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Research Article

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PREDICTION OF CORROSION RESISTANCE OF MAGNALIAS

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Abstract. *In the presented work the factors influencing the strength and corrosion rate in seawater of magnalium aluminum-magnesium alloy were considered. It was shown that in unsaturated solid alpha solutions the main form of magnesium in the aluminium structure was the electronic compound* Mg_2Al_4 *entering the rhombic subsystem of aluminium cells. The calculation showed that the more aluminium cells contain* Mg_2Al_4 *group as a rhombic subsystem, the higher the strength of these alloys. The mechanism of destruction by halogen ions of pure aluminium cells and aluminium cells containing the* Mg_2Al_4 *group was determined by the PM3 method. Destruction of both types of cells occurred by the same scenario, through the detachment by halogen ions of the central atom in the upper edge of cells bordering. It was shown that in seawater the corrosion rate of aluminium cells containing* Mg_2Al_4 *group was higher than the corrosion rate of pure aluminium cells. A mathematical model has been developed that allows calculating the change in the corrosion rate of magnesium alloys with low magnesium mass fraction (up to 3.5 % magnesium inclusive) in seawater. The model allowed to take into account the change of influence of the mass fraction of the main alloying elements (Mg, Cr, Mn, Zn, Ti, Cu) on the corrosion rate. Change of corrosion rate in seawater of three aluminium-magnesium alloys variants was calculated using this model. These aluminium alloy variants include a magnesium content of 2.6 mass % with higher levels of the alloying elements Cr and Mn.*

Keywords: Corrosion, aluminum-magnesium alloy, magnalium, aluminium, cubic subsystem, halogens, quantum-chemical calculations.

1. Introduction

Aluminium alloys are used in various industries due to their low density, high corrosion resistance and low cost [1]. Modelling of the alloys structure depending on the quantitative composition of the alloy is one of the ways to accelerate the search and prediction of improved alloy compositions. For example, a hybrid model on a combination of neuro-fuzzy and physical models for predicting the flow stress and microstructural evolution during thermomechanical processing has been developed in the paper [2]. Comparison with experimental data have shown generally good agreement for Al -Mg alloy with 1 mass % of Mg deformed under thermomechanical processing conditions. Using of machine learning for molecular material modelling of Al, Mg and Al-Mg alloy samples is shown in [3]. Ability to create uniformly accurate models of potential energy surfaces with a minimum amount of reference data is shown on the basis of the active learning procedure.

Another example of a complex study (experimental and numerical) is the work [4]. Reducing the number and size of Al_3Fe intermetallic particles in aluminum alloy leads to an increase in the corrosion resistance of the material. This result was obtained on the basis of electron microprobe analysis and transmission electron microscopy. A large number of works [5- 9] have been devoted to the study of the corrosion process and methods of protection against it. The works were carried out both experimentally [5-

7] and with the involvement of numerical calculations and mathematical models [8, 9]. Therefore, the creation of calculation methods capable of predicting with good accuracy the corrosion resistance of new and modified alloys is an urgent task.

The purpose of this work was to develop a methodology for predicting the corrosion resistance of aluminium-magnesium alloys with a percentage of magnesium not exceeding 3.5 mass %. This allows to significantly reduce research costs and increase the speed of development of new alloy modifications.

2. Materials and experimental details

The structure of magnalium and other samples have calculated using the parametric method 3 (PM3), which was specially developed for calculations of compounds containing aluminum and halogen atoms [10]. In the aluminium unit cell model 14 atoms were used for the calculations. It was taken 14 atoms in the cell of AMg-aluminium-magnesium (AMg) alloys, as in the cell of pure aluminum.

Considering that the cells of AMg alloys have had the same number of atoms as in the cell of pure aluminum (14 atoms). The density of AMg alloys was calculated with different numbers of magnesium atoms in the structural cell. The calculation was started with the condition that all cells of the AMg alloy contain 1 magnesium atom, and all other atoms in the cells are aluminum atoms (13 aluminum atoms). A model of an aluminum cell consisting of 9 atoms have been used in order not to take into account the same aluminum atoms twice in the calculations. This sell was called a calculated aluminium cell. The number of magnesium atoms changed depending on the concentration of magnesium in the alloy. Only one halogen atom - chlorine was used for modeling interaction cells with seawater.

In order to clarify the corrosion resistance of AMg alloys in seawater, samples of pure aluminium (analytic grade - 99.99 % Al), AMg2, AMg3 and AMg6 identical in size and external surface area were placed for 72 hours in 5% iodine solution in ethanol. Samples with dimensions of 1cm*1.5cm*2 mm were used. The gravimetric method was used to measure the corrosion rate in the samples - the samples were weighed before and after being placed in iodine solution. The mass of samples was measured on electronic scales RADWAG AS 60/220.R2 with an accuracy of 10^{-4} grams.

3. Results and discussion

The structure of the pure aluminium cell has been known from X-ray diffraction analysis [11]. A schematic representation of the aluminum cell structure obtained as a result of the PM3 calculation is shown in Figure 1. The aluminium cell is a face- centred cubic lattice of 14 aluminium atoms, consisting of two subsystems: cubic and rhombic (Figure 1). There are no aluminium atoms in the centre of the aluminium cell, which accounts for the good ductility of pure aluminium. Under normal conditions, these aluminium cells on the surface of products are partially oxidised. The cubic subsystem of the aluminium cell lattice on the surface is oxidised. It is reason why pure aluminum does not corrode in fresh water. However, pure aluminium has low strength and hardness and has currently very limited use, e.g. for producing electrical wires.

