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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Effect of Aluminates on Electrochemical Characteristics of the Aluminum–Indium–Tin Alloy

S. B. Alekseev, N. A. Kudryavtsev, V. V. Nikol'skii, V. N. Naraev, V. N. Varypaev, and Yu. M. Kozyreva

Rigel' Battery Open Joint Stock Company, St. Petersburg, Russia
St. Petersburg State Technological Institute, St. Petersburg, Russia

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Abstract—Electrochemical dissolution of an Al–In–Sn alloy in 2–4 M NaOH solutions containing 0–3 M of sodium aluminate at temperatures of 40 and 75°C was studied by measuring potentiodynamic curves and chronopotentiograms.

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The researchers' interest in the electrochemical behavior of aluminum is due to prospects for its use as an anodic material for chemical power cells (CPCs), which is due to its high electrochemical activity (especially in alkaline solutions), high theoretical specific capacity, comparatively low cost, wide occurrence, and easy accessibility.

Because of the high rate of self-discharge accompanying the dissolution of aluminum in alkalis, use of pure aluminum as an anode material seems to be impossible. The problem of diminishing the influence of the negative-difference effect is being solved by a search for new aluminum alloys that are produced by its doping with other elements having the most electronegative potential and the slowest self-dissolution rate [1–3]. The main result of studies of this kind was that there appeared several patents [4, 5] which suggested to use such elements as indium, tin, gallium, and lead as alloying components for the aluminum anode.

At present, aluminum alloys are widely used in alkaline aluminum-air CPCs [6]. In addition, pilot samples of a cell based on the electrochemical system Al/NaOH/AgO, in which an aluminum–indium–tin alloy is used as the anode material, have been tested and the effect of various factors on its characteristics has been analyzed [7]. The results obtained in this study indicate that accumulation of aluminum dissolution products (aluminates) in the electrolyte strongly affects the working efficiency of an alkaline power cell with an aluminum anode. Therefore, it seems important to reveal the role of aluminates in electrochemical oxidation of aluminum and its alloys in alkaline solutions.

However, data on the electrochemical behavior of aluminum anodes in alkaline solutions containing aluminate ions are rather scarce and refer to a pure, unalloyed metal [8]. A study of the influence exerted by an aluminate on the electrochemical dissolution of aluminum and its alloys is complicated by the fact that, despite numerous attempts to develop a theory of the structure of alkaline-aluminate solutions and to explain their behavior in various conditions, the structure of aluminate ions in alkaline solutions has not been determined so far [9–12]. Some researchers consider aluminates as salts of meta- and orthoaluminic acids, $HAlO_2$ and H_3AlO_3. At the same time, studies of the properties of Al_2O_3–Na_2O–H_2O solutions indicate that complex interactions occur between the components of this system and suggest that intrecate complex compounds of variable composition exist in the solutions under consideration. This follows from the results obtained in the analysis of their electrical conductivity and viscosity and in measurements of their optical density. For example, aluminate ions are most frequently represented as complex ions $Al(OH)_4^-$, $Al(OH)_5^{-2}$, and $Al(OH)_6^{-3}$, with the ion $Al(OH)_4^-$ considered to be the most stable.

The present study is concerned with the anodic behavior of an aluminum–indium–tin alloy in an alkaline–aluminate solution in a wide range of aluminate

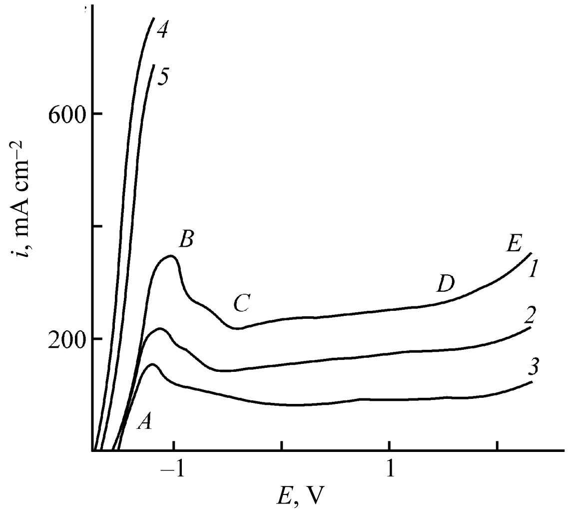

Fig. 1. Anodic potentiodynamic curves of the aluminum–indium–tin alloy in 6 M NaOH solution. Potential sweep rate 4 mV s^{-1}. (*i*) Current density and (*E*) anode potential. Aluminate concentration (M): (*1, 4*) 1, (*2*) 2, (*3, 5*) 3. Temperature (°C): (*1–3*) 40 and (*4, 5*) 75.

concentrations (0–3 M) at NaOH concentrations of 2, 4, and 6 M at temperatures of 40 and 75°C.

