of β -phase particles, but mostly on its form and distribution in the structure.

Microstructures with continuous layer of β -phase (Fig. 3) are more susceptible to corrosion, while randomly distributed β -phase in the structure (Fig. 2) provides better corrosion resistance.

Table 1.

Chemical composition of investigated materials

Material	Element concentration [%]						
	Al	Mg	Zn	Cr	Fe	Mn	Cu
AlMg2.5	95.7-97.7	2.2-2.8	-	0.15-0.35	max. 0.4	max 0.05	max. 0.05
AlMg5Mn	92.9-95.4	4.5-5.6	-	0.05-0.2	max. 0.4	0.05-0.2	max. 0.1
AlZn5Mg1	91-94.7	1-1.8	4-5	0.06-0.2	max. 0.4	0.2-0.7	-

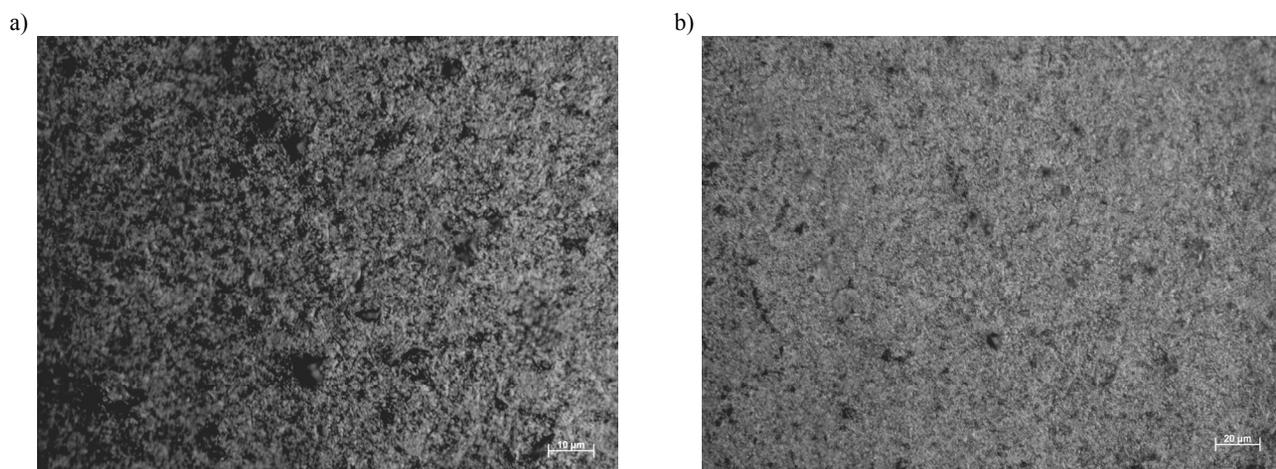


Fig. 2. The structure of aluminium AlMg2.5 alloy, a) 500x, b) 1000x

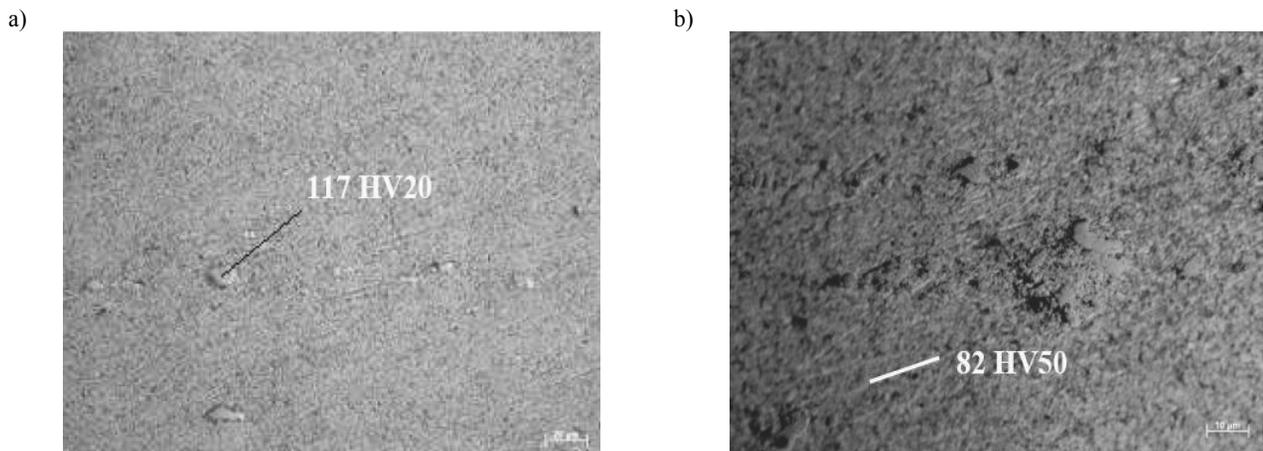


Fig. 3. The precipitations in the banding system in solution matrix α aluminium AlMg5Mn alloy, a) 500x, b) 1000x

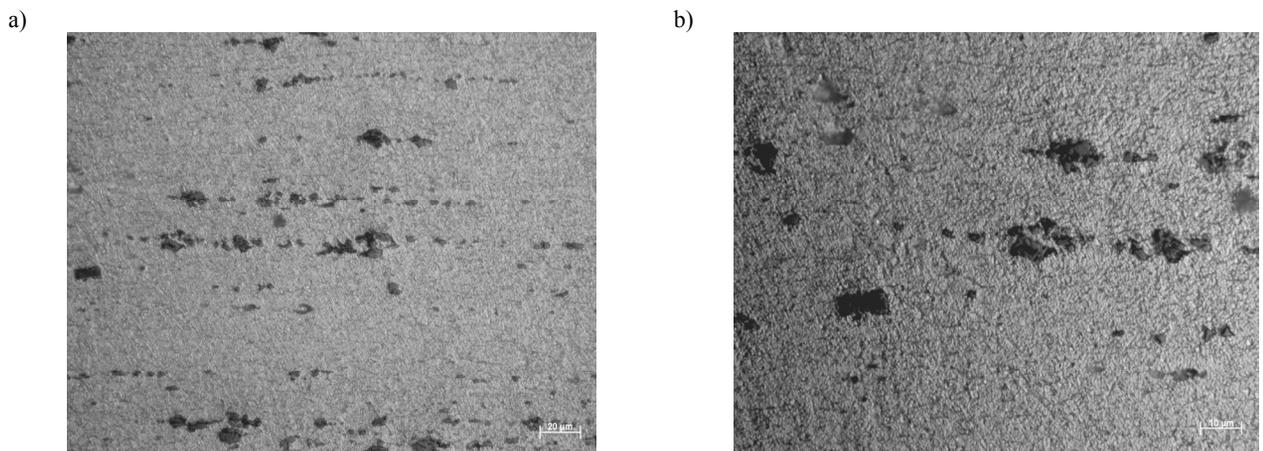


Fig. 4. The structure of AlZn5Mg1 alloy in the initial state, a) 500x, b) 1000x

Iron in percentage 0.3 decrease solubility of magnesium in aluminium and influence on precipitation of Al_3Fe phase, which doesn't dissolve in solid solution during solution heat treatment.

This phase is characterized by occurred envelope, which is caused by change of the solid solution composition round this phase (Fig. 2).

The research of the samples made of examined aluminium alloy showed diverse corrosion resistance in 3.5% NaCl solution.

On the basis of measurement it was stated that the corrosion potential value of AlMg2.5 samples was in the range $E_{corr} = -755$ – -750 mV. The recorded anodic polarization curves indicate the existence of passive range. The values of breakdown potential, below which the metal surface remains passive and above which pitting corrosion starts to grow on the metal surface equal to $E_{np} = -652$ –(-554) mV.

When the current density reached 10 mA/cm^2 the direction of anodic polarization of samples was changed.

On the basis of the Stern-Geary equation additional parameters describing the corrosion resistance of investigated

samples were determined: polarization resistance R_p and corrosion current density i_{corr} .

The values of the corrosion parameters were in the range $R_p = 6,5$ – $8,3 \text{ k}\Omega\text{cm}^2$, $i_{cor} = 0,0031$ – $0,004 \text{ mA/cm}^2$ (Table 2, Fig. 5)

Further research was carried out on the AlMg5Mn samples. It was stated that the corrosion potential value was in the range $E_{corr} = -762$ do -750 mV.

The recorded anodic polarization curves also indicate the existence of passive range. The values of breakdown potential equal to $E_{np} = -670$ – (-639) mV.

