

# Corrosion of indium doped E-AlMgSi aluminum conductor alloy (Aldrey)

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## Abstract

The effect of impurities on the electrical conductivity of aluminum has been studied in detail. The electrical conductivity of aluminum is 65.45% of that of copper. The tensile strength of aluminum wire is 150–170 MPa which, at equal conductivity, is about 65% of the strength of copper wire. This strength of aluminum wire is sufficient for bearing the wire's own weight but may be too low in case of snow, ice or wind overloads.

One way to improve the strength of aluminum wire is to use aluminum alloys having higher strength combined with sufficiently high electrical conductivity, e.g. the E-AlMgSi alloy (Aldrey). The key strengthening agent of the E-AlMgSi alloy (Aldrey) is the Mg<sub>2</sub>Si phase which imparts high mechanical strength to aluminum.

In this work we present experimental data on the kinetics of high-temperature oxidation and electrochemical corrosion of indium doped E-AlMgSi aluminum conductor alloy (Aldrey). Thermal gravimetric study has shown that indium doping and high temperature exposure increase the oxidation rate of E-AlMgSi alloy (Aldrey), with the apparent alloy oxidation activation energy decreasing from 120.5 to 91.8 kJ/mole. Alloy oxidation rate data determined using a potentiostatic technique in NaCl electrolyte media have shown that the corrosion resistance of the indium doped alloy is 20–30% superior to that of the initial alloy. With an increase in NaCl electrolyte concentration the electrochemical potentials of the alloys decrease whereas the corrosion rate increases regardless of alloy composition.

## Keywords

E-AlMgSi aluminum alloy (Aldrey), thermal gravimetric method, potentiostatic technique, oxidation rate, apparent activation energy, NaCl electrolyte, corrosion and pitting potentials, corrosion rate.

## 1. Introduction

The main requirements to conductor aluminum alloys are high electrical conductivity, mechanical strength, atmospheric corrosion resistance and susceptibility to pres-

sure mechanical treatment, primarily hot or cold rolling and drawing [1, 2].

The main parameters of conductors are the electrical resistivity and its thermal coefficient. The electrical conductivity of pure metals is a periodical function of the

atomic number of the metal, though this function is not clearly expressed unlike other physicochemical properties of Periodical table elements [3].

A drawback of aluminum as a conductor is its low mechanical strength. For this reason pure aluminum is often replaced for its alloy E-AlMgSi (Aldrey) having the composition Al + 0.5 wt.% Mg + 0.5 wt.% Si. The magnesium to silicon ratio in the alloy should correspond to the composition of the Mg<sub>2</sub>Si phase which forms in the alloy and acts as a strengthening agent imparting high mechanical strength to the alloy [4].

The strengthening mechanism of the Mg<sub>2</sub>Si phase is accounted for by a decrease in its solubility in solid aluminum with a decrease in temperature. If an Aldrey-type alloy is heated to temperatures of above 773 K, at which all Mg<sub>2</sub>Si is in the solid solution, and is rapidly cooled, a supersaturated Mg<sub>2</sub>Si solid solution in aluminum forms. Upon natural or artificial aging of the alloy (at 423–473 K) surplus Mg<sub>2</sub>Si precipitates from the solid solution in the form of a fine-grained structural component which increases the mechanical strength of the alloy. The tensile strength of Aldrey is twice that of aluminum [1]. The atmospheric corrosion resistance of aluminum is provided for by a continuous thin oxide film covering its surface [5].

The aim of this work is to study the effect of indium doping on the high temperature corrosion (oxidation) and electrochemical corrosion of the E-AlMgSi aluminum conductor alloy (Aldrey).

## 2. Experimental

The oxidation of E-AlMgSi alloys (Aldrey) was studied using a thermal gravimetric method based on continuous weighing of specimens. The experiments were conducted on the custom-assembled test system the operation principle of which was described earlier [6–12]. The crucible with the test metal was placed into the isothermal zone of the furnace. The temperature was increased at a 2–3 K/min rate. Before furnace heating the cathetometer was set in accordance with the spring pointer, the reference points were recorded at the scale and the change in the specimen weight was monitored during heating. A new reference point was recorded upon achieving the preset mode.

The change in the specimen weight was monitored based on spring elongation with a KM-8 cathetometer. The crucibles were made of aluminum oxide and had diameters of 18–20 mm and heights of 25–26 mm. Before the experiment the crucibles were annealed at 1273–1473 K in an oxidizing medium for 1.5 h until a constant weight was achieved. The weight of test alloy specimens was monitored before and after the experiment on an analytical balance.

The temperature was recorded with a PP-63 potentiometer. Upon the end of the experiment the system was cooled down, the crucible with the metal was weighed and the reaction surface area was measured. Then the ox-

ide film was removed from the specimen surface and its structure was studied under a scanning electron microscope.

The experimental error can be calculated using the initial formula of oxidation rate constant:

$$k = \frac{g}{st},$$

where  $g$  is the metal weight,  $s$  is the reaction surface and  $t$  is time.

The calculated relative error consists of the sum of relative errors:

$$\frac{\Delta k}{k} = \left( \frac{\Delta g}{g} \right)^2 + \left( \frac{\Delta s}{s} \right)^2 + \frac{\Delta t}{t}.$$

The value of the error was  $\frac{\Delta k}{k} = (2.71)^2 + (1.5)^2 + 0.027 = 9.62\%$ .