EXPERIMENTAL

As object of study was used an aluminum–indium–tin alloy containing up to 0.20% tin and up to 0.25% indium in the form of 1 × 1× 0.1 cm plates with a working surface area of 2.3 cm^2. Prior to any experiment, the electrode surface was cleaned, degreased with ethanol, and washed with distilled water. A 2–6 M NaOH solution with addition of 0–3 M of sodium aluminate served as the electrolyte. The working solution was thermostated on a water bath at $T = 75 \pm 1.0$°C (in some cases, at 40 ± 1.0°C). Polarization measurement were performed in a standard three-section electrochemical glass cell with a P-5848 potentiostat. For polarization in obtaining chronopotentiometric dependences served a B5-46 dc power source; the voltage in the anode–electrode circuit was measured with a Shch-1413 high-input-resistance digital voltmeter. Nickel plates served as auxiliary electrodes, and a saturated silver chloride electrode, as reference. The electrode was polarized for 15 min after being preliminarily kept in solution for 30 s to activate the surface. Potentiodynamic curves were measured at potentials of –2.0 to +2.0 V at a potential sweep rate of 4 and 8 mV s^{-1}. Chronopotentiograms were obtained at current densities of 100, 300, and 600 mA cm^{-2}. All the potentials are given relative to a standard hydrogen electrode.

The effect of the concentration of sodium aluminate in an alkaline solution on the rate of the anodic dissolution of the aluminum alloy is illustrated by Fig. 1. Curves obtained at the other potential sweep rate are similar, which points to a high stability of the results obtained.

It follows from Fig. 1 that the *i*–*E* dependences of anodic dissolution of the alloy under study at 40°C have a complex nature. For example, the *AB* portion of curve 1 corresponds to the active dissolution region, in which the rate of the anodic reaction depends on the potential. At a potential $E_\text{p} = -1.18$ V, the reaction rate reaches the maximum value $i_\text{p} = 345$ mA cm^{-2} and then decreases to a value of 220 mA cm^{-2} (portion *BC*), with the bend observed in this portion indicating that the passivation process is hindered to a certain extent at potentials of –0.75...–0.50 V. Then, a rather wide range of potentials is observed (–0.45 to +1.52 V, portion *CD*), within which the change in the current density does not exceed 40 mA cm^{-2}. Judging from its value, a conclusion can be made that the electrode surface passes to a semi-passive state. At potentials more positive than +1.52 V, the oxidation rate again increases (portion *DE*) and the metal finds itself in the repassivation region or in the transpassive state.

Soluble metallic anodes are passivated because a protective layer creating a kinetic barrier for metal dissolution is formed. The available published results obtained in studies of the anodic dissolution of aluminum in alkaline solutions demonstrate that the formation mechanism and structure of passive films produced on the surface of the dissolving metal are rather complex [13]. Aluminate ions, the final product of aluminum oxidation, are produced via a number of successive stages, in one of which there appear intermediate compounds that form an oxide film on the anode surface and are further partly dissolved in the alkaline medium. In the general form, these processes can be represented by the reactions [14]:

$$\mathrm{Al + 3OH} + \frac{(x-3)}{2}\,\mathrm{H_2O} \longrightarrow \frac{1}{2}\,\mathrm{Al_2O_3 \cdot \mathit{x}H_2O} + 3e, \qquad (1)$$

$$\mathrm{Al_2O_3 \cdot \mathit{x}H_2O + 2OH^-} \longrightarrow 2\mathrm{Al(OH)_4^-}$$
$$+ (x-3)\,\mathrm{H_2O} \qquad (2)$$

The maximum of the current density, observed at point *B* (Fig. 1, curve *1*), is associated with attainment of a dynamic equilibrium between the process of conversion of the metal to the oxide film [reaction (1)] and that of dissolution of this film in the electrolyte [reaction (2)]. At more positive potentials, the rate of reaction (1) increases to such an extent that diffusion fails to remove aluminate ions from the electrode surface, with the result that the process of film dissolution by reaction (2) is hindered because of the saturation on the near-anode layer by dissolution products and becomes rate-limiting.

The hindrance to the passivation of the alloy under study, which gives rise to a bend in the *BC* portion of curve *1*, is possibly due to occurrence, simultaneously with the main process of aluminum oxidation, of parallel current-forming reactions involving the alloying components present in the alloy. It has been shown previously that the alloying components strongly affect the efficiency of the anodic dissolution of aluminum alloys [1–3].