Table 2. Results of the corrosion investigations of AlMg2.5 alloy

Sample No	Corrosion potential E_{cor} , mV	Polarization resistance R_p , $\text{k}\Omega\text{cm}^2$	Corrosion current density i_{corr} , mA/cm^2	Breakdown potential E_{np} , mV
1	-755	6.81	0.0038	-553.9
2	-750	6.51	0.0040	-651.5
3	-750	8.25	0.0031	-584.9

When the current density reached 10 mA/cm^2 the direction of anodic polarization of samples was changed.

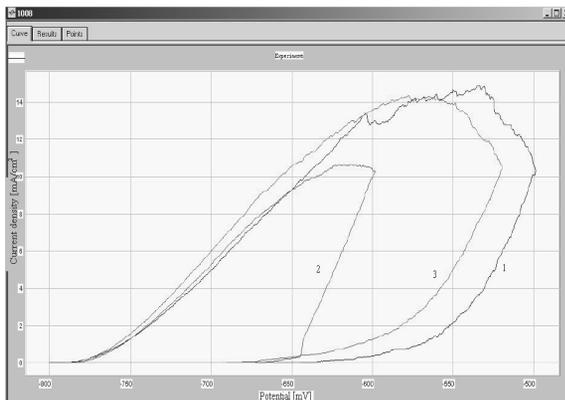


Fig. 5. Anodic polarization curves of samples made of AlMg2.5 aluminium alloys

Additional parameters describing the corrosion resistance of investigated samples were determined using the Stern-Geary equation: polarization resistance R_p and corrosion current density i_{corr} .

The values of the corrosion parameters were in the range $R_p = 0.136\text{-}0.482 \text{ k}\Omega\text{cm}^2$, $i_{\text{corr}} = 0.0539\text{-}0.1912 \text{ mA/cm}^2$ (Table 3, Fig. 6).

Table 3. Results of the corrosion investigations of AlMg5Mn alloy

Sample No	Corrosion potential E_{cor} , mV	Polarization resistance R_p , $\text{k}\Omega\text{cm}^2$	Corrosion current density i_{corr} , mA/cm^2	Breakdown potential E_{np} , mV
1	-755	0.136	0.1912	-699.9
2	-750	0.482	0.0539	-639.6
3	-762	0.247	0.1053	-673.4

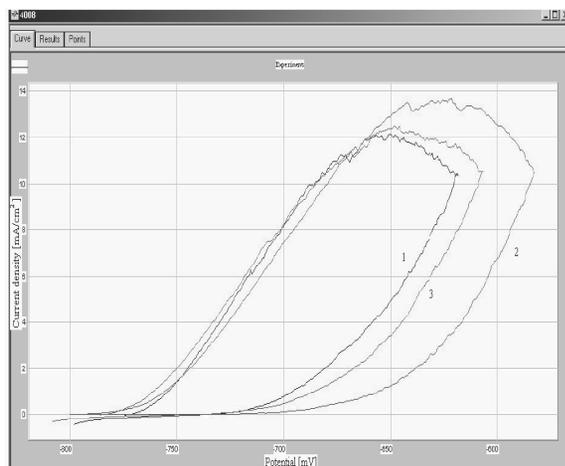


Fig. 6. Anodic polarization curves of samples made of AlMg5Mn aluminium alloys

Performed electrochemical analysis revealed that the open circuit potential for all the AlZn5Mg1 samples established itself after 1800s. The course of changes of current density in a function of potential for the sample investigated in 3.5% NaCl solution is presented in Fig. 7 and Table 4.

The value of corrosion potential E_{cor} was equal -890 mV , polarization resistance R_p was $11.79 \text{ k}\Omega\text{cm}^2$ and the density of corrosion current i_{corr} determined basing on the Stern-Geary equation was equal 0.0022 mA/cm^2 .

When the current density reached 10 mA/cm^2 the direction of anodic polarization of samples was changed.