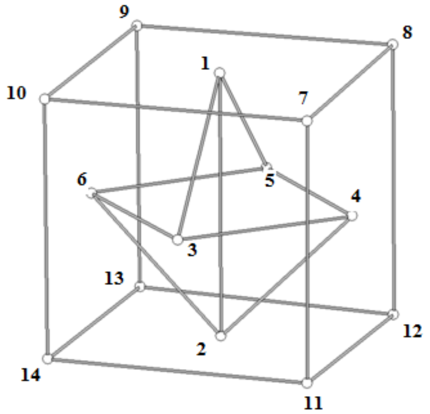


Fig.1. Structure of the pure aluminium cell (atoms 1-6 form the rhombic subsystem of the aluminium cell).

Alloys of aluminium with magnesium (magnalia) are widely used for technological purposes. These alloys have significantly higher hardness and strength than pure aluminium, Table 1 [12]. It is known that the strength of magnesium increases with increasing magnesium content in the alloy in the series from AMg1, AMg2, AMg3, AMg4, AMg6 (the figure indicates the percentage of magnesium content in the aluminium alloy by mass). An almost linear dependence of magnesium strength increase on magnesium percentage is observed (Table 1).

Table 1. Mechanical characteristics of aluminium alloys [12]

	Tensile strength, MPa	Yield strength, MPa	Brinell hardness, Kgs/mm^2
Pure aluminium	70	25	25
AMg1	140	50	30
AMg2	170	80	45
AMg3	200	100	58
AMg4	250	120	75
AMg5	280	150	65
AMg6	320	160	100

There are 14 atoms in the cells of AMg alloys as in the cells of pure aluminium. There is a homogeneous distribution of magnesium and other alloying elements in AMg alloys, as is known from X-ray diffraction analysis [13]. It is believed that the increase in the strength of alloys of aluminium with magnesium (magnalium) compared to pure aluminium is due to the emergence of strengthening phases in these alloys in the form of intermetallic compounds of magnesium and aluminium [14].

In further, issues related to the structural formula of intermetallic compounds of magnesium with aluminum in each type of AMg alloy, their localization in the structure of cells and their influence on the strength of the alloys as a whole were considered. Table 2 presents data on the density of AMg alloys depending on the mass content of magnesium atoms [15]. A large mass fraction of magnesium in an aluminum alloy leads to a lower density of the alloy. The density of AMg alloys at different number of magnesium atoms in the structural cell was calculated taking into account that in the cells of AMg alloys the same number of atoms as in the cell of pure aluminium (14 atoms). As a starting calculation, the condition was adopted that each cell of the AMg alloy contains one atom of magnesium. All other atoms in the cells were aluminium atoms (13 aluminium atoms). Below, the algorithm for calculating the density of the AMg alloy containing a given number of magnesium atoms was considered.

Table 2. Basic initial parameters of pure aluminium and alloys (magnalias) and alloy cell modelling parameters

	PA*	AMg1	AMg2	AMg3	AMg4	AMg5	AMg6	AMn*
Density, kg/m^3	2700	2690	2680	2670	2660	2650	2640	2730
Average number of magnesium atoms N per cell of AMg alloy**	-	0,25	0,5	1	-	-	2	-
Percentage of cells containing Mg_2Al_4 group	0%	12%	25%	50%	-	-	100%	-
Alloy tensile strength	70 MPa	140 MPa	170 MPa	200 MPa	-	-	250 MPa	-
Corrosion, mm per year	0,75	-	0,4	-	0,73	-	1,5	0,32

Here
* - PA (pure aluminium) - aluminium with 99.99 % purity; AMn - aluminium-manganese alloy with percentage of manganese 1.5 mass %;
** - average number of magnesium atoms in each magnalium cell.

The calculation took into account the fact that the aluminum atoms forming cell faces of 14 atoms are simultaneously part of two bordering cells. The computational aluminium cell included the first 4 aluminium atoms (atoms 9, 10, 13, 14 in the Figure 1) of the cubic subsystem (there are 8 atoms in the cubic subsystem of the physical cell). The rhombic subsystem of the physical cell contained 5 aluminium atoms (atoms 1-3, 5, 6 in the Figure 1). Atoms 4, 7, 8, 11, 12 of the physical cell belonged in the computational model to the neighboring computational cell.

Then 8 aluminium atoms and one magnesium atom was used in the calculated aluminium cell model. Both types of cells (physical and the cell used for calculations) contained one magnesium atom. It was considered that the magnesium atom is localised in the rhombic subsystem of the physical cell.

1) The total mass of 1 m^3 of pure aluminum (Mone Al) is determined for all aluminum atoms occupying positions with a given number (e.g. atoms 10, Figure 1) in all calculated aluminium cells. The density of pure aluminium is 2700 kg/m^3.

$$M_{one\ Al}= 2700\ kg/\ 9\ aluminium\ atom= 300\ kg. \qquad (1)$$

The total masses of aluminium atoms under any other numbers in all cells in 1m^3 are the same.