It is known that the aluminum–indium alloy is a mixture of a solid solution and an aluminum–indium eutectic, with the solid solution predominant in the alloy at mass fractions of indium of up to 0.2%. In anodic dissolution of alloys of this kind, indium atoms are oxidized together with aluminum atoms by the electrochemical mechanism to give indate ions InO_2^-.

In [15], the electrochemical behavior of indium in solutions of an alkali was studied and it was shown that transition of the indium anode to the passive state via formation of a passivating film on the surface of metallic indium occurs at a potential of –0.55 V. The passivation onset potential of indium corresponds to the position of the bend in the *BC* portion of the potentiodynamic curve of dissolution of the Al–In–Sn alloy. This fact confirms the previously made conclusion about the role of indium in the kinetics of anodic dissolution of the aluminum alloy and also indicates that products formed in dissolution of not only aluminum, but also indium, are involved in the passivation of the alloy under study.

As the concentration of the aluminates increases to 2–3 M (Fig. 1, curves *2* and *3*), the passivation onset potential E_p shifts in the negative direction and takes values of –1.08 and –0.99 V at aluminate concentrations of 2 and 3 M, respectively, with i_p decreasing to 215 and 150 mA cm^{-2}. This means that the region of active dissolution of the alloy becomes narrower at these aluminate concentrations.

In addition, as the aluminate concentration increases, the passive state of the electrode surface is enhanced, which is manifested in a more than twofold decrease in the current density in the passivity zone, with the range of potentials corresponding to the passive state simultaneously becoming wider. Apparently, this occurs because the increase in the content of the aluminate in the electrolyte enhances the diffusion limitations. As a result of saturation of the near-anode layer by dissolution products, and the subsequent passivation of the anode surface occur at more negative potentials. The shift of the dynamic equilibrium toward the formation of an oxide film by reaction (1) in solutions with a higher aluminate concentration is also indicated by an analysis of the Pourbet diagram for the aluminum–water system, reported in [16].

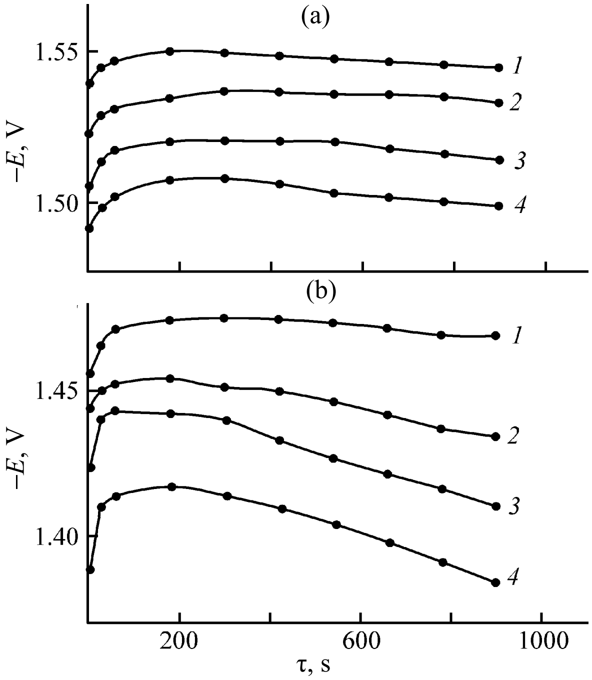

Fig. 2. Chronopotentiogram of anodic dissolution of the aluminum–indium–tin alloy in 6 M NaOH solution at 75°C. (*E*) Anode potential and (τ) time. Current density (mA cm^{-2}): (a) 300 and (b) 600. Aluminate concentration (M): (*1*) 0, (*2*) 1, (*3*) 2, and (*4*) 3.

As temperature increases, the solubility of aluminum oxide in a sodium hydroxide solution grows [12], as also does the diffusion rate, which leads to a change of the run of the i–E dependence of anodic dissolution of the aluminum alloy. Indeed, the anodic polarization curves at a temperature of 75°C (Fig. 1, curves *4* and *5*) correspond only to active dissolution of aluminum: the rate of the anodic process is higher than that at 40°C and there are no indications of passivation of the anode surface even at current densities exceeding 600 mA cm^{-2}. This circumstance is highly important when the alloy under study is used as the anode material for a power cell, because it allows discharge at high current densities.

