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## Chronopotentiometry at platinum electrode in KF-NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> melt\*

Some features of the mechanism of the anode process on platinum in KF-NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> melt at 750–780 °C depending on the of anodic current density (0.5 mA/cm<sup>2</sup> to 2.0 A/cm<sup>2</sup>) and anodic pulse duration have been studied using chronopotentiometry method.

In curves of change in the platinum anode potential a small peak at current densities of 10–30 mA/cm<sup>2</sup> and a clear peak at current densities of 0.5–2.0 A/cm<sup>2</sup> are recorded when the current is cut on. Analysis of dependencies of the transition time on the current density indicates that the first peak in curve is associated with the formation of an oxide compound on the platinum surface, and the second one is related to hindering the diffusion for delivery of electroactive particles to its surface.

**Key words:** Chronopotentiometry, mechanism of the anode process, platinum anode, aluminium

\* The study was supported by the Russian Foundation for Basic Research (grant № 13–03–00829 A).

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### Introduction

At the present time research is directed to the development of physicochemical bases of technology for production of aluminum by electrolysis of KF-NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> melt at 750–850 °C using non-consumable anodes conducting in the world [1–3]. In order to avoid a rapid corrosion of the anodes it is necessary to select both its formulation and a method of manufacturing, and optimal electrolysis modes. The latter implies the establishment of regularities of kinetics of

oxygen release at the anode using electrochemical methods of analysis. Platinum can serve as an experimental model of a non-consumable anode.

Earlier [4] a comparative analysis of experimental and modeling stationary polarization curves for platinum in KF-NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> melt at 725–800 °C has been conducted.

It has been shown that the primary charge transfer to form O<sub>ads</sub> particles adsorbed on platinum is accompanied by

their desorption by physical or electrochemical mechanism. A more complete description of the mechanism features of the process under study can be achieved as the result of using the complex of electrochemical analysis methods, including non-stationary ones.

## Experiment

Experiments were performed in alundum crucible [4], which was placed in a quartz cell purged with argon or oxygen. The auxiliary nichrome electrode was placed in a porous alundum tube that serves as a diaphragm. As the working electrode platinum purity of 99.9926 % (JSC "Revda Non-Ferrous Metals Processing Works") was used. As the reference electrode a gas carbon electrode [5] in the equilibrium mixture of CO and CO<sub>2</sub> served. Measurements were carried out in the melt (wt. %):

## Results and discussion

Figure 1 shows typical curves of change in the potential of the platinum anode obtained on platinum in KF-NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> melt at 750–780 °C when cutting on and cutting off the anode current. A peak in cut on curve is observed at low current densities (up to ≈30 mA/cm<sup>2</sup>). Increasing the anode current density from 0.5 to 30 mA/cm<sup>2</sup> results in shifting of a peak potential from ≈ 0.44 to 0.58 V in respect of the carbon electrode and reducing the transition time from 1.1 to 0.005 s. In our view, electrochemical platinum oxidation accompanied by filling its surface by oxidation product can act as the process in said section. Despite the instability of platinum oxide at temperatures above 560 °C [6] electrochemical formation of platinum oxide was observed in

The present work is devoted to the experimental study of non-stationary anode process on platinum by chronopotentiometry in KF-NaF-AlF<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> melt at 750–780 °C.

39.6KF-7.1NaF-47.3AlF<sub>3</sub>-6.0Al<sub>2</sub>O<sub>3</sub> at temperature 750–780 °C.

Chronopotentiograms were obtained at anodic current densities from 0.05 mA/cm<sup>2</sup> to 2.0 A/cm<sup>2</sup> with a sampling frequency up to 750 kHz using PG-STAT AutoLab 320N and software NOVA 1.10 (Eco Chemie, the Netherlands). To calculate the anode overvoltage using the procedure «I-Interrupt» ohmic resistance in the section of polarizing circuit included in the measuring circuit were determined.

a cryolite-alumina melt at 1000 °C [7]. The diffusive character of the dependence of the transition time on the current density at that may be caused by limiting oxygen delivery to the platinum through the oxidized layer (or the growth rate of the oxide film).