2) The total mass of magnesium atoms in 1 m^3 of AMg alloy was calculated, knowing the total mass of aluminum atoms under a certain number $M_{one\ Al}$, the mass of a magnesium atom, which is 0.901 of the mass of an aluminum atom, and the number of magnesium atoms N in aluminum cells. If 1 magnesium atom N in the cells equals 1, then all magnesium atoms in this case are 1/9 of the total number of atoms in the alloy:

$$M_{one\ Mg}= M_{one\ Al} * 0.901 * N = 270.3\ kg; \qquad (2)$$

3) The total mass of aluminum atoms $M_{tot\ Al}$ in 1 m^3 of the AMg alloy was found for a given number of magnesium atoms N in the elementary cells of the alloy.

$$M_{tot\ Al}= M_{one\ Al} * (9 - N); \qquad (3)$$

There were 270.3 kg of magnesium and 2400 kg of aluminium for 1 m^3 of AMg alloy containing 1 magnesium atom in each cell. When they were summed up, it turned out that in 1 m^3 there is 2670.3 kg of the total mass of aluminium and magnesium (add up 8 mass fractions of aluminium and one mass fraction of magnesium). That is the density of the alloy in which in 100% of structural cells there are 8 atoms of aluminium and 1 atom of magnesium will be 2670,3 kg/m^3. This density corresponds to the alloy AMg3 (Table 2).

Assuming that one magnesium atom is in every second real physical cell (N=0.5) of the alloy. It was got the density of the alloy 2682.15 kg/m^3. The number of magnesium atoms by condition is 2 times less than in the alloy AMg3 and the total mass of magnesium in 1 $m^3$of this alloy was 134.15 kg. The mass of aluminium in 1 $m^3$of this alloy was 2548 kg. The value is 2682.15 kg/m^3 which is close in density to the AMg2 alloy. In this case, it was assumed that only half of the cells of the AMg2 alloy contain a magnesium atom and the other half of the cells were pure aluminium cells.

If a magnesium atom was contained in every fourth physical cell of N= 0.25 aluminum, then alloy density would be 2692.6 kg/m^3. The number of magnesium atoms by the condition was 4 times less than in the alloy AMg3 and the total mass of magnesium in 1 m^3 of this alloy is 67,575 kg. The mass of aluminium in 1 m^3 of this alloy was 2625 kg, which is close to the density of the alloy AMg1. In this case, it is assumed that only 25% of the cells of the alloy contain a magnesium atom and 75% of the cells are pure aluminium cells.

Also consider the case when in all real physical cells of pure aluminium 2 atoms of aluminium out of 14 atoms of cells were replaced by atoms of magnesium (2 atoms of magnesium + 12 atoms of aluminium; N=2) in 1m^3 of AMg alloy there were 540,6 kg for magnesium and 2100 kg for aluminium. When they were summed up, it turned out that 1m^3 contains 2640.6 kg of the total mass of aluminium and magnesium, which corresponds in density to the alloy AMg6 (Table 2). At the average content of magnesium atoms in the cell N=2 it is unlikely that there are cells of pure aluminium in the alloy AMg6.

Taking into account the data of Table 1 and Table 3, we could conclude that the strength of AMg alloys increases as the number of aluminium cells containing magnesium atoms increases. Aluminium cells that containing a magnesium atom are the centres of strength. The situation is similar to the strengthening of iron structure by carbon. In steels, iron cells containing carbon compounds (carbides) are the centres of strength. The more cells containing carbon compounds (up to 2.14 % of the mass fraction), the harder and stronger is the iron structure.

Having determined the average statistical distribution of magnesium atoms in different AMg alloys (Table 2) it was necessary to determine the structural formula of compounds with aluminium atoms in AMg alloys. When considering the possible cell microstructure of AMg alloys, it should be taken into account that aluminium atoms are trivalent and magnesium atoms are divalent. In this regard, the localisation of atoms in the cubic subsystem of the face-centred cubic lattice of aluminium is unlikely. The localisation of magnesium atom in the cubic subsystem of the aluminium cell would lead to the creation of lattice defects in the form of vacancies, which in turn would lead to a decrease in the strength of the crystal cells, which contradicts the experimental data that any alloy of aluminium with magnesium is stronger than pure aluminium (Table 1). It has been observed that the strength of aluminium cell-based alloys increases significantly when the mass fraction of magnesium in the alloys increases, and consequently the number of magnesium atoms in aluminium cells [12].

Due to the fact that the localisation of magnesium atoms in the cubic subsystem is difficult, hence the localisation of magnesium atoms in the alloy is very likely to occur in the rhombic subsystem of aluminium cells (atoms 1, 2, 3, 4, 5, 6, Figure 1). A fact showing that strengthening intermetallic compounds can be formed on the basis of the rhombic subsystem of the aluminium cell is the known intermetallic compound of manganese in aluminium Al_6Mn [16]. The manganese in Al_6Mn compound has embedded inside the rhombic subsystem of the aluminium cell. There are 6 aluminium atoms per one manganese atom in this Al_6Mn intermetallide. Exactly 6 aluminium atoms are located in the rhombic subsystem of the aluminium cell. The aluminium cell containing the Al_6Mn group contains 15 atoms - 14 aluminium atoms and one manganese atom. It was showed the possible configuration of this Al_6Mn intermetalide inside the aluminium cell at Figure 1, Supplementary Material.