The temperature was measured with a platinum/platinum-rhodium thermocouple the hot solder of which was at the level of the specimen surface. The temperature measurement accuracy was  $\pm 2$  K. The temperature measurement error was

$$\frac{\Delta T}{T} = 2 \left( \frac{100\%}{900^\circ} \right) = 0.22\%.$$

This method of alloy oxidation kinetics study was described elsewhere [6–12].

The corrosion and electrochemical properties of the E-AlMgSi alloys (Aldrey) were studied using a potentiostatic technique on a PI-50-1.1 potentiostat with an LKD-4-002 recorder. The reference electrode was silver chloride, the auxiliary electrode being platinum. The potential sweep was 2 mV/s. The polarization curve recording method for the E-AlMgSi alloy (Aldrey) was described earlier [13–22].

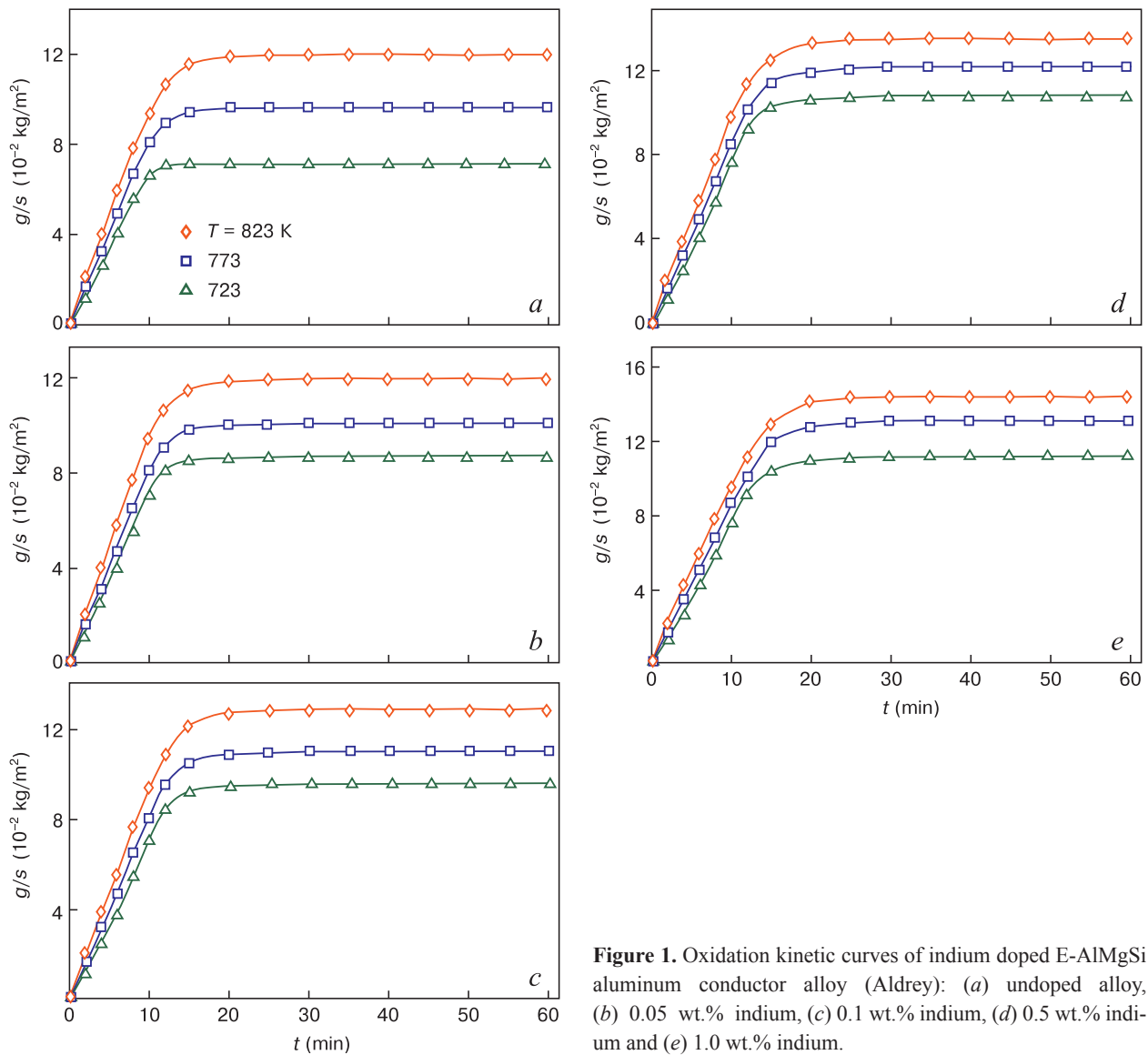
Based on the experimental polarization curve we determined the main electrochemical potentials of the alloys, i.e.,  $-E_{st}$  or  $-E_{fc}$  (the steady state potential or the free corrosion potential),  $-E_{rp}$  (the repassivation potential),  $-E_{pc}$  (the pitting corrosion potential),  $-E_{cor}$  (the corrosion potential) and  $-i_{cor}$  (the corrosion current).

