Principles of creating new alloy compositions for the production of cast protectors

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Abstract. Aluminum protectors are used in cathodic systems for protecting metal structures from electrochemical corrosion. The materials of the article are devoted to the selection of elements for alloying aluminum, based on the analysis of physicochemical, technological and electrochemical characteristics of the alloy base and elements of the periodic system named after D.I. Mendeleev. Zn, Mg, Mn, Ti and Zr were selected as the main alloying components by the tendency of elements to alloy formation and to obtain a homogeneous structure, taking into account their effect on the anodic activity and resistivity of oxides on the metal surface. The obtained research results are in good agreement with the well-known international standards for the chemical compositions of aluminum tread alloys, for which magnesium, zinc, and manganese are present as the main alloying components. For experimental studies, Mg, Zn, Mn were chosen as alloying additives, and Si, Fe as impurities. The optimal concentration range of the aluminum alloy will be as follows: for zinc, 3.6-5.4; for magnesium, 0.55-1.05; for manganese 0-0.3. The content of Si and Fe in the alloy is limited to 0.06 and 0.01\%, respectively. The maximum value of the CUE - 75.78\%.

1. Introduction
Aluminum protectors are widely used in cathodic protection systems of metal building and structures from electrochemical corrosion [1-7]. Known compositions of aluminum-based alloys do not fully meet modern requirements for sacrificial materials for basic electrochemical characteristics [8-13]. Due to the constant expansion of the fields of application of cathodic protection and the increasing requirements for its service life, it becomes necessary to create alloy compositions with new stably specified characteristics. To achieve this goal, it is necessary to single out solutions to the following tasks:
- increasing the current efficiency of alloys with reduced anode activity;
- increasing the electronegative potential of the alloys with increased anode activity;
- providing at least 80% of the actual current output of alloys having different anode activity.

The methodology for the synthesis of alloy compositions with desired properties is based on a combined consideration of the metal-chemical, technological and other special characteristics of the elements of the Periodic system in conjunction with the base element of the alloy [14-18].
This work sets out the basic principles for choosing alloying elements for aluminum on the base of a comparative assessment of their tendency to alloy formation, taking into account the nature of changes in the physical and electrochemical properties of alloys and dissolution products.

2. Methods
Experimental samples for research were obtained by pouring the melt into special forms. Electrochemical tests were carried out in a 3% aqueous NaCl solution during 14 days.

Calculations of the theoretical and actual current recovery of the experimental alloys were carried out according to the following formulas:

\[ Q_T = \frac{1000 \cdot a_{all}}{A \cdot h/kg} \]  
\[ Q_F = \frac{I \cdot T}{\Delta m} \cdot A \cdot h/kg \]

where \( a_{all} \) is the electrochemical equivalent of the alloy, g / A · h; 
\[ a_{all} = \Delta m_1 \cdot a_{m1} + \Delta m_{12} \cdot a_{m2} + \cdots + \Delta m_l \cdot a_{ml}, \ g/A \cdot h \]

\( a_{mi} \) is the electrochemical equivalent of the alloy component, g / A · h; 
\( \Delta m_{mi} \) is the mass fraction of the component in the alloy; 
I is the current strength, A; 
T is the time of the electrochemical tests, h; 
\( \Delta m \) is the change in mass of the sample, kg.

The average values of the actual current output were determined by three parallel samples. The coefficient of use efficiency (CUE) was determined by the formula:

\[ \eta = 100 \cdot \left( \frac{Q_F}{Q_A} \right), \ % \]

To study the structure of samples from these alloys, we used the light microscopy method, which allows us to study the metal structure on sections using a Nikon Epiphot TME200 microscope.

3. Results and discussion
An analysis of information on the manufacturability of the alloying process by comparing the melting temperatures and densities of aluminum and elements (Fig. 1) indicates the possibility of separating elements into fields A, B and C, closed by semicircles with radii \( R_a, R_b \) and \( R_c \), respectively. Obviously, the elements of field A should be considered as maximally favorable for aluminum alloying, while those located in field C are unacceptable due to significant deviations of physical properties comparable with aluminum. The separation of elements into I-III groups (Table 1) characterizes the degree of manufacturability of elements from the process of alloy formation.