It was revealed that in alloy AMg3 in all cells of the alloy contains on the average on 1 atom of magnesium after calculation of average statistical distribution of magnesium atoms. At the same time, all cells of the alloy still contain 14 atoms, of which the rhombic subsystem contains six atoms. If the embedded atoms of magnesium in AMg alloys led to an increase in the number of atoms in the unit lattice, an increase in the density of AMg alloys would be observed. However, this did not occur. For example, in the aluminium alloy AMn (containing 1.5 mass % manganese), 10% of the alloy cells have 15 atoms in their composition, which led to an increase in density to 2730 kg/m^3 (the density of pure aluminium is 2700 kg/m^3).

The analysis showed that five trivalent aluminium atoms and one divalent magnesium atom cannot form a one-position heterovalent solid solution. There is always one unoccupied valence bond and this makes the compound unstable. Therefore, if it assumes that in the alloy AMg3 in half of the cells there is no magnesium, in the other half of the cells there are two atoms each of magnesium in the rhombic subsystem of the AMg alloy cell in the form of solid solution Mg_2Al_4, then the average statistical distribution of magnesium atoms in the AMg3 alloy will still be as follows equal to one (Figure 2, Supplementary Material). Mg_2Al_4 is an electronically coupled alpha phase solid solution. There are 2 magnesium atoms and 4 aluminium atoms at the 6 atoms in the rhombic subsystem. Aluminium atoms 1 and 2, Figure 1 have been replaced by magnesium atoms in the rhombic subsystem. Half of the cells of AMg3 alloy not containing magnesium atoms are actually pure aluminium cells (Figure 2). In these cells, as in pure aluminium, the aluminium atoms of the rhombic subsystem are not completely oxidised. This is the reason for the corrosion of pure aluminium cells in seawater. Mg_5Al_8 compound was found in AMg10 alloys but it cannot be formed in AMg1, AMg2, AMg3 alloys due to low magnesium concentration and uniform distribution of magnesium in the alloy structure [13].

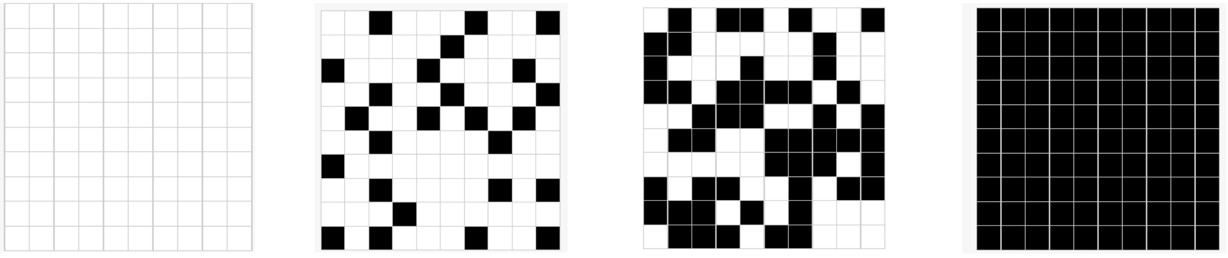

a) b) c) d)

Fig.2. Variant of the average statistical distribution of aluminium cells containing Mg_2Al_4 groups in different AMg alloys. The cells containing Mg_2Al_4 groups are marked in black: a) pure Al; b) AMg2; c) AMg3; d) AMg6.

Then in the alloy AMg2, taking into account the average statistical distribution of magnesium atoms in the alloy cells (Table 2) and taking into account the structure of the compound Mg_2Al_4, two magnesium atoms are contained in 25% of the alloy cells. On the other hand, the alloy AMg2 contains 75% of pure aluminium cells.

In the alloy AMg1 12% of cells contain the group Mg_2Al_4 and 88% of cells of pure aluminium. In alloy AMg6, on average, all cells of the alloy contain two magnesium atoms in the rhombic subsystem of aluminium Mg_2Al_4 cells. 100% of the cells of AMg6 alloy contain two magnesium atoms (Figure 2).

Thus, it is possible to assert that for magnesium from AMg1, AMg2, AMg3 to AMg6 the regularity is determined that the more aluminium cells contain the compound Mg_2Al_4 located in the solid solution of the rhombic subsystem, the higher the strength of the alloy (Table 2).

Corrosion of AMg alloys.

It is known that aluminium and all magnesiums have no corrosion in the atmosphere and in fresh water. In [12] data on corrosion of different AMg alloys in seawater were given. This data was showed in Table 2. Table 2 shows that the least corrosion in seawater in the range of alloys AMg (AMg2, AMg4, AMg5, AMg6) and PA (pure aluminium) for the alloy AMg2. According to Table 2, the corrosion rate of AMg2 alloy in seawater is 2.34 times less than that for pure aluminium. It is believed that the corrosion rate in seawater increases significantly when the mass fraction of magnesium in the alloy increases. The corrosion rate in seawater of AMg4 alloy is 45% higher than that of AMg2, while that of aluminium is 46.5% higher than that of AMg2. At the same time there is no direct dependence of corrosion rate in seawater on the magnesium content in the alloy.