The corrosion current was calculated taking into account the Tafel slope  $b_k = 0.12$  V on the cathodic curve because pitting corrosion of aluminum and its alloys in neutral media depends on the cathodic oxygen ionization reaction. The corrosion rate is in turn considered to be a function of the corrosion current and is calculated using the following formula:

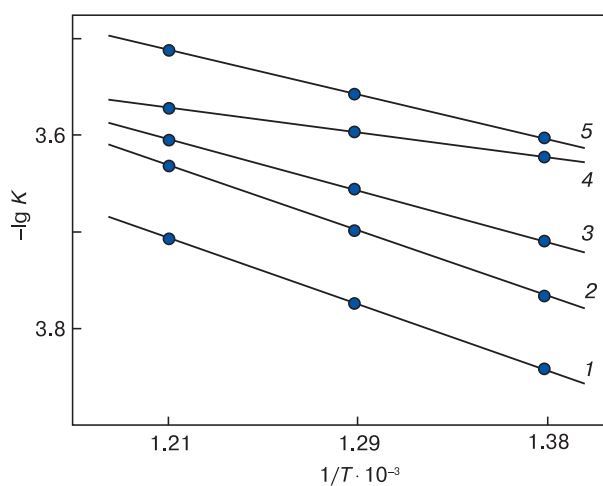
$$K = i_{cor}k,$$

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

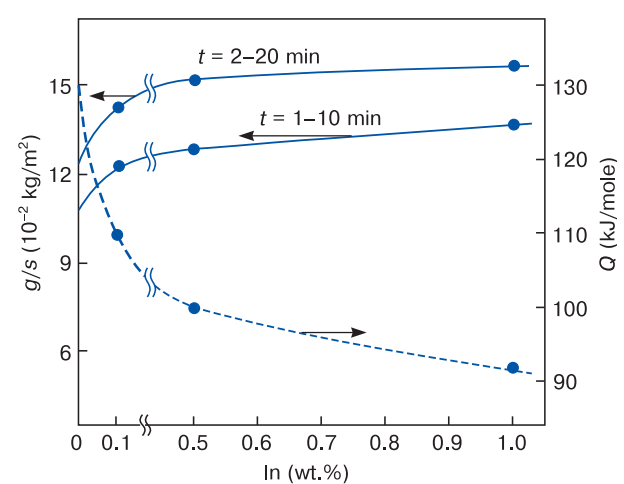
The alloys were synthesized in a SShOL type resistance shaft experimental laboratory furnace at 1023–1073 K. The charge for the synthesis of the E-AlMgSi alloy (Aldrey) was A6 Grade aluminum doped with the rated quantity of silicon and magnesium. Silicon doping was conducted taking into account the quantity of



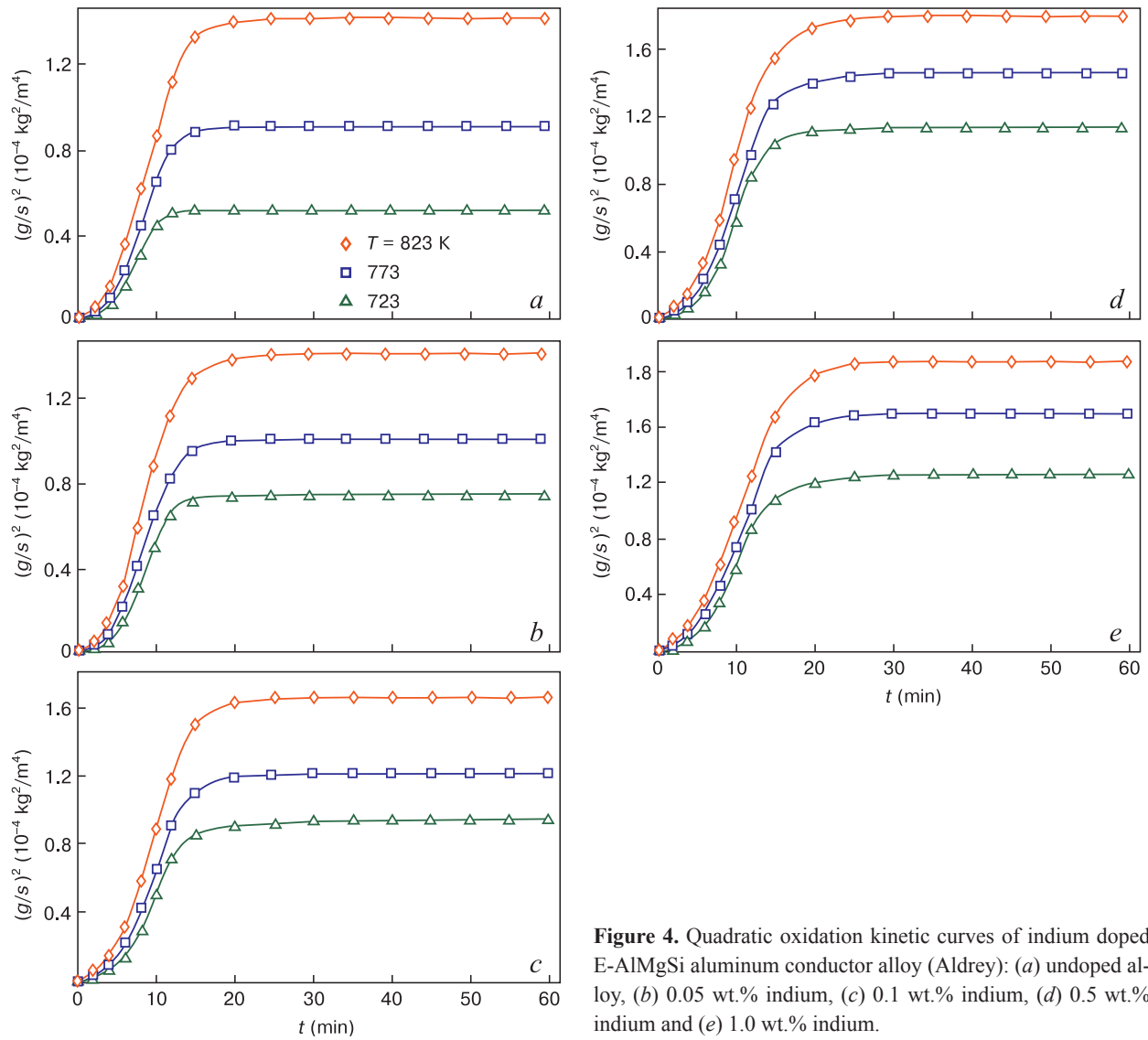
**Figure 1.** Oxidation kinetic curves of indium doped E-AlMgSi aluminum conductor alloy (Aldrey): (a) undoped alloy, (b) 0.05 wt.% indium, (c) 0.1 wt.% indium, (d) 0.5 wt.% indium and (e) 1.0 wt.% indium.



**Figure 2.**  $\lg K$  as a function of  $1/T$  for indium doped E-AlMgSi aluminum conductor alloy (Aldrey): (a) undoped alloy, (b) 0.05 wt.% indium, (c) 0.1 wt.% indium, (d) 0.5 wt.% indium and (e) 1.0 wt.% indium.



**Figure 3.** Oxidation isochrones of indium doped E-AlMgSi aluminum conductor alloy (Aldrey) at 823 K.



**Figure 4.** Quadratic oxidation kinetic curves of indium doped E-AlMgSi aluminum conductor alloy (Aldrey): (a) undoped alloy, (b) 0.05 wt.% indium, (c) 0.1 wt.% indium, (d) 0.5 wt.% indium and (e) 1.0 wt.% indium.

**Table 1.** Kinetic and energy oxidation parameters of solid indium doped E-AlMgSi aluminum conductor alloy (Aldrey)

Indium content in alloy (wt.%)	Oxidation temperature (K)	True oxidation rate ( $10^4 \text{ kg}/(\text{m}^2 \cdot \text{s})$ )	Apparent oxidation activation energy (kJ/mole)
0	723	2.67	128.5
	773	2.89	
	823	3.28	
0.05	723	2.76	114.1
	773	2.95	
	823	3.39	
0.1	723	2.86	109.6
	773	3.05	
	823	3.47	
0.5	723	3.04	99.4
	773	3.20	
	823	3.57	
1.0	723	3.14	91.8
	773	3.27	
	823	3.70	

metallic silicon contained in raw aluminum (0.1 wt.%). Magnesium wrapped in aluminum foil was introduced in the melt using a bell. Metallic indium was also added to the melt wrapped in aluminum foil. Chemical analysis of the alloys for silicon and manganese content was conducted at the Central Factory Laboratory of the Tajikistan Aluminum Company. The alloy composition was tested by weighing the charge and the final alloys. The alloys were synthesized again if the alloy weight deviation was more than 1–2 %. Then slag was removed from the alloys and specimens for corrosion and electrochemical tests were cast into a graphite mold. The specimens had a cylindrical shape and were 10 mm in diameter and 140 mm in length [13].

### 3. Effect of indium on oxidation kinetics of solid E-AlMgSi aluminum conductor alloy (Aldrey)

The oxidation kinetics of indium doped E-AlMgSi conductor alloy (Aldrey) was studied for a batch of alloy specimens containing 0.05, 0.1, 0.5 and 1.0 wt.% indium. Alloy oxidation process data are presented in Figs. 1–4 and Tables 1 and 2.

The pattern of the oxidation kinetic curves of the E-AlMgSi conductor alloy (Aldrey) suggests that oxidation occurs rapidly at an early stage as indicated by the growth of the specific weight of the specimens (Fig. 1 a). The true E-AlMgSi alloy (Aldrey) oxidation rate as a function of temperature varied from  $2.67 \cdot 10^{-4}$  to  $3.28 \cdot 10^{-4}$  kg/(m<sup>2</sup> · s). The apparent oxidation activation

energy calculated from the  $\lg K(1/T)$  dependence slope tangent was 128.5 kJ/mole (Table 1).

Solid E-AlMgSi conductor alloy (Aldrey) containing 0.05 wt.% indium was oxidized at 723, 773 and 823 K. The alloy oxidation kinetic curves are shown in Fig. 1 b. The alloy oxidation rate increases slightly with an increase in time and temperature. However the growth of the specific weight of the specimen becomes constant after 20 min of oxidation upon reaching  $3.39 \cdot 10^{-4}$  kg/m<sup>2</sup> at 823 K. The apparent oxidation activation energy is 114.1 kJ/mole (Table 1).

Indium doping of the E-AlMgSi alloy (Aldrey) to 0.1 and 0.5 wt.% slightly increases the true oxidation rate (Fig. 1 c and d) and hence leads to a decrease in the oxidation activation energy in comparison with the alloy containing 0.05 wt.% indium. For example, at 723 and 823 K the true oxidation rate for the alloy containing 0.1 wt.% indium varies from  $2.86 \cdot 10^{-4}$  to  $3.47 \cdot 10^{-4}$  kg/(m<sup>2</sup> · s) at an activation energy of 109.6 kJ/mole, whereas the oxidation rate for the E-AlMgSi alloys (Aldrey) containing 0.5 and 1.0 wt.% indium varies at these temperatures from  $3.04 \cdot 10^{-4}$  to  $3.57 \cdot 10^{-4}$  kg/(m<sup>2</sup> · s) and from  $3.14 \cdot 10^{-4}$  to  $3.70 \cdot 10^{-4}$  kg/(m<sup>2</sup> · s), respectively. The apparent oxidation activation energies are 99.4 and 91.8 kJ/mole, respectively (Table 1).

Figure 2 shows  $\lg K(1/T)$  dependences for the indium doped E-AlMgSi alloy (Aldrey). It can be seen from Fig. 2 that the oxidation rate increases with an increase in temperature and indium content. Oxidation of the alloys is accompanied by a slow but gradual increase in the thickness of the oxide film which completely inhibits oxidation at  $t = 20$  min. With an increase in the thickness of the oxide film the oxidation rate drops dramatically but increases with an increase in temperature. Indium dop-

**Table 2.** Oxidation curve polynomials of solid indium doped E-AlMgSi aluminum conductor alloy (Aldrey)

Indium content in alloy (wt.%)	Oxidation temperature (K)	Alloy oxidation curve polynomials	Regression coefficient (R <sup>2</sup> )
0	723	$y = -0.6 \cdot 10^5 x^4 + 0.001x^3 - 0.044x^2 + 0.973x$	0.981
	773	$y = -0.6 \cdot 10^5 x^4 + 0.001x^3 - 0.038x^2 + 1.109x$	0.988
	823	$y = -0.6 \cdot 10^8 x^4 + 0.001x^3 - 0.041x^2 + 1.289x$	0.994
0.05	723	$y = -0.5 \cdot 10x^4 - 0.001x^3 - 0.021x^2 + 0.889x$	0.983
	773	$y = -0.5 \cdot 10x^4 - 0.001x^3 - 0.028x^2 + 1.042x$	0.989
	823	$y = -0.5 \cdot 10x^4 + 0.001x^3 - 0.039x^2 + 1.267x$	0.992
0.1	723	$y = -0.5 \cdot 10^3 x^4 - 0.001x^3 - 0.001x^2 + 0.779x$	0.985
	773	$y = -0.5 \cdot 10^2 x^4 - 0.001x^3 - 0.012x^2 + 0.967x$	0.991
	823	$y = -0.5 \cdot 10^2 x^4 - 0.001x^3 - 0.019x^2 + 1.164x$	0.993
0.5	723	$y = -0.5 \cdot 10^4 x^4 - 0.001x^3 + 0.007x^2 + 0.775x$	0.986
	773	$y = -0.5 \cdot 10^3 x^4 - 0.001x^3 - 0.001x^2 + 0.934x$	0.992
	823	$y = -0.5 \cdot 10^3 x^4 - 0.001x^3 - 0.018x^2 + 1.169x$	0.994
1.0	723	$y = -0.5 \cdot 10^4 x^4 - 0.001x^3 + 0.006x^2 + 0.798x$	0.991
	773	$y = -0.5 \cdot 10^4 x^4 - 0.001x^3 + 0.004x^2 + 0.920x$	0.995
	823	$y = -0.5 \cdot 10^3 x^4 - 0.001x^3 - 0.013x^2 + 1.158x$	0.997

Notations: y is the relative weight gain of alloys; x is the oxidation time.

ing to within 0.05 wt.% affects the oxidation rate of the E-AlMgSi conductor alloy (Aldrey) but slightly. Further increase in the indium concentration in the alloy increases the oxidation rate of the initial E-AlMgSi alloy (Aldrey).

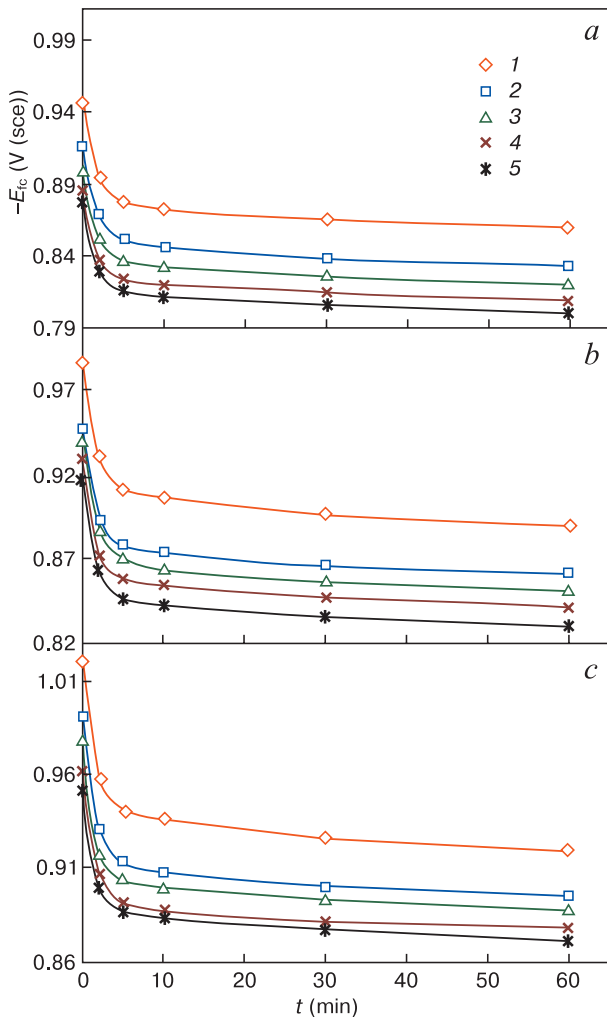
Table 2 shows processing data for quadratic alloy oxidation kinetic curves in the  $(g/s)^2$  vs  $t$  form for the E-AlMgSi conductor alloy (Aldrey) containing up to 1.0 wt.% indium (Fig. 4). It should be noted that the alloy oxidation curve pattern is hyperbolic because the parameter  $n$  in the equation  $y = kx^n$  varies from 2 to 4 (Table 2).

An increase in the oxidation rate of the E-AlMgSi alloy (Aldrey) as a result of indium doping is accounted for by the mechanism whereby the forming indium oxide  $In_2O_3$  phase affects the main oxidation protection product, i.e.,  $Al_2O_3$ . Spinel-like oxides  $Al_xIn_yO_z$  do not form between the  $Al_2O_3$  and  $In_2O_3$  oxides. Therefore indium oxide  $In_2O_3$  forming as a result of oxidation penetrates into aluminum oxide from the reaction surface and im-

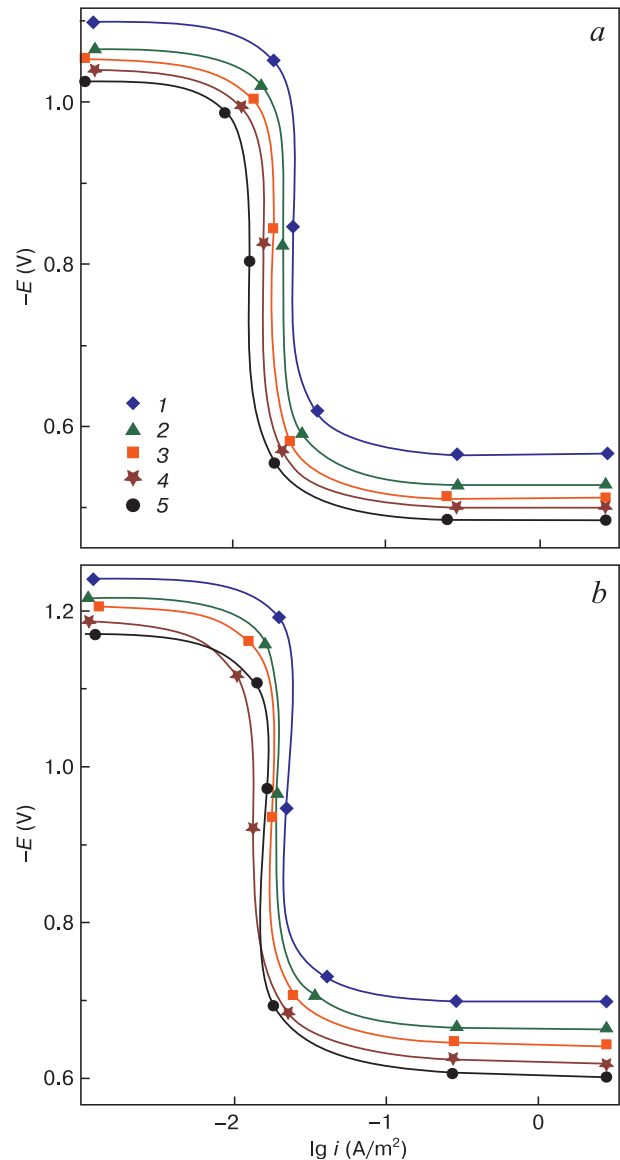
pairs its protection properties due to the growth of the porosity of the  $Al_2O_3$  film thus increasing oxygen delivery rate to the reaction surface.

#### 4. Effect of indium on corrosion and electrochemical behavior of E-AlMgSi aluminum conductor alloy (Aldrey) in NaCl electrolyte media

Results of corrosion and electrochemical studies for the E-AlMgSi aluminum alloy (Aldrey) in NaCl electro-



**Figure 5.** Time dependence of free corrosion potential (sce) ( $-E_{fc}$ , V) of indium doped E-AlMgSi aluminum conductor alloy (Aldrey) in (a) 0.03%, (b) 0.3% and (c) 3% NaCl media: (1) undoped alloy, (2) 0.05 wt.% indium, (3) 0.1 wt.% indium, (4) 0.5 wt.% indium and (5) 1.0 wt.% indium.



**Figure 6.** Anodic polarization curves (2 mV/s sweep) of indium doped E-AlMgSi aluminum conductor alloy (Aldrey) in (a) 0.03%, (b) 0.3% and (c) 3% NaCl media: (1) undoped alloy, (2) 0.05 wt.% indium, (3) 0.1 wt.% indium, (4) 0.5 wt.% indium and (5) 1.0 wt.% indium.