Table 4. Results of the AlZn5Mg1 alloy corrosion investigations

Sample No	Corrosion potential E_{cor} , mV	Polarization resistance R_p , $\text{k}\Omega\text{cm}^2$	Corrosion current density i_{corr} , mA/cm^2	Breakdown potential E_{np} , mV
1	-894	9.96	0.0026	-825.4
2	-894	13.81	0.0018	-772.9
3	-890	11.79	0.0022	-830.6

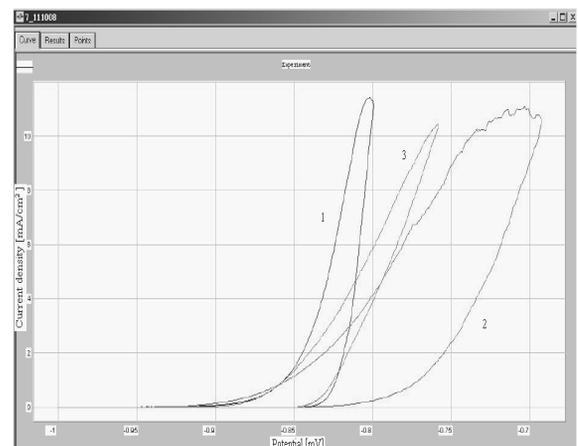


Fig. 7. Anodic polarization curves of samples made of AlZn5Mg1 aluminium alloys

Performed electrochemical analysis in 3.5% NaCl solution, which simulated artificial sea water revealed that the AlMg5Mn aluminium alloy is characterized by the lowest corrosion resistance in analyzed conditions (the density of corrosion current i_{corr} is on the level 0.1168 mA/cm^2).

The results of corrosion research suggested that the highest corrosion resistance was observed for the AlZn5Mg1 alloy. The average value of the corrosion current was about 0.0022 mA/cm^2 .

With the corrosion current values of all alloys correlated the results of the polarization resistance R_p . Evaluated polarization resistance of AlZn5Mg1 alloy indicate on the fact, that this alloy shows the best corrosion behavior in examined solution ($R_p = 11.79 \text{ k}\Omega\text{cm}^2$).

In the case of AlMg5Mn aluminium alloy the significant decrease of polarization resistance value was stated.

Table 5.
The average parameters characterize the corrosion process of investigated alloys

Alloy	Corrosion potential E_{cor} , mV	Polarization resistance R_p , $k\Omega cm^2$	Corrosion current density i_{cor} , mA/cm ²	Breakdown potential E_{np} , mV
AlMg2.5	-752	7.19	0.0036	-421.4
AlMg5Mn	-756	0.296	0.1168	-670.9
AlZn5Mg1	-890	11.79	0.0022	-809.6

The metallographic observations of the surface morphology of the samples after corrosion investigations let to estimate the kind and the stage of corrosive damages. Conducted investigations showed, that analyzed aluminum alloys after investigations in 3.5 % NaCl solution have diverse character of the damages of the surface.

In the case of alloy AlMg2.5 (Figs. 8 and 9) it was stated the presence of localized corrosion - pitting corrosion mainly as the oval pits and micropores.

This kind of corrosion is extremely insidious, as it causes little loss of material with small effect on its surface, while it damages deep structures of the metal. The pits on the surface are often obscured by corrosion products.

The driving power for pitting corrosion is the lack of oxygen around a small area. This area becomes anodic while the area with excess of oxygen becomes cathodic. The corrosion penetrates the mass of the metal, with limited diffusion of ions, further pronouncing the localized lack of oxygen [15].

Pitting can be initiated by a small surface defect, being a scratch or a local change in composition, or a damage to protective coating.

Similar corrosion effects were observed in the AlMg5Mn (Figs. 10 and 11). The presence of chlorides in sea water, significantly aggravates the conditions for formation and growth of the pits through an utocatalytic process.

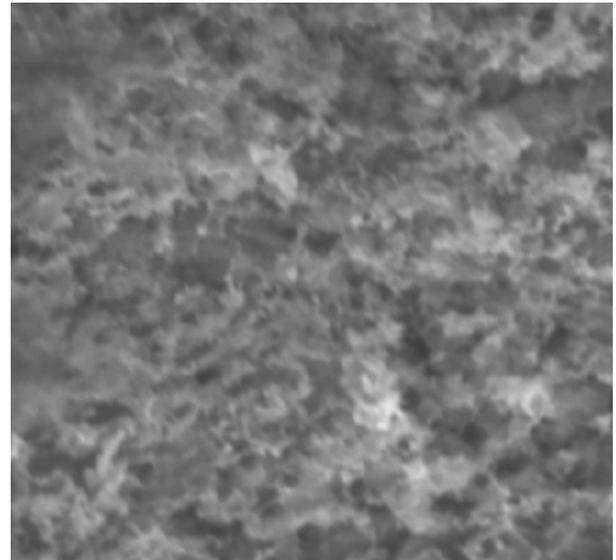


Fig. 9. Micropores and coorision pits on specimen surface of AlMg2.5 alloy after potentiodynamic tests