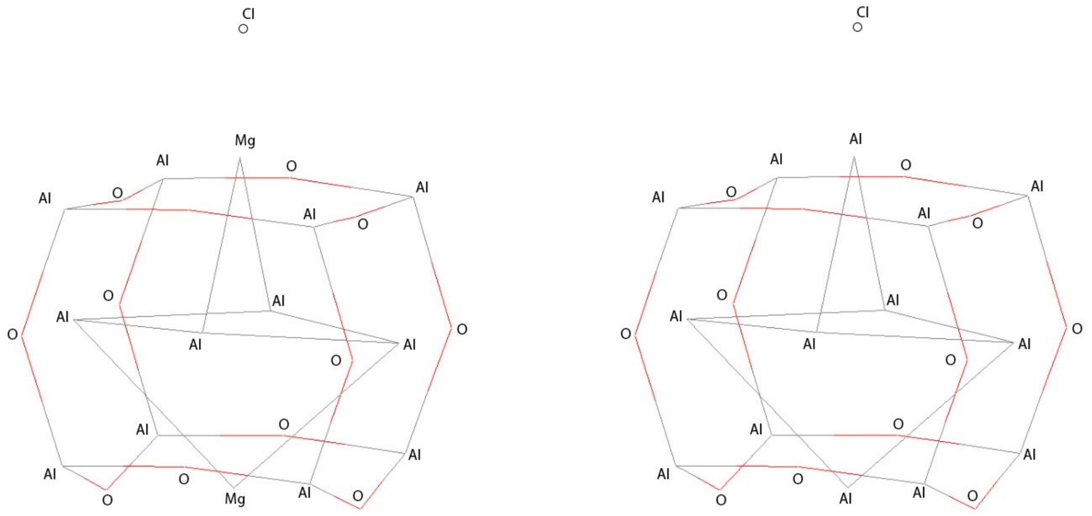
The following questions arose when analysing the data in Table 2:

Why is the corrosion rate of AMg2 alloy much lower than in pure aluminium?

Why do alloys containing more magnesium than AMg2 alloy have significantly higher corrosion rates than AMg2 alloy?

It was shown in [17] that in pure aluminium cells, corrosion of aluminium cells was possible only through the central aluminium atom 1 of the upper plane of aluminium cells (Figure 1) bordering with seawater. Aluminium atom 1 is part of the rhombic subsystem of the cubic face-centred lattice of aluminium. It was shown in [17] that corrosion of pure aluminium in seawater is caused by corrosion of the rhombic subsystem of aluminium cells, in which aluminium atoms are not oxidised. At the same time, the cubic subsystem of pure aluminium on the surface of products is completely oxidised.

Comparative calculations of the structure of pure aluminium cells and aluminium cells containing the Mg_2Al_4 group were carried out using the PM3 method (Figure 3). Since corrosion occurs on the surface of the products, it was taken into account that both types of cells were partially oxidised (cubic subsystems of cells were oxidised).



a) b)

Fig.3. Proposed detachment mechanisms of atom 1 (see Figure 1) from aluminium cells containing Mg_2Al_4 group (a), from pure aluminium cells (b).

The experiment showed that AMg2 alloy is significantly more stable in halogen solution than AMg3 alloy and pure aluminium. The calculation by the PM3 method showed that negative halogen ions produce detachment of magnesium atoms from the cells of aluminium containing the Mg_2Al_4 group. At the same time, the calculation showed that negative halogen ions produced detachment of atoms from the cells of pure aluminium in the case of pure aluminium cells (Figure 3, a), negative halogen ions could not destroy the cubic lattice subsystem in which each aluminium atom has three covalent bonds with oxygen atoms in partially oxidized cells containing Mg_2Al_4 group on the surface of products (Figure 3, b). At the same mechanism of destruction of cells in the alloy AMg2 in comparison with pure aluminium, a much lower corrosion rate was observed (Table 2). Given the data in Table 2, a question arised. If 25% of aluminium cells contain Mg_2Al_4 group, and 75% of cells are pure aluminium, and the corrosion mechanism in both types of cells is the same, then why in AMg2 alloy the corrosion rate in seawater is 46% lower than in pure aluminium?

In contrast to the works [5, 6], which focus on the corrosion processes in the interphase spaces of magnalium, our work investigates the corrosion process inside crystal grains of magnalium.

4. Experiment

In order to clarify the corrosion resistance of AMg alloys in seawater, the studied samples were placed for 72 hours in 5% iodine solution in ethanol. The experiment showed that the alloy AMg2 is significantly more resistant in halogen solution than pure aluminium and alloys AMg3, AMg6. The difference in weight loss between samples AMg2 and AMg3 was 16.8 %, between samples AMg2 and AMg6 the difference in weight loss was 23%. Between samples of AMg2 and pure aluminium (PA) the difference in weight loss was 42%, between samples of AMg6 and aluminium was 25%. The obtained results do not contradict the data of Table 2. It was necessary to consider in more detail the chemical composition of AMg2 and AMg3 alloys for explaining the obtained results, Table 3 [15]. The main alloying elements in AMg alloys are manganese, chromium, zinc, titanium. Copper in dosages from 0.15 to 0.22 has an anticorrosive effect [18].