**Table 3.** Corrosion and electrochemical parameters of indium doped E-AlMgSi aluminum conductor alloy (Aldrey) in NaCl electrolyte

NaCl concentration (wt.%)	Indium content in alloy (wt.%)	Electrochemical potentials (V (sce))				Corrosion rate	
		$-E_{fc}$	$-E_{cor}$	$-E_{pc}$	$-E_{rp}$	$I_{cor}$ ( $10^2$ A/m <sup>2</sup> )	$K$ ( $10^3$ g/(m <sup>2</sup> · h))
0.03	–	0.860	1.100	0.600	0.720	0.049	16.41
	0.05	0.833	1.070	0.580	0.700	0.046	15.41
	0.1	0.820	1.055	0.568	0.692	0.044	14.74
	0.5	0.809	1.043	0.557	0.686	0.042	14.07
	1.0	0.800	1.030	0.544	0.681	0.040	13.40
0.3	–	0.890	1.180	0.680	0.768	0.066	22.11
	0.05	0.861	1.154	0.648	0.748	0.064	21.44
	0.1	0.852	1.137	0.637	0.740	0.061	20.43
	0.5	0.843	1.120	0.629	0.737	0.059	19.76
	1.0	0.830	1.109	0.620	0.735	0.057	19.09
3.0	–	0.919	1.240	0.735	0.800	0.082	27.47
	0.05	0.895	1.214	0.708	0.771	0.075	25.12
	0.1	0.887	1.209	0.700	0.765	0.073	24.45
	0.5	0.878	1.198	0.691	0.764	0.071	23.78
	1.0	0.870	1.187	0.680	0.755	0.068	22.78

lyte media are summarized in Table 3 and illustrated in Figs. 5 and 6. Figure 5 shows the graphical dependence of the free corrosion potential ( $-E_{fc}$ , V) on time for the indium doped E-AlMgSi alloy (Aldrey) in NaCl electrolyte media. It can be seen from Fig. 5 that immersion of the specimens into NaCl electrolyte results in a shift of the free corrosion potential towards positive values.

Generalized data on the corrosion and electrochemical properties of the alloys summarized in Table 3 suggest that indium doping of the initial E-AlMgSi alloy (Aldrey) to within 0.05–1.0 wt.% shifts the corrosion, repassivation and pitting potentials in the test media towards positive values.

Indium doping of the E-AlMgSi alloy (Aldrey) reduces its corrosion rate by 20–30% in all the test media. An increase in the NaCl electrolyte concentration (chloride ions) favors an increase in the corrosion rate of the alloys. The corrosion rate and corrosion current of the E-AlMgSi alloy (Aldrey) are the lowest at an indium concentration of 1.0 wt.%. Thus this alloy composition is the optimum one with regards to corrosion properties.

The anodic branches of the polarization curves for the indium doped E-AlMgSi aluminum conductor alloy (Aldrey) are shown in Fig. 6. It can be seen from the curve patterns in Fig. 6 that with an increase in the content of the third component, i.e., indium, all the electrochemical potentials shift towards positive values in NaCl electrolyte media which suggests a decrease in the cathodic dissolution rate of the indium doped alloys. The shift of the electrochemical potentials towards positive values and a decrease in the E-AlMgSi alloy (Aldrey) corrosion rate as a result of indium doping can be ac-

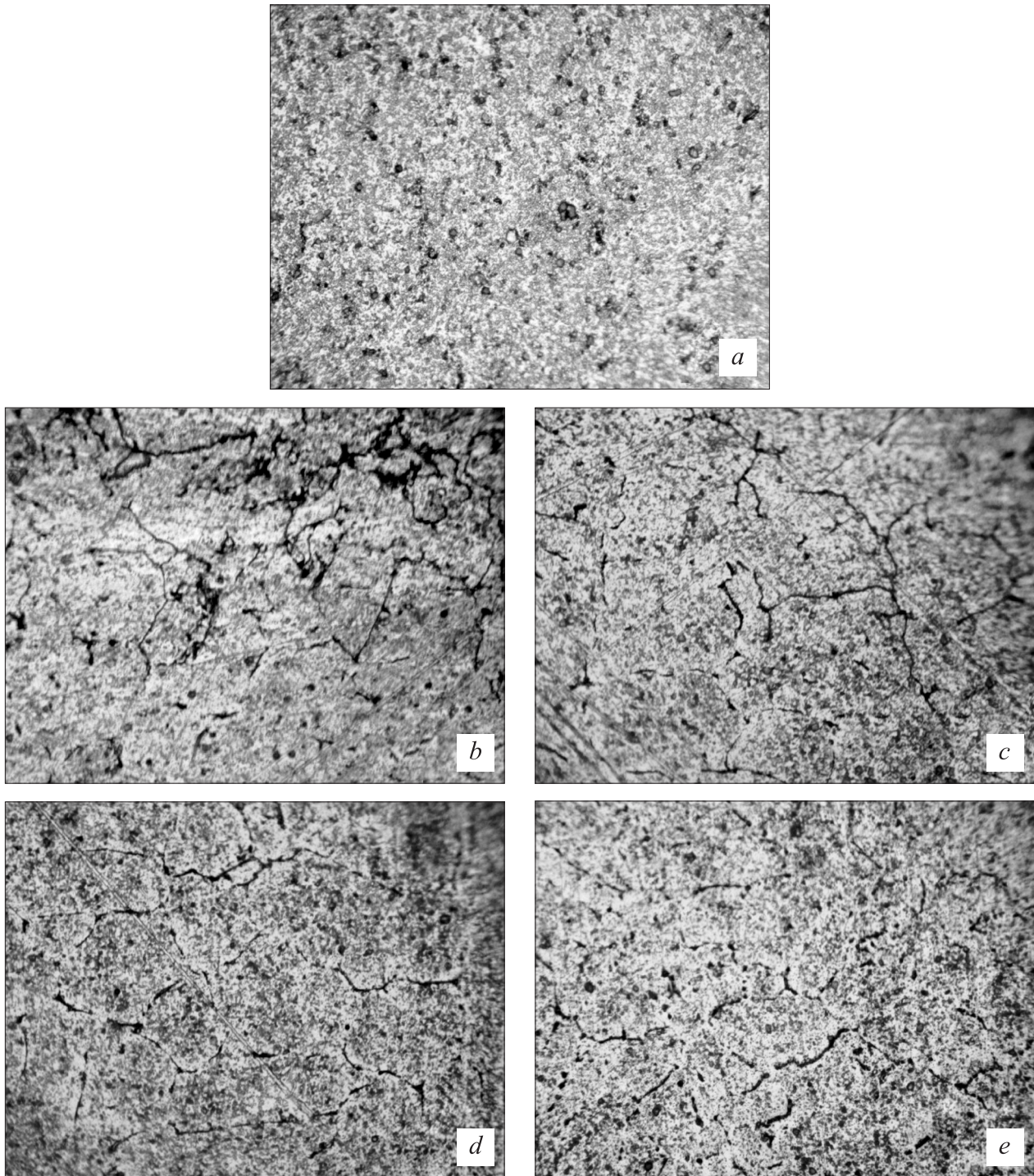
counted for by an increase in the heterogeneity of the alloy structure (Fig. 7).

The standard electrode potential of aluminum is  $\varphi_{Al^{3+}/Al}^0 = -1.66$  V indicating its low thermodynamic stability. In the air aluminum is immediately covered with an  $Al_2O_3$  aluminum oxide film the thickness of which may reach 5.0–20.0 nm. The formation of the  $Al_2O_3$  oxide film increases the electrode potential of aluminum. For example, the electrode potential of aluminum in 3.0% NaCl electrolyte media is  $-0.55$  V.

At this electrode potential aluminum may undergo corrosion in neutral electrolyte solutions and in water, its dissolution occurring with both oxygen and hydrogen depolarization.

The interaction of primary corrosion products ( $Al^{3+}$  cations and  $OH^-$  anions) at  $pH > 4$  leads to the formation of difficultly soluble  $Al(OH)_3$  hydroxide on the electrode surface. This aluminum corrosion product eventually transforms to aluminum oxide  $Al_2O_3 \cdot nH_2O$ . The oxide and hydroxide films forming as a result of corrosion have protective properties and therefore aluminum has a high corrosion resistance in neutral solutions.

Aluminum doping with indium the standard electrode potential of which is  $-0.342$  V, i.e., far higher than that of aluminum, provides for the higher corrosion resistance of the Al–In system alloys in NaCl electrolyte media (Table 3). Along with  $Al(OH)_3$  and  $Al_2O_3 \cdot nH_2O$  corrosion products, corrosion of these alloys may lead to the formation of  $Al(OH)_3 \cdot Ga(OH)_3$  type hydroxides and  $Al \cdot Ga_2O_3 \cdot nH_2O$  oxides which provide for a higher corrosion resistance of the alloys in electrochemical media.



**Figure 7.** Microstructure images ( $\times 650$ ) of indium doped E-AlMgSi alloy (Aldrey): (a) undoped alloy, (b) 0.05 wt.% indium, (c) 0.1 wt.% indium, (d) 0.5 wt.% indium and (e) 1.0 wt.% indium.

## 5. Conclusion

The oxidation kinetics of the indium doped E-AlMgSi aluminum conductor alloy (Aldrey) was studied using the thermal gravimetric method. Indium doping and high temperature exposure increase the oxidation rate of the initial alloy in the solid state which is confirmed by a decrease in the apparent oxidation energy of the E-AlMgSi

alloy (Aldrey) from 128.5 to 91.8 for the alloy containing 1 wt.% indium.

The polynomials of alloy oxidation kinetic curves showed that oxidation occurs by a thin-film mechanism and obeys a  $y = kx^n$  type hyperbolic equation where  $n$  is 2 to 4.

The anodic behavior of the E-AlMgSi aluminum conductor alloy (Aldrey) was studied in NaCl electrolyte me-



dia with a potentiostatic technique at a potential sweep of 2 mV/s. Indium doping of the initial alloy shifts the main electrochemical potentials of the alloys towards positive values.

We showed that indium doping increases the corrosion resistance of E-AlMgSi alloy (Aldrey) in NaCl electrolyte media by 20–30%. With an increase in NaCl electrolyte concentration (chloride ions) the electroche-

mical potentials of the alloys decrease, this being accompanied by an increase in the corrosion rate of the alloys regardless of their composition.

Based on the results of this study we developed an alloy composition the corrosion resistance of which is 20–30% superior to that of the currently used E-AlMgSi aluminum conductor alloy (Aldrey).

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