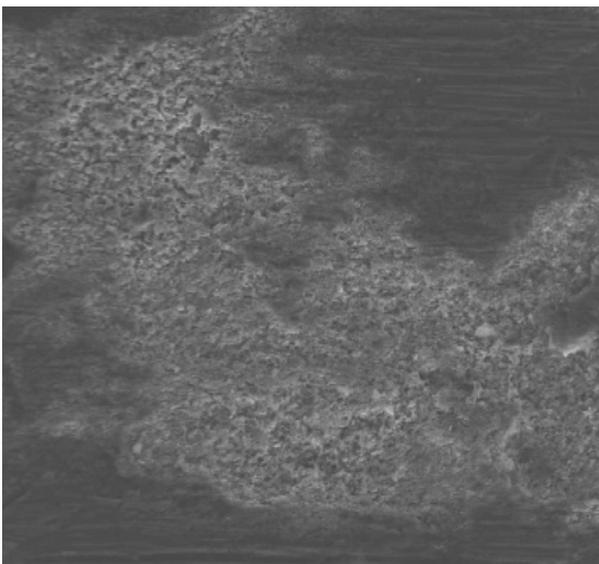


Fig. 8. The surface of AlMg2.5 alloy after corrosion tests

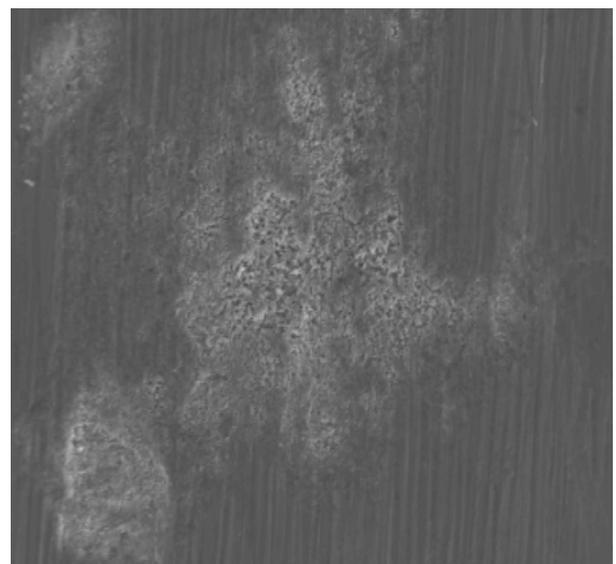


Fig. 10. Corrosion pits on a surface of AlMg5Mn alloy after corrosion tests

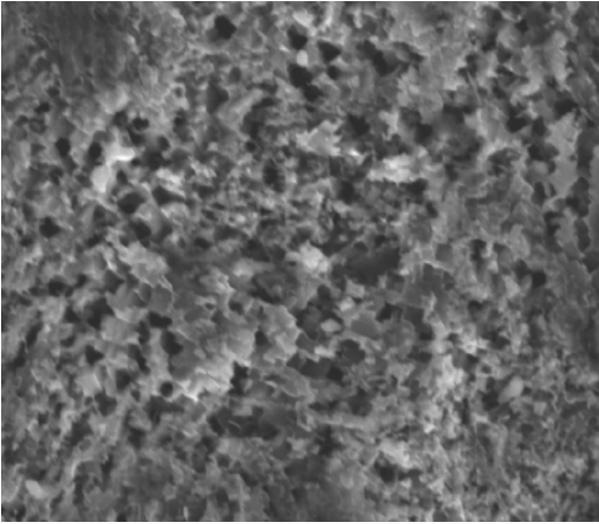


Fig. 11. Micropores and corrosion pits on specimen surface of AlMg5Mn alloy after potentiodynamic tests

The pits become loaded with positive metal ions through anodic dissociation. The Cl^- ions become concentrated in the pits for charge neutrality and encourage the reaction of positive metal ions with water to form a hydroxide corrosion product and H^+ ions. The pits are weakly acidic, which accelerates the process.