Table 3. Chemical composition of aluminium alloys AMg2, AMg3.

Mass fraction of elements, mass %							
	Mg	Mn	Cr	Zn	Ti	Cu	Fe
AMg2	2.6	0.6	0.05	0.15	0.15	0.15	0.5
AMg3	3.8	0.6	0.05	0.2	0.1	0.1	0.5

One atom of alloying elements per cell is sufficient to either completely block the corrosion of the aluminium cell (manganese, chromium, titanium atoms) or to increase the rate of cell failure (iron). The influence of alloying element atoms was considered in more detail:

1) Aluminum cells containing manganese in the form of the intermetallic compound Al_6Mn are not destroyed in sea water, moreover, they are centers of strength, which increases the wear resistance and microhardness of AMg alloys. Also the Al_6Mn compound can capture iron atoms to form the Al_5MnFe compound (iron is usually present in aluminium and its alloys as a harmful impurity and reduces the corrosion resistance of the alloy). The formation of Al_5MnFe compounds inside aluminium cells does not allow halogens to destroy these cells and increases the strength of these cells compared to cells containing Al_6Mn compounds. Manganese atoms in aluminium alloys neutralise iron atoms, which leads to strengthening of the alloys.

2) As shown in [19], in alloys, any increase in the number of bonds with chromium atoms increased the corrosion resistance in seawater. For example, this occurs when the number of chromium atoms in the alloy was increased. Trivalent chromium atoms could be incorporated into both the cubic and rhombic subsystems of the aluminium cell lattice to form various intermetallic compounds such as $Al_{13}Cr$ (Figure 3, Supplementary Material). Also, atoms of chromium and manganese can simultaneously be in the aluminium cell, forming the compound $Al_{12}CrMn$, but given the small concentrations of chromium and manganese in the alloy AMg2, AMg3 the number of cells containing this compound is insignificant.

Taking into account the above, it can be stated that in seawater, aluminium cells containing chromium or manganese atoms, or chromium and manganese atoms simultaneously, do not corrode.

3) The embedded of titanium creates intermetallic compounds in the alloy structure that do not interact with halogen ions. This reduces the grain structure, which decreases structural corrosion.

4) Implantation of zinc into AMg alloys leads to the disappearance of anisotropy of mechanical properties in tensile strength of samples. Zinc atoms as well as magnesium atoms are divalent and at interaction of zinc with magnesium in aluminium cells instead of Mg_2Al_4 structure the compound $MgZnAl_4$

is formed. At a mass fraction of not more than 0.5 mass % zinc has an anticorrosive effect on aluminium and its alloys [8].

5) Iron is always contained as a harmful impurity in aluminium alloys - free iron always impairs corrosion resistance [3, 19].

The percentage of aluminium cells containing each of the listed atoms was calculated. The number of cells containing a certain type of atoms of alloying elements, it was calculated knowing the density of the alloys under consideration, the spatial structure of the alloy cells, and the mass fraction of each of the alloying elements in each of the alloys. The results of calculations were shown in Table 4.

Table 4. Chemical composition of aluminium alloys AMg2, AMg3.

	% of protected cells						
	Mn	Cr	Ti	Cu	Zn	Fe	Total percentage of protected cells
AMn (1,5 mass %)	10%	0%	-	-	-	-	+10
AMg2, (Mg 2.6 mass %, Cr 0.05 mass %, Mn 0.6 mass %, Zn 0.15 mass %, Ti 0.15 mass %, Cu 0.15 mass %)	+4,1	+0,36	+1.18	+0.89	+0,86	-3.36	+4.03
AMg3, (Mg 3.8 mass %, Cr 0.05 mass %, Mn mass 0.6 %, Zn 0.2 mass %, Ti 0.1 mass %, Cu 0.1 mass %)	+4.08	+0.36	+0.75	+0.6	+1.14	-3.34	+3.59

First, the maximum number of structural cells was calculated in which the atoms of these alloying elements can be located (at the rate of one alloying element atom per one structural cell). It was calculated for each alloying element, taking into account its mass fraction in alloys. The plus sign (+) in the cell of Table 4 before the figure shows that this result increases the degree of protection of the alloy from corrosion. The minus sign (-) before the figure in the cell of the table shows that this result reduces the degree of protection from corrosion. The results of calculation of the total number of protected from corrosion cells (taking into account the positive and negative influence of alloying elements) of aluminium in AMg2 and AMg3 alloys correlate with the results of our experiment on comparative corrosion of AMg2 and AMg3 alloys in seawater. The more protected from corrosion structural cells, the lower the corrosion rate of the alloy. The calculation showed that in the alloy AMg2 (Table 4) the total number of cells protected from corrosion is 11% higher than in the alloy AMg3 (Table 4). We believe that the corrosion rate of alloys is directly related to the number of corrosions protected cells of the alloy. The difference in the number of protected from cell corrosion is equal to the difference in the corrosion rate of alloys. In the case of the considered alloys AMg2 and AMg3, the theoretically calculated difference in the corrosion rate of alloys in ΔV_{teor} was equal to 11%. This result was close to the result obtained by us in the experiment on comparative corrosion of alloys AMg2 and AMg3. Experimentally determined corrosion rate in seawater in alloy AMg2 was16.8% less than in alloy AMg3 (ΔV_{exp}= 16.8%).

Some difference between the result of this model and the experimental result is due to the different number of pure aluminium cells in AMg2 and AMg3 alloys. According to the average statistical model of cell calculation (Figure 2) in the alloy AMg2 the number of pure aluminium cells is twice as much as in the alloy AMg3. In the alloy AMg3, half of the cells contain pure aluminium and the other half contains the compound Mg_2Al_4. The PM3 calculation showed that the corrosion mechanism in seawater for both types of cells is the same, but the rate of interaction with halogen ions is different. For practical use of this model of corrosion rate calculation it is necessary to use a correction factor:

$$\Delta V_{exp}= \Delta V_{teor} +K, \tag{4}$$

where K= 5.8% correction factor - for investigated alloys AMg2 and AMg3 of the given composition.

The value of K depends on the percentage of aluminium cells containing Mg_2Al_4 group. The greater the percentage, the greater the value of K, and the greater the corrosion rate of the studied alloy AMg. The corrosion rate of aluminium cells containing Mg_2Al_4 in seawater is higher than the corrosion rate of pure aluminium cells.

In the AMg3 alloy the number of cells containing Mg_2Al_4 group is 50% of the total number of cells. In alloy AMg2 number of cells with group Mg_2Al_4 is 25% less. In the case of the studied alloys AMg2 and AMg3 correction factor K = 5.8% is due to 25% difference in the number of cells containing the group Mg_2Al_4. Then for AMg alloys containing any number of cells (from AMg0.2 to AMg3.5) the correction factor K was calculated by the formula.

$$K= 0.232 * \Delta N, \qquad (5)$$

where, ΔN is the difference between the percentage of cells containing Mg_2Al_4 in the alloy AMg2 and the percentage of cells with Mg_2Al_4 in the studied AMg alloy. The alloy AMg_2 contains 25% of cells with Mg_2Al_4 group. For analysed AMg alloys with a percentage of cells with Mg_2Al_4 group less than 25%, the correction factor is applied with a minus sign.

It is possible to calculate the change in the corrosion rate of known AMg alloys with a fairly good accuracy when changing the percentage of alloying elements, using the calculation model that takes into account the average percentage of alloy cells protected from corrosion. The model is not intended for calculation of corrosion resistance of AMg alloys with magnesium content in the alloy of 4 and more %of the mass fraction. This limitation on the use of the model is due to the fact that starting from 4% of magnesium content the solid alpha solution of AMg alloy is oversaturated with magnesium) [20].

For example, it was calculated the change in corrosion rate of the modified alloy AMg2+Mn (0.2 mass %) (Mg - 2.6 mass %, Cr -0.05 mass %, Mn - 0.8 mass %, Zn -mass 0.15 mass %, Ti -0.15 mass %, Cu - mass 0.15%, Fe -mass 0.5%). Since the percentage of cells containing the Mg_2Al_4 group has not changed the correction factor is not used. In this alloy the mass fraction of manganese is increased by 0.2 mass % in comparison with the standard alloy AMg2 (Mg - 2.6 mass%, Cr -0.05 mass %, Mn - 0.6 mass %, Zn - 0.15 mass %, Ti - 0.15 mass %, Cu - 0.15 mass %). It is known that if the mass fraction of Mn is less than 1 mass %, the brittleness of aluminium alloys does not increase. In this way increasing the mass fraction of manganese in the alloy AMg2 up to 0.8 mass % should increase the strength of the alloy and corrosion resistance, without increasing brittleness. The change in the number of corrosion-protected cells of alloy AMg2 was calculated when the mass fraction of manganese increases by 0.2 mass %. The percentage of corrosion-protected cells of AMg2 alloy increased to 5.04% of the total number of cells of the alloy. Increasing the number of corrosion-protected cells should reduce the corrosion rate by 14% compared to the standard alloy AMg2.

Further it was calculated the change in corrosion rate of modified alloy AMg2+ Cr 0.55%, (Mg - 2.6 mass %, Cr - 0.6 mass %, Mn- 0.6 mass %, Zn- 0.15 mass %,Ti - 0.15 mass %, Cu- 0.15 mass %, Fe - 0.5 mass %). Since the percentage of cells containing Mg_2Al_4 group did not change the correction factor is not used. In the studied alloy AMg2 the chromium content is increased to 0.6 mass %. It is known that there are no technical problems in melting aluminium alloy if the mass fraction of chromium does not exceed 0.7 mass % [21]. When the mass fraction of chromium is 0.6 mass % in AMg2 alloy, the percentage of cells protected by chromium will increase to 4.32 mass %, of the total number of cells. The total number of protected cells at increasing the mass fraction of chromium to 0.6 mass % in the alloy AMg2 increased to 8%. At the same time, the corrosion rate of AMg2 alloy decreased by 34% compared to the standard AMg2 alloy with chromium content of 0.05 mass %.

Furthermore, it was calculated the modified alloy AMg2 in which the mass fractions of manganese and chromium were increased simultaneously AMg2 + Cr 0.55 mass % +Mn0.2 mass % (Mg - 2.6 mass %, Cr - 0.6 mass %, Mn - 0.8 mass %, Zn - 0.15 mass %, Ti - 0.15 mass %, Cu - 0.15 mass %, Fe - 0.5 mass %). Since the percentage of cells containing Mg_2Al_4 group has not changed the correction factor is not used. In this modification of AMg2 alloy, the percentage of protected cells reached 13.4 %, which reduced the corrosion rate by 54.9 % compared to the standard AMg2 alloy (Table 2).