Typical chronopotentiograms of anodic dissolution of the alloy under study are shown in Figs. 2a and 2b. It can be seen in Fig. 2a that dissolution in an electrolyte containing no aluminate ions (curve *1*) is distinguished by the stability of the E–τ characteristic. The change in potential during 900 s does not exceed 0.01 V, whence follows a conclusion that the buildup of the electrode polarization through accumulation of oxidation products in the near-anode layer is rather slow. Introduction of aluminate ions does not affect significantly the run of the E–τ dependence: chronopotentiograms measured at aluminate concentrations of 1–3 M (Fig. 2a, curves *2–4*) do not differ fundamentally from curve *1*. In each case, however, the electrochemical dissolution of the alloy occurs at a more positive potential than those in solutions with a lower content of the aluminate, which indicates that the influence exerted by the aluminate on the dissolution potential of the aluminum alloy gradually increases as the aluminate concentration in the electrolyte becomes higher.

An increase in the current density to 600 mA cm^{-2} (Fig. 2b) impairs the stability of the dissolution potential of the alloy in the course of time, with this tendency being more pronounced in solutions with higher aluminate concentrations. In a pure NaOH solution (Fig. 2b, curve *1*), the chronopotentiogram of alloy dissolution differs only slightly from a similar curve in Fig. 2a. At the same time, in solutions containing 1–2 M of the aluminate (curves *2, 3*), the change in the potential in the course of dissolution is 0.02–0.03 V, and further increase in the aluminate concentration to 3 M (curve *4*) results in a sharp shift of the potential into the region of positive values already during the first seconds after the beginning of polarization.

Potential of the aluminum–indium–tin alloy in NaOH solutions with various aluminate concentrations at different current densities

c_{NaOH}, M	i, mA cm^{-2}	E, V, at indicated $c(\text{Al(OH)}_4^-)$ concentration, M			
		0	1	2	3
2	100	−1.58	−1.50	s*	s
	300	−1.49	−1.42	s	s
	600	−1.38	−1.27	s	s
4	100	−1.60	−1.61	−1.54	s
	300	−1.53	−1.51	−1.48	s
	600	−1.44	−1.43	−1.34	s
6	100	−1.62	−1.63	−1.62	−1.59
	300	−1.56	−1.54	−1.50	−1.47
	600	−1.47	−1.44	−1.43	−1.39

* s, solution saturation with the aluminate.

In dissolution of the alloy in 2 and 4 M NaOH solutions, the behavior observed in Fig. 2 is mostly preserved. It should, however, be noted that the 4 M NaOH solution containing 3 M of the aluminate is unstable and decomposes with precipitation of aluminum hydroxide. In a 2 M NaOH solution, a similar pattern is observed even at aluminate concentrations of 2 M, in agreement with the solubility isotherms of the Al_2O_3–Na_2O–H_2O system, reported in [12].

The table lists the average values of the potential of the alloy under study in the course of anodic polarization at current densities in the range 100–600 mA cm^{-2} in solutions with various concentrations of NaOH and Na[Al(OH)4] at 75°C.

The data in the table demonstrate the complex nature of the influence exerted by the electrolyte composition on the dissolution potential of the alloy under study. As, for example, the NaOH concentration increases from 2 to 6 M, the anodic dissolution potential shifts toward negative values, with this shift being the stronger, the higher the current density. In addition, the electronegative potential continues to decrease in less concentrated solutions as the aluminate concentration increases up to the electrolyte saturation concentration. In the process, the change in the potential upon an increase in the aluminate concentration in solution becomes more pronounced on passing from more concentrated NaOH solutions to less concentrated solutions. For example, the change in the potential in a 6 M NaOH solution containing 0 to 3 M of the aluminate does not exceed 0.04 V at a current density of 100 mA cm^{-2}, whereas in a 2 M NaOH solution at the same current density, the potential decreases by 0.08 V, compared with a pure electrolyte, even at an aluminate concentration of 1 M, and at a current density of 600 mA cm^{-2}, this decrease is as large as 0.12 V. This circumstance, taken together with the overall decrease in the potential in less concentrated NaOH solutions, points to an enhanced negative influence of the aluminate on the alloy dissolution potential.

CONCLUSIONS

(1) The anodic dissolution of the aluminum–indium–tin alloy in alkaline electrolytes both in the presence and

in the absence of aluminates has no passivity region at 75°C. At 40°C, passivation is observed, together with active dissolution, in a wide range of potentials, with the passivation current density decreasing as the aluminate concentration becomes higher.

(2) The dissolution potential of the alloy at 75°C is distinguished by stability, but shows a complex dependence on the solution composition. The potential shifts in the negative direction as the alkali concentration increases, and in the positive direction, as the content of aluminates becomes higher, with the last circumstance being the most characteristic of dilute solutions.

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