Fractographic analyses of the AlZn5Mg1 samples (Figs. 12 and 13) allowed to evaluate the type of corrosion damages.

It was revealed the pits occurrence - typically in chloride solutions and uniform corrosion. The observed corrosion products are related to the chemical composition because zinc fulfills a function of positive electrode relative to the aluminium.

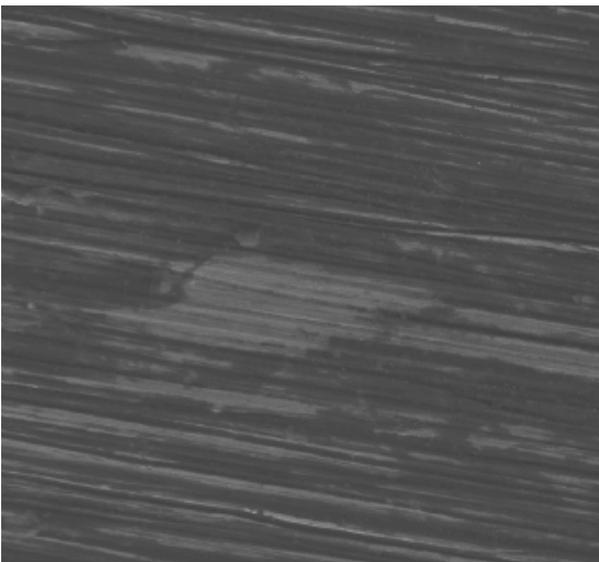


Fig. 12. The surface of AlZn5Mg1 alloy after corrosion tests

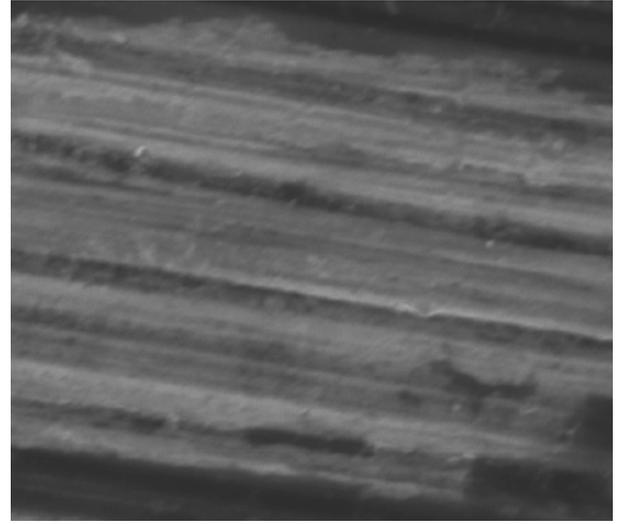


Fig. 13. Micropores and corrosion pits on specimen surface of AlZn5Mg1 alloy after potentiodynamic tests

It was stated the proceeding of the zinc anodic digestion till the moment of establishing conditions of balance investigated surface - solution.

4. Conclusions

In the structure of AlMg2.5 it was found uniformly distributed precipitations with diversified size in solution matrix α .

The precipitations in the AlMg5Mn and AlZn5Mg1 alloys occurred in the banding systems.

Metallographic surface observation of the samples after corrosion tests showed the corrosion damages diversity.

The susceptibility of Al-Mg alloys to different forms of corrosion depends not only on the presence of β -phase particles, but mostly on its form and distribution in the structure.

Numerous corrosion pits were observed after investigations of the AlMg2.5 aluminium alloy in 3.5% NaCl solution. The same corrosion effects were revealed after corrosion examinations of AlMg5Mn. Fractographic analyses of AlZn5Mg1 alloy show that this alloy gives into uniform corrosion.

According to the results of potentiodynamic analyses it was found that the samples of examined AlMg2.5 or AlMg5Mn alloys show poor corrosion resistance in the NaCl solution. It was found that with the increase of the Mg quantity the corrosion resistance decreases.

The highest corrosion resistance was revealed in the AlZn5Mg1 aluminium alloy ($i_{\text{cor}} = 0.0022 \text{ mA/cm}^2$, $R_p = 11.79 \text{ k}\Omega \times \text{cm}^2$). The observed corrosion products are related to the chemical composition - zinc behaves as anode relative to Al-matrix.

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