Increasing the length of the anode current pulses of value up to ≈30 mA/cm<sup>2</sup> (Fig. 1a), does not give rise to the second peak in the cut on curve associated with hindering the diffusion for delivery of electroactive oxygen-containing Al-O-F component from the melt content to the layer near the anode. Its expression is observed for the system under study with an increase in the magnitude of anode current density from 0.5 A/cm<sup>2</sup> (Fig. 1b), at that the transition times are from 2 ms to 10–15 s.

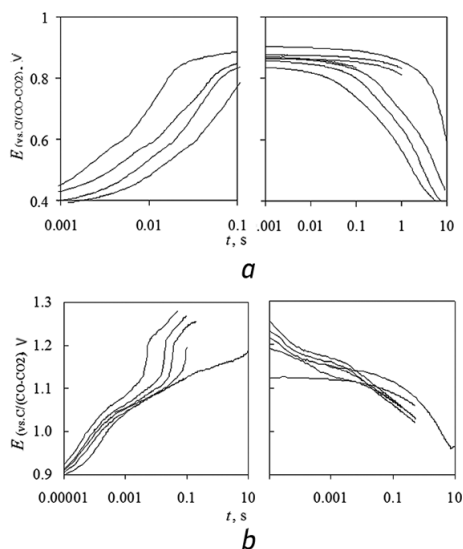


Fig. 1. Cut on and cut off curves of current on platinum in  $\text{KF-NaF-AlF}_3\text{-Al}_2\text{O}_3$  melt at  $780\text{ }^\circ\text{C}$  and current densities of  $0.5\text{--}30\text{ mA/cm}^2$  (a) and  $0.5\text{--}2.0\text{ A/cm}^2$  (b). Atmosphere is argon, the reference electrode is a carbon electrode

Analysis of curves of change in the platinum potential under current interruption points indicates a long period of term relaxation of the platinum potential as after the anode current density pulse of value of  $30\text{ mA/cm}^2$  ( $30\text{--}35\text{ s}$ ), so after pulses of value of  $0.5\text{--}2.0\text{ A/cm}^2$  ( $10\text{--}15\text{ s}$ ).

Data from curves of change in the platinum potential for small (**1**, **2**) and high

## Conclusion

Nonstationary anodic process on platinum in  $\text{KF-NaF-AlF}_3\text{-Al}_2\text{O}_3$  melt at  $750\text{--}780\text{ }^\circ\text{C}$  depending on the duration and magnitude of anode current density (from  $0.5\text{ mA/cm}^2$  to  $2.0\text{ A/cm}^2$ ) have been studied using chronopotentiometry method.

It is shown that when the anodic current densities are from  $0.5\text{ A/cm}^2$  the process under study is limited by diffusion of the electroactive particles to the

(**3**) anodic current density values were built in the coordinates  $it^{1/2}$  to  $i$  (Fig. 2). Enhancement of  $it^{1/2}$  (**1**) with increasing  $i$  for small values of anode current densities indicates the electrode process (platinum oxidation) followed by slow desorption of products [8], whereas at high anodic current densities constancy of  $it^{1/2}$  value (**3**) is observed, which points at slow diffusion of electroactive particles to the electrode surface. The value of the diffusion coefficient of the electroactive particles for high anode current densities at  $750\text{--}780\text{ }^\circ\text{C}$  estimated from the Sanda equation [8] amounted to  $0.7\text{--}1.5 \times 10^{-5}\text{ cm}^2/\text{s}$ .