It should be noted that the known compositions of aluminum sacrificial alloys [19, 20] contain alloying components, usually located in the favorable zone (Fig. 1, Table 1). Subsequent screening of elements of groups I and II (Table 1) with the exception of toxic, rare-earth, and noble ones was carried out taking into account the metal-chemical (tendency of the elements to form single-phase structures) and electrochemical characteristics.
**Figure 1.** Melting point and density of metals.

| Group | The name of the region according to Fig. 1 | Conventional designation according to Fig. 1 | Elements in a group | Alloy formation tendency |
|-------|---------------------------------|---------------------------------|-------------------|-------------------------|
| I     | Zone I + field A                | Pb, Bi, Cd, In, Zn, Sb, Te, Se, Ga, Sn, Mg, Ba, Ge, La, Si, Be, (Cs), Cd | Most favorable     |
| II    | Zone II + field B              | Ce, Nb, Cu, Mn, Fe, Zr, V, Y, Ti, Sr, Ni, Co, Au, Ag | Favorable          |
| III   | Zone III                       | Mo, W, Os, Re, Ta, Ir, Tc, Hf, Rh, Th, Pt, Pd, (U), (Cr) | Unfavorable        |
Assuming that the electrochemical characteristics of aluminum alloys vary depending on the phase composition, Table 2 provides information on the phase regions of alloys containing recommended elements as alloying components [21].

Table 2. The main types of interaction in the Al-element system

| Element | The range of concentrations (% by weight) of the alloying element in the phase region |
|---------|----------------------------------------------------------------------------------|
|         | α | α + β_{sec} | α + β_{n}(AlB_{1}) |
| **Limited Solid Solutions** | | | |
| Zn      | 0 – 4.0 (100 °C) | 4.0 - 31.6 | > 31.6 |
| Cd¹     | 0 – 0.0002 (165 °C) | 0.0002 - 0.4 (640 °C) | > 0.4 |
| Ga      | 0 – 0.5 | > 0.5 | 0.5 - 100 |
| In¹     | 0 – 0.0085 (560 °C) | 0.085 - 0.175 | > 0.175 |
| Be      | 0 – 0.01 (500 °C) | - 0.06 | > 0.006 |
| **Limited Solid Solutions and Chemical Compounds** | | | |
| Mg      | 0 – 1.9 | 1.9 - 17.4 | > 17.4 |
| Ti      | 0 – 0.07 (400 °C) | 0.07 – 0.14 | 0.14 – 62.82 |
| Zr      | 0 – 0.001 (20 °C) | 0.001 – 0.28 | 0.28 – 47.01 |
| V       | 0 – 0.37 (638 °C) | 0.37 | > 0.37 |
| Nb      | 0 – 0.001 (20 °C) | 0.001 | > 0.001 |
| Mn      | 0 – 0.35 (500 °C) | 0.35 – 1.4 | 1.4 – 20.0 |

Note: ¹ Limited miscibility of elements in the liquid state.

According to the type of interaction, the elements are grouped in terms of their beneficial effect on the formation of an aluminum alloy homogeneous from the electrochemical viewpoint.

At the same time, elements that do not change or increase the electronegative potential of aluminum will be favorable for alloying aluminum; on the contrary, elements significantly ennoblement of aluminum are classified as unfavorable.

All things being equal, a single-phase structure is most preferred for producing an electrochemically homogeneous alloy. From the elements considered (Table 2), in the order of decreasing their solubility in aluminum (% by mass) during the formation of the structure of α-solid solutions, the following series can be constructed: Zn (4.0), Mg (1.9), Mn (0.35); upon the formation of the structure α + β_{sec}: V (0.37), In (0.1), Ti (0.07), Zr (0.28).

An important role in the selection of elements as alloying is given to the comparative assessment of current efficiency and standard potentials for the main electrode processes in binary systems “aluminum – element” (Fig. 2). Obviously, Be, Ti, Mg, La, Cs with respect to aluminum, the thermodynamic tendency of which corresponds to the standard potential (-1.66 V), can be used to obtain alloys with increased anodic activity. When analyzing the actual value of the potential of aluminum, Ti, Zn, Mn, Nb, V, Zr may also be of interest for alloys of general technical purpose and a reduced anode activity. The last group may also include Ga, In, Sn, Cd.

Since the anodic activity of the alloys is determined by the specific resistance of the film surface of the dissolution products (oxides and hydroxides), Fig. 3 shows their numerical values.
The difference in the standard ($\phi_{0}^{Al} = -1.66$ V) and stationary ($\phi_{c}^{Al} = -1.66$ V) potentials of aluminum is due to the high resistivity of aluminum oxide ($\rho = 1 \cdot 10^{14}$ Ohm · m). As it can be seen, zinc, tin and indium play an activating role, contributing to a decrease in the resistivity of the oxide film. Conversely, magnesium with a high electrical resistivity of magnesium oxide does not activate aluminum, although it has a high electronegative potential ($\phi_{0}^{Mg} = -2.37$ V). These comparisons suggest that the activating additives can be Sn, In, Ga, Zn, Nb, and V. Some interest follows with respect to Mg, Be and La, which have higher thermodynamic activity than aluminum at comparable resistivity’s of their oxides.

A comparative analysis of the data on the thermodynamic activity, current transfer, and electrical resistance of oxide suggests that promising alloying elements are Be, La, Cs, Ti, Nb, and V.

Table 3 shows the main properties of aluminum sacrificial alloys and preferred over other elements responsible for the manifestation of the corresponding properties.

| Property | Element |
|----------|---------|
| Alloy formation tendency: | Pb, Bi, Cd, Zn, Sb, Te, Se, Ga, Sn, Mg, Ba, Ge, La, Si, Be, Cs, Si, Ce, Nb, Cu, Mn, Fe, Zr, V, Y, Ti, Sr, Ni, Co |
| 1 Most favorable: | |
| 2 Favorable | |
| Structure: | Zn, Cd, Ga, In, Si, Be, Sn |
| $\alpha_0$ | Mg, Ti, Zr, V, Nb, Mn |
| $\alpha + \beta_{sec}$ | |
| Improving the electrochemical properties of alloys: | Be, Ti, Mg, Cs, La |
| 3 decreased anode activity | Ti, Zn, Mn, Nb, V, Zr, Si |
| general technical purpose | |
| increased anode activity | |
An analysis of these aggregate data allows us to conclude that, according to a set of properties (indicated by numbers in brackets in accordance with Table 3), the following alloying elements can be recommended: Zn (1-4); Mg (1-3); Mn (1-3); Ti (1-3); Zr (1-3); Be (1-3); V (1-4); Nb (1-4); Cd (1-3); Ga (1-4); In (1-4); Sn (1-4); La (1.4); Cs (1.4).

For experimental studies, Mg, Zn, Mn were chosen as alloying additives, and Si, Fe as impurities. When choosing the ground level and ranges of elements variation from the alloying complex (Mg, Mn, Zn) and the group of harmful impurities (Fe, Si), we took into account not only the nature of the elements interaction with each other (and with aluminum) and the type of phase diagrams, but also well-known experimental data on technological and operational properties of aluminum cast alloys. For magnesium and zinc, the specified range of variation is selected on the basis of experimental data on the interaction of base metals of sacrificial alloys; for manganese and iron. The selected range of variation provided the content of these elements at levels found in the foundry practice of aluminum alloys. The levels of variation for silicon and iron are selected based on the limitations of their alloy content (Table 4).

Mathematical processing of the results of an active experiment made it possible to obtain the regression equation in natural form: CUE = 76.81 + 8.79 Mg + 5.21 Mn – 0.42 Zn – 7.28 Si – 38.83 Fe – 4.63 Mg² – 109.0 Mn² + 0.13 Zn² – 0.31 MgZn + 0.63 MgSi + 3.13 MnZn + 7.50 MnSi – 25.0 MnFe + 0.25 ZnSi + 7.50 SiFe.

Testing by the F-criterion confirmed the adequacy of the equation, since Fcalc = 127.1 >> Ftab (22-1); (22-16) = 3.88 for α = 0.05. The maximum value of the CUE (75.78%) of the aluminum alloy in the given ranges of variation occurs with the following values of the independent variables: Mg = 0.83%; Mn = 0.11%; Zn = 4.50%; Si = 0.06%; Fe = 0.010%. The optimal composition of the aluminum alloy will be as follows: Al + 4.5% Zn + 0.83% Mg + 0.11% Mn. The content of Si and Fe in the alloy is limited to 0.06 and 0.01%, respectively. Tolerances for the content of alloying components (Δ) are determined from the following expression: Δ = (0.25-0.65)√C, where C is the concentration of the element in the alloy [15]. With this in mind, the concentration range is, %: for zinc, 3.6-5.4; for magnesium, 0.55-1.05; for manganese 0-0.3. Silicon and iron are the main impurities in primary aluminum. For practical use, it is economically feasible to use A85 grade aluminum as the basis of sacrificial alloys.

4. Conclusions

Based on the analysis of metal-chemical and technological characteristics, groups of elements favorable for alloy formation with aluminum are identified. According to the results of an additional comparison of the values of current recovery and standard potentials for the basic electrochemical
processes in binary aluminum-element systems, as well as the values of the potentials of the elements and the electrical resistivity of their oxides, Zn, Mg, Mn, Ti, Zr, V, Be, Cd, In, La, Nd, Cs was proposed as alloying. Experimental studies on the effect of Zn, Mg, and Mn on the basic electrochemical properties of aluminum have confirmed the feasibility of their application as alloying components. In this case, the maximum composition under the conditions of the adopted restrictions is ensured by the following composition: Al (grade A85) + (3.6–5.4)% Zn (grade TSV) + (0.55–1.05)% Mg (grade Mg95) + (0–0.3)% Mn (grade Mr0). The alloy has the following electrochemical properties: \( \varphi_C = -690-710 \text{ mV}; \varphi_n = -570-600 \text{ mV}; \text{CUE} = 72-78%; \ Q_F = 2150-2350 \text{ Ah/kg}; K = 0.08-0.11 \text{ mm/year}. \)

The results obtained are in good agreement with the standards (Russian standard 26251-84 and others) on the compositions of aluminum tread alloys in which magnesium, zinc and manganese are the main alloying components.

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