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Research Article

Corrosion and electrohemical behavior of aluminum conductor E-AlMgSi (Aldrey) alloy with tin in a medium electrolite NaCl

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Abstract

The economic feasibility of using aluminum as a conductive material is explained by the favorable ratio of its cost to the cost of copper. In addition, one should take into account the factor that the cost of aluminum has remained virtually unchanged for many years. When using conductive aluminum alloys for the manufacture of thin wire, winding wire, etc. Certain difficulties may arise in connection with their insufficient strength and a small number of kinks before fracture. In recent years, aluminum alloys have been developed, which even in a soft state have strength characteristics that allow them to be used as a conductive material.

One of the promising areas for the use of aluminum is the electrical industry. Conducting aluminum alloys type of the E-AlMgSi (Aldrey) are representatives of this group of alloys and belong to heat-strengthened alloys. They are distinct by high strength and good ductility. These alloys, with appropriate heat treatment, acquire high electrical conductivity. The producing made from it are used almost exclusively for overhead power lines.

The paper presents the results of a study of the anodic behavior of aluminum E-AlMgSi (Aldrey) alloy with tin in a medium electrolyte of 0.03; 0.3 and 3.0% NaCl. Corrosion-electrochemical studies of the alloys were carried out by the potentiostatic method in potentiostat PI-50-1.1 at a potential sweep speed of 2 mV/s. It is shown that alloying E-AlMgSi (Aldrey) alloy with tin increases its corrosion resistance by 20%. The main electrochemical potentials of the E-AlMgSi (Aldrey) alloy, when doped with tin, shift to a positive range of values, and from the concentration of sodium chloride in the negative direction of the ordinate.

1. Introduction

Aluminum and its alloys are widely used in electrical engineering as a conductor and constructural material. As a conductive material, aluminum is characterized by high electrical and thermal conductivity (after copper, the maximum level among all technically used metals) [1].

Aluminum also has a low density, high atmospheric corrosion resistance and resistance to chemicals. Despite this, aluminum alloys in a certain condition and in harsh operating conditions can be exposed to dangerous types of corrosion damage. Of particular interest is the corrosion of aluminum in solutions that are close and neutral $(6 < pH < 8)$. It includes corrosion in natural environments such as sea, lake and river water, drinking water and precipitation. Under these conditions, at ordinary temperatures, the speed of H + ions or H_2O molecules with hydrogen evolution is negligible [2].

The economic feasibility of using aluminum as a conductive material is explained by the favorable ratio of its cost to the cost of copper. In addition, one should take into account the factor that the cost of aluminum remains practically unchanged for many years [1–4].

When using conductive aluminum alloys for the manufacture of thin wire, such as winding wire, etc. Certain difficulties may arise in connection with their insufficient strength and a small number of kinks before fracture.

In recent years, aluminum alloys have been developed, which even in a soft state have strength characteristics that allow them to be used as a conductive material [1–3].

One of the conductive aluminum alloys is the alloy E-AlMgSi (Aldrey), which refers to heat-strengthened alloys. It is characterized by high strength and good ductility. This alloy, with appropriate heat treatment, acquires high electrical conductivity. The wires made from it are used almost exclusively for overhead power lines [4, 5].

Due to the fact that power lines of aluminum and its alloys are operated in an open atmosphere, issues of increasing the corrosion resistance of alloys are relevant.

The aim of this work is study the effect of tin alloying of corrosion electrochemical behavior of E-AlMgSi (Aldrey) conductor aluminum alloy with the following chemical composition: 0.5 wt.% Si, 0.5 wt.% Mg, balance Al.

2. Experimental

The synthesis of alloys was carried out in a shaft laboratory furnace of resistance of the SSHOL type in temperature of 750–800 °C. A6 grade aluminum, which was additionally doped with the calculated amount of silicon and magnesium, was used as a charge in the preparation of the E-AlMgSi alloy.When doping aluminum with silicon, the metallic (0.1 wt.%) silicon present in primary aluminum was taken into account. Magnesium wrapped in aluminum foil was introduced into the molten aluminum using a bell. The metalic tin was introduced into the

melt in a form wrapped in aluminum foil. The alloys were chemically analyzed for silicon and magnesium contents at the Central Industrial Laboratory of the State Unitary Enterprise Tajikistan Aluminum Company. The alloy compositions were controlled by weighing the charge and the alloys. Synthesis was repeated if the alloy weight deviated from the target one by more than 1–2% rel.u. Then the alloys were cleaned from slag and cast into graphite molds in order to obtain samples for electrochemical corrosion study. Then, slag was removed from the melt and the samples were cast for corrosion-electrochemical studies into a graphite mold The cylindrical samples had a diameter of 10 mm and a length of 140 mm.

The tests were carried out in neutral solutions containing different NaCl concentrations pursuant to the recommendations of GOST 9.017-74 Standard, i.e., in a seawater imitating media, for studying the effect of chloride ions on the electrochemical corrosion behavior of tin containing E-AlMgSi (Aldrey) aluminum alloy.

The studies were carried out with a PI-50.1.1 potentiometer and a LKD-4-002 recorder. The reference electrode was a silicon chloride one (**SCE**) and the auxiliary electrode was a platinum one. The potential sweep rate was $2 \text{ mV} \cdot \text{s}^{-1}$.

The samples for electrochemical studies were positively biased relative to the potential which established upon submersion into the test solution (E_{fc} is the free corrosion potential or the steady state potential) until the current density started to increase drastically (Fig. 1, Curve *1*). The samples were then reverse biased (Fig. 1, Curves *2* and *3*) to –1.3 V which resulted in oxide film dissolution. Finally the samples were again positively biased (Fig. 1, Curve *4*), and the potential of the cathodic to anodic current transition was considered as the passivation onset potential (E_{po}).
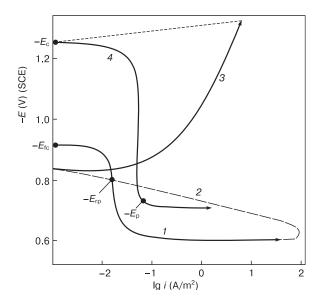

Figure 1. Full polarization (2 mV/s) curve of the E-AlMgSi (Aldrey) alloy, in electrolyte medium of 3% NaCl.

The resultant polarization curve was used for determining the main electrochemical potentials of the alloys, i.e., $-E_{ss}$ or $-E_{fc}$ (the steady state potential or the free corrosion potential), $-E_{rp}$ (the repassivation potential), $-E_{p}$ (the pitting potential), $-E_{c}$ (the corrosion potential) and $-i_{c}$ (the corrosion current).

The corrosion current was calculated taking into account the Tafel slope ($A = 0.12$ V) of the cathodic curve since pitting corrosion of aluminum and its alloys in neutral media is controlled by the oxygen ionization cathodic reaction. In turn the corrosion rate is a function of the corrosion current and calculated using the following formula:

$$K = i_c k_C,$$

where $k = 0.335$ g/(A · h) for aluminum.

The method of measuring alloy polarization curves is described in detail earlier [6–15]. The results of electrochemical corrosion study for tin containing E-AlMgSi (Aldrey) aluminum alloy are summarized in the Table 1 and illustrated in Figs 2–5. Figure 2 shows the experimental curve of free corrosion potential as a function of time for tin containing E-AlMgSi (Aldrey) aluminum alloy samples in NaCl electrolyte. It can be seen from Fig. 2 that submersion into NaCl electrolyte shifts the $-E_{fc}$ potential towards positive values.

The result of corrosion electrochemical properties of the alloys presented in the Table 1 show that 0.05 to 1.0 wt.% tin alloying of E-AlMgSi (Aldrey) aluminum alloy shifts its corrosion, repassivation and pitting corrosion potentials in the test media towards positive values.

As was shown earlier [16] the difference between the pitting corrosion potential and the free corrosion potential of metals (pitting corrosion resistance basis ΔE_{pc}) is used as a criterion of metals' pitting corrosion susceptibility in a specific media. Analysis of the experimental data from the viewpoint of this criterion suggests that tin addition affects the pitting corrosion resistance basis ΔE_{pc} of E-AlMgSi (Aldrey) aluminum alloy but slightly.
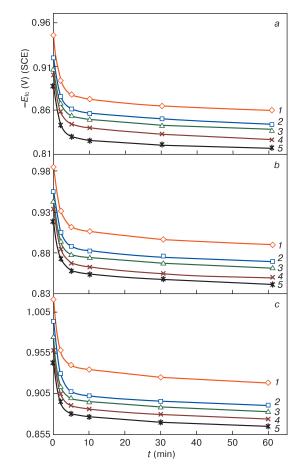

Figure 2. Temporal dependence of the potential (SCE) of free corrosion ($-E_{fc}$, V) of the E-AlMgSi alloy (Aldrey) (*1*) containing tin, wt.%: 0.01 (*2*); 0.05 (*3*); 0.1 (*4*); 0.5 (*5*), in the medium electrolyte 0.03% (*a*); 0.3% (*b*) and 3% (*c*) NaCl.

The anodic branches of the tin containing E-AlMgSi (Aldrey) aluminum alloy polarization curves are shown in Fig. 3. The curve pattern (Fig. 3) suggests that an increase in the third component (tin) content shifts all the electrochemical potentials of the alloy in NaCl electrolyte to-

Table 1. Electrochemical corrosion properties of tin containing E-AlMgSi (Aldrey) aluminum alloy in NaCl electrolyte.

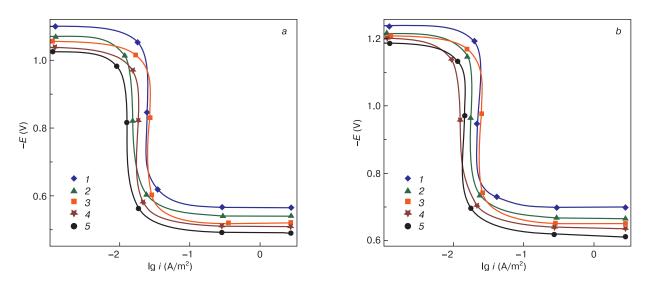| NaCl, wt.%	Tin content in alloy, wt.%	Electrochemical potentials, V (SCE)					Corrosion rate	
		$-E_{fc}$	$-E_{c}$	$-E_{p}$	$-E_{rp}$	ΔE_{rp}	$i_c \cdot 10^{-2}$, A/m²	$K \cdot 10^{-3}$, g/(m²·h)
0.03	–	0.860	1.100	0.600	0.720	260	0.049	16.41
	0.05	0.836	1.077	0.589	0.707	247	0.045	15.07
	0.1	0.829	1.058	0.578	0.701	251	0.042	14.07
	0.5	0.820	1.047	0.570	0.698	250	0.040	13.40
	1.0	0.812	1.038	0.557	0.698	255	0.038	12.73
0.3	-	0.890	1.180	0.680	0.768	210	0.066	22.11
	0.05	0.866	1.158	0.654	0.750	212	0.063	21.10
	0.1	0.855	1.140	0.640	0.750	215	0.060	20.10
	0.5	0.846	1.127	0.632	0.745	214	0.057	19.09
	1.0	0.837	1.110	0.626	0.742	211	0.054	18.09
3.0	-	0.919	1.240	0.735	0.800	184	0.082	27.47
	0.05	0.890	1.218	0.712	0.774	178	0.078	26.13
	0.1	0.883	1.210	0.704	0.770	179	0.075	25.12
	0.5	0.874	1.202	0.698	0.765	176	0.073	24.45
	1.0	0.865	1.194	0.690	0.758	175	0.071	23.78

Figure 3. Anode polarization (2 mV/s) curves of the E-AlMgSi (Aldrey) alloy (*1*) containing tin, wt.%: 0.01 (*2*), 0.05 (*3*), 0.1 (*4*), 0.5 (*5*), in a medium electrolyte 0.03% (*a*) and 3% (*b*) NaCl.

wards positive values and hence the anodic corrosion rate of tin containing E-AlMgSi (Aldrey) aluminum alloy is lower. The positive shift of the electrochemical potentials and the corrosion rate reduction for E-AlMgSi (Aldrey) aluminum alloy due to tin alloying can be accounted for by an increase in the heterogeneity of the alloy structure.

The dependence of the corrosion rate of the E-AlMgSi alloy (Aldrey) on the tin content in the electrolyte medium of 0.03, 0.3, and 3.0% NaCl is shown in Fig. 4. The addition of tin to the E-AlMgSi alloy (Aldrey) reduces its corrosion rate in all the studied NaCl electrolyte media (Fig. 4). Moreover, an increase in the concentration of NaCl electrolyte (chloride ion) contributes to an increase in the corrosion rate of alloys (Fig. 5). The corrosion rate and corrosion current density of the E-AlMgSi alloy (Aldrey) have a minimum value at a concentration of 1.0 wt.% tin. Therefore, the specified composition of the alloys is optimal in terms of corrosion.
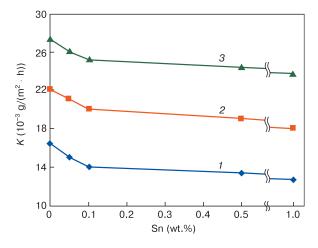
3. Results and discussion

According to the data of [17], the passivated oxide formed on aluminum in neutral media has low electronic conductivity. It inhibits almost completely not only the anodic reaction of metal dissolution, but also the conjugate cathode reduction of oxygen dissolved in the electrolyte. Oxide films on aluminum of technical purity and its alloys are more conductive. This explains the significant acceleration of oxygen reduction and, consequently, the corrosion of aluminum-based alloys. In neutral solutions, oxide films on aluminum exhibit a high protective effect, corrosion proceeds uniformly, with a minimum speed, mainly on individual defects of the oxide film.

The results of the corrosion-electrochemical study of the E-AlMgSi (Aldrey) alloy doped with tin are presented in the Table 1. The dynamics of the free corrosion potential with an increase in the exposure time in the

Figure 4. Dependence of the corrosion rate of the E-AlMgSi (Aldrey) alloy on the concentration of tin in a medium electrolyte 0.03% (*1*); 0.3% (*2*) and 3.0% (*3*) NaCl.
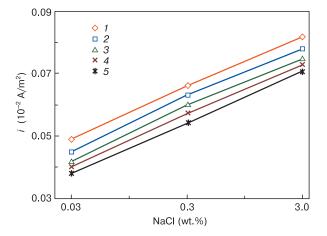
Figure 5. The dependence of the current density of the corrosion of the alloy E-AlMgSi (Aldrey) (*1*) containing tin, wt.%: 0.01 (*2*); 0.05 (*3*); 0.1 (*4*); 0.5 (*5*) of the concentration of NaCl.

NaCl solution (Figure 2) indicates the rate of formation of the protective oxide layer on the alloy surface. So, if for the initial E-AlMgSi (Aldrey) alloy stabilization of the potential of free corrosion within 1 hour, then for alloys doped with tin, this process is completed within 30–40 minutes, which indicates the acceleration of the formation process protective oxide layer in tin alloyed alloys in comparison with the initial alloy. In tin alloyed alloys, with an increase in the exposure time, a shift in the free corrosion potential to a region of more positive values is observed. The most positive value of the potential (–0.812 V) has the E-AlMgSi alloy (Aldrey) alloyed with 1.0% Sn in a medium of 0.03% NaCl. The addition of tin, regardless of its amount, increases the potential for free corrosion. In this case, the potential shift to the region of positive values is about 54 mV in comparison with the E-AlMgSi (Aldrey) alloy in a medium of 3% NaCl. In accordance with the change in the value of the free corrosion potential over time, the most intensive formation of the protective oxide film on the electrode surface occurs within the first 3–5 min after immersion of the electrode in the solution (Fig. 2).

Corrosion and electrochemical characteristics of the investigated alloys are presented in Table 1, show that the alloying of the E-AlMgSi (Aldrey) alloy with tin promotes a shift in the electrochemical potentials in a positive direction. The free corrosion potential of all investigated alloys is in the passive region, i.e. between the potentials of corrosion and pitting. In general, ternary alloys both in terms of electrochemical characteristics and corrosion resistance are superior to the initial E-AlMgSi (Aldrey) alloy. For example, alloys containing 1.0 wt.% tin are 20–30% more corrosion resistant than the original E-AlMgSi (Aldrey) alloy.

The mechanism of corrosion of pure aluminum in neutral environments is described by the equations [17].

$$Al + 3OH^- = Al(OH)_3 + 3e, \qquad (1)$$

$$Al(OH)_3 + OH^- = Al(OH)_4^-. \qquad (2)$$

The process is limited by the rate of OH ion delivery to the electrode surface. The depolarizer in aerated neutral solutions is oxygen. Its recovery at the metal interface (the solution proceeds according to the equation

$$O_2 + 2H_2O + 4e = 4OH^-. \qquad (3)$$

The process is limited by diffusion to the electrode of oxygen dissolved in the electrolyte, which ultimately determines the rate of metal corrosion. As an intermediate product of the interaction of the metal with OH^- ions, a hydrated oxide of the general formula $Al_2O_3 \cdot nH_2O$ is deposited on the surface. Various modifications of aluminum oxide and hydroxide are readily soluble in alkaline and acidic media, but practically insoluble in neutral solutions. For this reason, the field of practical use of aluminum and its alloys in liquid media mainly covers only solutions that are close to neutral. In such solutions, oxide films on aluminum exhibit a high protective effect, and uniform corrosion of aluminum and its alloys, as a rule, is small and occurs on individual defects of the oxide film [17]. The mechanism of dissolution of the E-AlMgSi (Aldrey) alloy doped with tin can be explained as follows [18]. Upon contact of the alloys with the tin solution as an electrochemical active component [19], it partially partially dissolves from the solid solution, increasing the concentration of vacancies in the surface layer, and partially interacts with water oxygen to form SnO_2, which accumulates on the surface. The thermodynamic activity of aluminum in a defective surface layer increases, which contributes to the formation of a dense and less defective layer of aluminum oxyhydroxides with high protective properties [reactions Eqs. (1), (2)]. SnO_2 oxide accumulates in the upper part of this layer, whose density is higher than the density of Al_2O_3 [19]. The corrosion potential of an alloy coated with a dense low-defective layer of aluminum oxyhydroxides and tin oxide increases, and the depolarization reduction rate and, accordingly, the tin corrosion rate of the containing alloy decreases. Insoluble in aqueous solutions and not forming mixed oxides with aluminum due to the difference in the periods of the crystal lattices, SnO_2 accumulates on the surface, mechanically blocking it and preventing both the dissolution of the alloy during anodic polarization and the formation of pits.

4. Conclusion

Thus, on the basis of the conducted studies, an alloying element was selected, the small additives of which allow increasing the corrosion resistance of the E-AlMgSi alloy (Aldrey). The developed alloy in corrosion resistance exceeds almost 20–30%, currently used as a conductor E-AlMgSi (Aldrey) alloy.

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