The presence of the electrochemical oxidation of platinum is supported by the following:

- the estimated value of the electric double layer capacity ( $C_d$ ) in the initial section of curves of change in the platinum potential (times to  $\approx 5 \times 10^{-4}\text{ s}$ ) when the current is cut on according to expression  $C_d = i / (d\eta/dt)$  [1] was  $400\text{--}560\text{ uF/cm}^2$ , which is characteristic of the formation of several oxide compound layers;
- dependence of  $it^{3/2}$  on  $i$  (Fig.2, **2**) is linear at low current densities, that points at the growth of the oxide film resulting from the electrochemical process [7].

surface of the platinum anode, while at low current densities preceding stage is recorded.

Analysis of dependencies of  $it^{1/2}$  on  $i$  from curves of changes of the potential platinum when anode current is cut on according to equations describing the slow diffusion of electroactive particles and the growth of the oxide film on the electrode surface indicates the electrochemical oxidation of platinum.

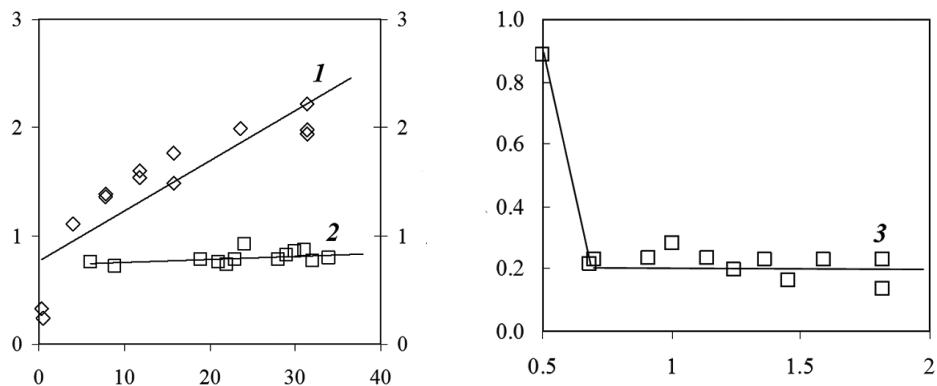


Fig. 2. Dependencies of  $it^{1/2}$  and  $it^{3/2}$  on  $i$ , built up from cut on curves on platinum for small (1, 2) and high (3) anode current densities

For high current densities values of the diffusion coefficient of electroactive particles to the platinum anode and the capacity of the electrical double layer were estimated, which amounted to, respectively,  $0.7\text{--}1.5 \times 10^{-5} \text{ cm}^2/\text{s}$  and  $400\text{--}560 \text{ uF}/\text{cm}^2$ .

The new obtained data can be used to specify the scheme of the process un-

der study and create a theoretical model enabling estimation of the effect of the parameters of the anodic process on platinum and other oxygen-releasing electrodes in  $\text{KF-NaF-AlF}_3\text{-Al}_2\text{O}_3$  melt and other oxide-fluoride melts in a wide temperature range.

1. Nekrasov V. N., Suzdaltsev A. V., Limanovskaya O. V., Khramov A. P., Zaikov Yu. P. Theoretical and experimental study of anode process at the carbon in  $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$  melts. *Electrochim. Acta.* 2012;75: 296.
2. Yang J., Hryn J. N., Davis B. R., Roy A., Krumdick G. K., Pomykala Jr. J. A. New opportunities for aluminum electrolysis with metal anodes in a low temperature electrolyte system. *Light Metals.* 2004;321.
3. Helle S., Pedron M., Assouli B., Davis B., Guay D., Roue L. Structure and high-temperature oxidation behaviour of Cu-Ni-Fe alloys prepared by high-energy ball milling for application as inert anodes in aluminium electrolysis. *Corrosion Science.* 2010;52: 3348. DOI: 10.1016/j.corsci.2010.06.011.
4. Nekrasov V. N., Limanovskaya O. V., Suzdaltsev A. V., Khramov A. P., Zaikov Yu. P. Stationary anodic process at platinum in  $\text{KF-NaF-AlF}_3\text{-Al}_2\text{O}_3$  melts. *Rus. Metallurgy.* 2014;8: 664. DOI: 10.1134/S0036029514080084.
5. Suzdaltsev A. V., Khramov A. P., