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REASON OF CORROSION OF ALUMINIUM PRODUCTS IN SEA WATER

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In this paper, the cause of corrosion of aluminium products in sea water is proposed. Corrosion is caused by incomplete oxidation of aluminum cells on the surface of products. Incomplete oxidation of aluminium cells occurs due to lack of energy in oxygen molecules. It is necessary to significantly increase the energy of oxygen molecules for oxidation the rhombic subsystem of a cubic face-centered aluminum cell. It is shown a significant decrease in the rate of the chemical reaction for the treated aluminium foil interacted with iodine in alcohol solution. The foil was in contact with oxygen heated to 450 °C and subjected to ultraviolet irradiation at the same time. It was pretreated for 12 hours. It is assumed that 12 hours of contact the foil with reactive oxygen species, most of the aluminium cells on the surface of the foil samples have been completely oxidised. This foil doesn't react chemically with halogens.

Keywords: Quantum-chemical calculations, aluminium, alumina, cubic subsystem, oxidation, halogens.

1. Introduction

Due to the fact that the development of new alloys with given properties is a time-consuming and expensive process, the use of techniques that allow to exclude obviously inefficient areas of research is a very relevant task [1-6]. One of the most promising methods for such a choice is quantum-chemical calculation methods. However, when using these methods, the question of confidence in them very often arises. In order to find out the degree of such trust, it is possible to carry out verification calculations of known objects and to determine the degree of correspondence of the results of such calculations to reality. If the results of the calculations coincide with experimental data, these types of calculations can already be used to predict the properties of newly developed alloys [2, 5].

On the other hand, to conduct quantum chemical calculations require large computing power, while the amount of time used depends on the number of electrons in the electron shell of the atoms of the investigated metals. The number of electrons in the electron shell increases too with increasing order number of metal in the periodic table. It dramatically increases the complexity and time of quantum-chemical calculations. In this regard, it was decided to test possibility to calculate the crystal structure of metals. The calculation is carried out on the example of light metal atoms, located in the first 3 rows of the periodic system of Mendeleev. For such calculations semi-empirical parametric method 3 can be used which allows calculating parameters of atoms having electrons on s- and p- electron shells in atoms [7].

In addition, this parametric method 3 was originally designed to calculate compounds containing elements such as aluminium, oxygen and all halogens [8].

Therefore, the metal aluminium, which is widely used in production and whose properties are fairly well known, is the most suitable object for the verification calculations.

2. Materials and experimental details

The structure of aluminium and its oxidised forms was calculated using the parametric method 3, which was specially developed for calculations of compounds containing aluminium and halogen atoms [8]. In the aluminium unit cell model 14 atoms were present for the calculations. When modeling the oxidation process of the cubic subsystem of the face-centered cubic lattice of aluminium, 12 atoms of oxygen were added. To determine the effect of oxygen simultaneously on the cubic and rhombic subsystems of the aluminium lattice, 13 to 21 oxygen atoms were used. Models in which there was a gradual increase in the number of oxygen atoms in the rhombic subsystem of the aluminium lattice with a fully oxidised cubic subsystem were used. The presence of even one oxygen atom in the rhombic subsystem completely stops the chemical interaction of the oxidised aluminium cell with halogen ions and a further increase in the number of oxygen atoms in the rhombic subsystem also blocks the chemical interaction with halogens.

Up to 4 halogen ions were used to evaluate the nature of the interaction of negative halogen ions with the lattice models of oxidised aluminium. Four different halogens (chlorine, bromine, iodine, fluorine) were used.

Experiments with different samples of untreated and treated aluminium were performed to verify the results of the calculations. Untreated aluminium foil samples, corundum (aluminium oxide, with a share of aluminium oxide more than 99 % wt.) and treated aluminium foil samples were used. All these samples were placed in an alcohol solution containing 5 % wt. of iodine. The mass of the samples before and after placing them in the solution was measured on a RADWAG AS 60/220.R2 electronic scale. The measurements were carried out with an accuracy of up to ten thousandths of a gram.

Untreated aluminium foil samples with a share of aluminium not less than 99,5 % were used for the experiment. Treated samples were obtained by heat treatment and treatment under an ultraviolet lamp of the air entering the surface of the samples. The aluminium foil samples and the air entering these samples were heated to a temperature of 450 °C with simultaneous irradiation of the incoming heated air by the ultraviolet radiation of the DRT-400 lamp. The DRT-400 lamp produces broadband ultraviolet radiation in the range from 220 nm to 340 nm.

3. Results and discussion

First of all, the parametric method 3 was used to calculate the structure of a single aluminium cell which can be represented as a rhombus within a cube, i.e. as a face-centered cubic lattice [9]. In such lattices each side of the cube has an aluminium atom in its centre - 8 aluminium atoms are in the nodes of the cubic subsystem (atoms 7-10 and 11-14) and 6 aluminium atoms are in the rhombic subsystem of the face-centered cubic lattice (the aluminium atoms of the rhombic subsystem are in the centre of the cube sides (atoms 1, 2, 3, 4, 5, 6), Figure 1. There are no atoms in the centre of the aluminium lattice, which makes aluminium well malleable. The numbering of aluminium atoms is the same in all the presented figures, Figures 1-5.

Calculation shows that on aluminium atoms of cubic subsystem of the cell positive charges are localised (from +0.1 the value of the electron charge (electron) to +0.2 electron), and on aluminium atoms of rhombic structure negative charges are localised (from -0.2 electron to -0.25 electron). This type of charge configuration gives more stability to the aluminium cell (each of the positively charged aluminium atoms in any of the faces is attracted to a negatively charged aluminium atom located in the centre of the face). At the same time localisation of enough big negative charges in the centre of aluminium cell faces stabilises geometry of aluminium cell (aluminium cell cannot collapse) because of electrostatic repulsion of negative charges located in the centre of every face from each other. The cell of pure aluminium can also be represented as a system consisting of three planes: the central negatively charged plane (atoms 3, 4, 5, 6) is attracted to the two positively charged outer planes, the upper (atoms 7, 8, 9, 10) and the lower (11, 12, 13, 14). Atoms 1, 2 have negative charges localised on them, Figure 1.

Further calculations were carried out for a partially oxidised aluminum cell. It is known that when interacting with oxygen, the surface of aluminium is covered with a strong, chemically inactive aluminium oxide film 30 Å or thicker [10]. This film protects pure aluminium from the aggressive effects of the external environment. The oxidation of the aluminium cell was calculated. Variants of the interaction of the aluminium cell with a varying number of oxygen atoms from one atom to twelve atoms were calculated (the variant in which complete oxidation of the face-centered cubic aluminium cell structure), Figure 2.

Calculations have shown that the oxygen atoms form covalent bonds with the aluminium atoms in the cubic lattice of the aluminium unit cell.

The general symmetry of the aluminium cell at full oxidation of the cubic subsystem practically does not change. Preservation of symmetry to a certain extent proves the correctness of the calculation, because under severe strain in the cells of oxidised aluminium a film of aluminium oxide, poorly adhering to the surface of pure aluminium and poorly protecting the surface of pure aluminium from chemical interactions, should arise. An example of this type of oxide film weakly adhering to the metal surface is the rust that forms on the surface of iron products during iron oxidation [11]. However, it is known that the oxide film on the surface of aluminium is very strongly bonded to the mass of pure aluminium underneath the film. During oxidation of cubic subsystem of aluminium cell the distribution of charges in the cell changes - on all oxidised aluminium atoms of cubic subsystem positive charges (+0.18 electron, +0.22 electron) are localised: on aluminium atoms number 1, 2, 4, 6 of rhombic subsystem very significant positive charges +0.7 electron are localised.

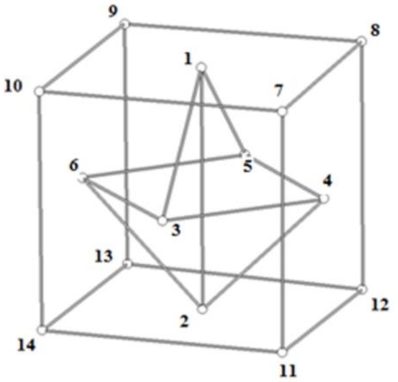

Fig.1. Schematic diagram of the pure aluminum crystal lattice.

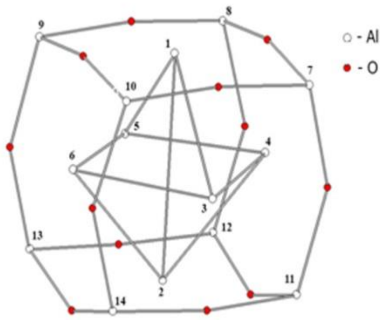

Fig.2. Face-centered cubic lattice of an oxidised aluminum cell. Only the cubic subsystem of the face-centered lattice is oxidised. Oxygen atoms are red circles.

Negative charges are localised on all oxygen atoms and aluminium atoms number 3, 5, Figure 2. Thus, around an aluminium cell with oxidised cubic subsystem an electrostatic field is established which allows chemical interaction of negative ions with an aluminium cell only if the negative ions are in close proximity to aluminium atom 1, Figure 2.

Nevertheless, some atoms can pass through the oxide aluminium film as it is known. For example, that the thickness of oxide layer on the surface of aluminium can be significantly increased when aluminium is heated up to 450 °C. The increase in thickness of oxide layer on aluminium surface indicates that this oxide layer is permeable to oxygen molecules or atoms. It is also known that seawater degrades aluminium products over time [12]. The degradation of the mass of pure aluminium under the aluminium oxide film can occur either from the destruction of the oxide film (unlikely as aluminium oxide is a chemically strong compound) or from the penetration of chemically active elements (such as halogen ions) under the oxide film [12].

In order to clarify the mechanism of aluminium surface destruction in seawater, calculations have been made for the interaction of aluminium cells with fully oxidised cubic lattice subsystems with halogen ions (chlorine, bromine, iodine, fluorine) present in large quantities in seawater [13]. Calculations have shown that there is no chemical interaction of negatively charged halogen ions with aluminium atoms located in oxidised cubic sublattices of aluminium cells. Any one of the aluminium atoms in the cubic sublattice is chemically bonded to the three nearest oxygen atoms, together forming an oxidised aluminium film, Figure 3. Thus, the negatively charged halogen ions present in seawater cannot destroy the structure consisting of oxidised aluminium atoms (the halogen ions are in physical interaction with the cubic lattice subsystem of aluminium, forming an ion- halogen shell around the aluminium surface).

However, it is known from experience that products made of aluminium in seawater corrode and cause damage to these products. Taking into account abovementioned facts we can draw conclusion that corrosion of aluminium ware in sea water occurs because of destruction of rhombic sublattice of aluminium cells (fully oxidised cubic sublattice of aluminium is chemically inert): halogen ions can cooperate only with aluminium atom located in the centre of outer surface of aluminium cell (in this atom is designated as atom number 1, this atom is a part of rhombic sublattice), Figure 1. Calculations showed a very strong interaction of negatively charged halogen ions with aluminium atom number 1 in the aluminium cell. In fact, the halogen ions tore this aluminium atom out of the cell structure aluminium, Figure 4.

Calculations showed that bromine and fluorine ions interact most strongly with the central atom of the aluminium surface. It was shown that bromine or fluorine ion interacts with the central aluminium atom number 1 of the outer plane of the oxidised aluminium cell, the bond length between the aluminium atoms number 1 and number 2 increases considerably and the aluminium atom number 1 extends beyond the aluminium cell, Figure 4. The bond length between aluminium atom number 1 and number 2 increases by 0.9 Å when interacting with the bromine ion (and by 1.3 Å when interacting with the fluorine ion), Figure 4. Actually, it corresponds to the tearing out of the structure of the non-oxidised cubic subsystem of the aluminium cell by aluminium atom number 1. When interacting with iodine and chlorine ions, the bond length increases by no more than 0.6 Å, i.e. the ions of these halogens also produce the destruction of the aluminium surface, but at a slower rate than the fluorine and bromine ions.

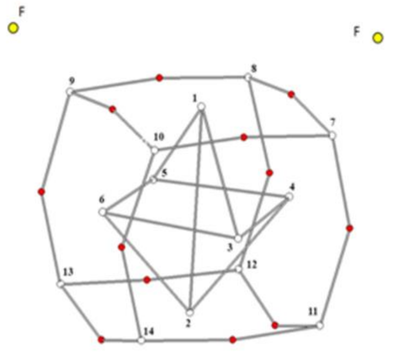

Fig.3. Scheme of the interaction of halogen ions with the oxidised cubic sublattice of aluminum cells.

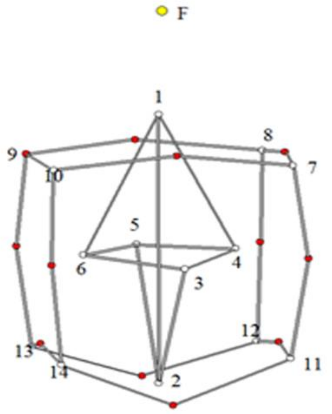

Fig.4. Interaction of the fluorine ion with the central atom of the aluminum cell.

In order to determine whether under normal conditions the oxidation of aluminium atoms in a rhombic subsystem was possible, we calculated the possible interaction of halogen ions with the oxidised aluminium cell taking into account that the oxygen atom localised in the centre of the aluminium cell with the formation of a covalent bond with the aluminium atom number 1 (this aluminium atom is in the centre of the aluminium cell outer plane) and aluminium atom number 2 (this aluminium atom is in the centre of the aluminium cell lower plane), Figure 4. It was assumed that the rhombic subsystem was a covalent bond with the aluminium atom number 1. All aluminium atoms (7, 8, 9, 10, 11, 12, 13, 14) of the cubic subsystem of the face-centered structure of the aluminium cell are covalently connected with oxygen atoms, Figure 5. That is, the whole cubic subsystem of the aluminium cell is oxidised, and in the rhombic subsystem aluminium atoms number 1 and number 2 are partially oxidised.

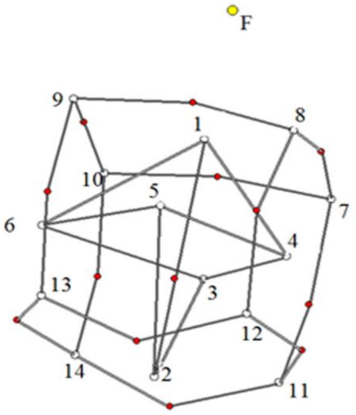

Fig.5. The interaction of the fluorine ion with the aluminum atom number 1. This aluminum atom is in a chemical bond with an oxygen atom that has penetrated into the center of the cell.

Calculations have shown that in the oxidised aluminium cell during the interaction of the aluminium atom number 1 with a negative fluorine ion (iodine, chlorine, bromine) the distance increased by 0.3 Å between the oxygen atom in centre of the cell and aluminium atom number 1, i.e. the distance is practically unchanged, Figure 5. This means that there is no tearing of aluminium atom number 1 from aluminium cell (no chemical reaction between negative halogen ion and aluminium atom number 1), Figure 5. There is no damage to the structure of aluminium cell. The variants of calculation of interaction of halogen ions with an aluminium cell with various degrees of oxidation of rhombic subsystem up to full oxidation of rhombic subsystem (with fully oxidised cubic subsystem) also revealed complete absence of chemical interaction of negative halogen ions with the central atom of the upper plane of the aluminium cell (aluminium atom number 1). If aluminium cells under normal conditions is fully oxidised both subsystems - cubic and rhombic (such system is known as corundum), it is known from practice that in seawater containing halogen ions (chlorine, iodine, bromine, fluorine) the destruction of aluminium products still occurs.

Further comparison of calculation results with known facts about corrosion of aluminium surface in sea water was made [12]. Thus, in normal conditions (medium temperature 20 °C, pressure 10^5 Pa., oxygen 21 vol. % in atmosphere oxidation of aluminium atoms (numbers 1, 3, 4, 5, 6, 2,) of rhombic subsystem of face-centered cubic lattice of aluminium cell does not occur Figure 2, 4 [14, 15].

It is due to the fact that under normal conditions the rhombic cell structure of aluminium products is not oxidised and corrosion of aluminium products in sea water occurs. This allows us to conclude that the destruction of the surface of oxidised aluminium in seawater begins at the central aluminium atom (atom 1 of aluminium) of the face (this square consists of atoms numbers 7, 8, 9, 10, 1) of the face-centered cubic lattice bordering sea water, Figure 4. All other aluminium atoms (numbers 7, 8, 9, 10) at the surface bordering seawater are in an oxidised state (chemically inert), Figure 3.

To verify the results of the calculations, experiments were carried out with different aluminium samples:

1) Untreated aluminium foil was placed for 24 hours in 5 % wt. of iodine in alcohol solution at 20 °C. The given aluminium foil sample has almost completely dissolved in iodine solution, which corresponds to the literature data [16]. It does not contradict results of the calculations according to which aluminium film in which cubic subsystem is completely oxidised, but rhombic subsystem is not, is destroyed through interaction of negative halogen ions with the central atom of the outer side of the oxidised aluminium cell.

2) A fully oxidised aluminium (corundum) grade plate was also placed at the alcohol solution of iodine. The mass of the corundum plate did not change during this period of time. The measurements were taken with an accuracy of ten thousandth of a gram on electronic brand scales. Corundum was used in the experiment as a fully oxidised form of aluminium in which both the cubic and rhombic subsystems were completely oxidised in all cells. The absence of change in the mass of the corundum plate is consistent with the calculation results that there is no chemical interaction with halogen ions in the aluminium cell with fully oxidised cubic and rhombic subsystems, Figure 5. That is, the experimental results showed a very strong interaction of the halogens with the aluminium surface where there are no fully oxidised aluminium cells. It also showed a complete lack of chemical interaction with the surface where all the aluminium cells are fully oxidised.

It was assumed, that the time of dissolution of common aluminium foil in iodine solution would increase, if a certain number of cells on the surface of the aluminium foil were completely oxidised: It was supposed that the more aluminium cells were completely oxidised, the longer would be the dissolution time of the aluminium foil. In order to develop a technique to create conditions for the complete oxidation of aluminium cells on the aluminium surface it was assumed that under normal conditions for the oxidation of the rhombic subsystem of the aluminium cell oxygen molecules do not have enough energy (vibrational and electronic energy of oxygen molecules) to overcome the potential barriers around the aluminium atoms of the rhombic subsystem. If the energy of oxygen molecules increases more than some value, aluminium atoms of rhombic subsystem will start to oxidise in aluminium cells bordering with the atmosphere containing oxygen.

In order to increase vibrational and electronic energy of oxygen molecules the samples of aluminium foil and incoming air were heated up to 450 °C with the simultaneous irradiation of incoming heated air by ultraviolet radiation (DRT-400 lamp). Heating the air to 450 °C increased the vibrational energy of oxygen molecules. Broad-band ultraviolet radiation (220 nm – 340 nm) generates ozone O_3 formation and transfers oxygen molecules from the basic chemically inactive triplet state $^3O_2$, to the excited singlet state $^1O_2$ (the singlet state energy $^1O_2$ is 0.98 electron volt higher than the basic triplet state $^3O_2$) [17]. Ozone O_3 and singlet oxygen $^1O_3$ have a significantly higher chemical activity than oxygen molecules in the ground triplet state [18]. Samples of aluminium foil were exposed to reactive oxygen species at 4 and 12 hours. The treated aluminium samples were then placed for 24 hours in containers with the alcohol solution of iodine. As a result, it was found that the aluminium sample placed under ultraviolet radiation at 450 °C for 4 hours lost during 24 hours in the alcohol solution of iodine ~ 70 % of its weight (the weight of the aluminium sample before placing it into the iodine solution was 0.0287 grams, after 24 hours the sample weight was 0.0088 grams, but it remained intact, unlike the sample of the same aluminium foil which has not undergone any treatment.

The aluminium foil sample that was placed under ultraviolet radiation at 450 °C for 12 hours lost only ~ 5 % of its weight in a 5 % wt. alcohol solution of iodine during one day (the weight of the foil sample before placing it into the iodine solution was 0.0367 grams, while after one day, the sample weighed 0.0350 grams). A protective layer has formed on the surface of the aluminium foil sample subjected to the 12-hour treatment. This protective layer doesn't react chemically with halogen ions. The fact that the sample of aluminium subjected to the 4-hour treatment isn't completely dissolved in a solution of iodine. It indicates that in this sample such a protective layer was also formed, but this protective layer didn't cover the entire surface of the sample. That is not in all cells of the aluminium on the surface of the aluminium foil occurred complete oxidation (Table 1).

Table 1. Weight loss of aluminium samples after being in an alcoholic solution of iodine, the surface of which was or wasn't subjected to surface treatment with reactive oxygen species.

	Untreated aluminium sample	Aluminium sample after 4 hours processing	Aluminium sample after 12 hours of processing	Corundum (100 % oxidized aluminium)
Weight loss of aluminium samples %	100 %	70 %	5,5 %	0 %

Thus, experimentally, a dependence of the magnitude of the protective effect of exposure to halogens on the time of exposure to ultraviolet radiation on the surface of aluminium products at 450 °C was found. The protective effect is due to the complete oxidation of a large number of aluminium cells on the surface of the products - the longer the time of exposure to oxygen active forms on the aluminium samples, the more completely oxidised aluminium cells are formed on the surface of the products, the lower the corrosion rate of the aluminium products. If all cells on the surface of aluminium products are completely oxidised (this condition is called corundum), corrosion of the aluminium product in halogen solution stops completely.

4. Conclusions

Thus, it is advisable to create a layer of fully oxidised aluminium cells on the surface of these products for increasing the wear-life of aluminium products in seawater.

1) It has been shown that parametric method 3 of the quantum-chemical calculation can be used to calculate the metals belonging to the first three periods of the Mendeleev table.

2) It has been shown by calculation and experiment that the failure of aluminium products is caused by incomplete oxidation of the surface aluminium cell structure (under normal conditions the rhombic subsystem of the aluminium cells is not oxidised, under fully oxidised cubic sub-system). Insufficient oxidation of aluminum cells leads to destruction of the rhombic subsystem of the cells by negative halogen ions, which are contained in large quantities in seawater. Destruction of rhombic subsystem of aluminium cells occurs because of chemical interaction of negatively charged halogen ions with aluminium atoms of rhombic subsystem: aluminium atoms of fully oxidised cubic subsystem do not enter into chemical interaction with halogen ions. The incomplete oxidation of aluminium cells is due to the lack of energy of oxygen molecules under normal conditions.

3) In order to increase the life span of aluminium products in seawater, it is recommended to create a monolithic corundum layer on the surface of these products (a layer in which all aluminium cells have a fully oxidised rhombic and cubic subsystem): the surface of aluminium products treated with ultraviolet irradiation and heated to 450 °C should be treated for at least 12 hours. It is necessary to create a monolithic layer of fully oxidised aluminium cells at least 1 cell thick on the surface of an aluminium product for achievement a protective effect.

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