Taking into account the results of the article [17], it was assumed that if cells without magnesium atoms are completely oxidized in the AMg2 alloy, these completely oxidized cells will stop to interact with halogen ions from seawater. The corrosion resistance of the treated AMg2 alloy will increase significantly. It is necessary to oxidize 75% of the alloy cells on the surface of the products.

AMg2 samples were placed in a 5% iodine solution in ethyl alcohol for 72 hours to test the hypothesis shown above. The corrosion resistance of untreated AMg2 samples and AMg2 samples exposed to ozone for 6 hours at a temperature of 190 °C. was studied. Ozone was generated by ultraviolet radiation from atmospheric oxygen. The experimental method is described in detail in the article [19]. The choice of a temperature of 190 °C during sample processing was chosen due to the fact that the source [13] shows that the physico-chemical properties of AMg alloys deteriorate sharply when these alloys are heated above a temperature of 210 °C. This phenomenon was caused by a change in the internal structure of the cells containing a magnesium atom, as the beta phase of Al_3Mg_2 is formed [14].

The surfaces of the untreated AMg2 sample after 72 hours in the iodine solution and the sample pretreated for 6 hours of ozone treatment with AMg2 after 72 hours in the iodine solution are shown in Figure 4.


a) b)

Fig.4. Photographs of the surface of samples exposed to alcohol solution of iodine for 72 hours: a) an untreated AMg2 sample; b) a sample treated with ozone for 6 hours.

Significant surface damage is recorded on the surface of the untreated AMg2 sample (Figure 4, a). Only a small pitting corrosion was observed on the surface of the ozone-treated AMg2 sample (Figure 4, b). If the untreated AMg2 alloy sample lost 5.74% of its mass in 72 hours, then the sample subjected to ozone treatment lost 4.23% of its mass within 6 hours. The experiment showed a significant increase in the corrosion resistance by 26% of the surface of the AMg2 alloy treated with ozone for 6 hours.

Thus, the surface treatment of AMg2 alloy products with ozone at a temperature of 190 ° C can be recommended in order to increase corrosion resistance in seawater.

5. Conclusions

1) The analysis showed that the corrosion resistance of AMg2, AMg3 alloys depends on the percentage of aluminium cells containing manganese, chromium, titanium, zinc, copper, iron and magnesium atoms. The combined effect of these elements increases or decreases the corrosion resistance of AMg alloys in seawater. In seawater destruction of structural cells in pure aluminium and in cells of AMg alloys containing Mg_2Al_4 compound occurs by the same mechanism, but at different rates. There is a detachment by the negative halogen ion of the central aluminium or magnesium atom located on the outer edge of the alloy cells. Aluminium cells containing the compound Mg_2Al_4 are destroyed faster than pure aluminium cells.

2) The developed model of calculation of change in corrosion resistance of AMg2 and AMg3 alloys showed results close to those obtained in the experiment.

3) It is recommended to use AMg2 alloys with increased manganese and chromium content in marine atmospheres:

a) In the modified alloy AMg2 (Mg - 2.6 mass %, Cr - 0.05 mass %, Mn - 0.8 mass %, Zn - 0.15 mass %, Ti - 0.15 mass %, Fe - 0.5 mass %) the amount of manganese has been increased by 0.2 mass % compared to the standard alloy AMg2. The corrosion rate in this modification of AMg2 alloy have been reduced by 14 % compared standard AMg2 alloy with manganese content of 0.6 mass %;

b) In the modified alloy AMg2 (Mg - 2.6 mass %, Cr - 0.6 mass %, Mn - 0.6 mass %, Zn - 0.15 mass %, Ti - 0.15 mass %, Cu - 0.15mass %, Fe - 0.5mass %) the amount of chromium has been increased by 14 times compared to the standard alloy AMg2. The corrosion rate in this modification of AMg2 alloy have been reduced by 34% compared to the standard AMg2 alloy with chromium content of 0.05 mass %;

c) In the modified alloy AMg2 (Mg - 2.6 mass%, Cr - 0.6 mass%, Mn - 0.8 mass%, Zn - 0.15 mass %, Ti - 0.15 mass%, Cu - 0.15 mass%, Fe - 0.5 mass%) the amount of chromium has been increased by 14 times in comparison with the standard alloy AMg2 and the amount of manganese have been increased by 0.2 mass% compared to the standard alloy AMg2. The corrosion rate in this modification of AMg2 alloy have been reduced by 54.9% compared to the standard AMg2 alloy with chromium content of 0.05 mass% and manganese content of 0.6 mass%.

d) Additional oxidation of the AMg2 alloy surface with ozone significantly reduces the rate of corrosion by 26% in seawater.

Conflict of interest statement
The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

CRediT author statement
Guchenko S.A.: investigation, writing - original draft; **Seldyugaev O.B.:** conceptualization, writing - review & editing; **Fomin V.N.:** investigation, formal analysis; **Afanasyev D.A.:** visualization, writing - review & editing.
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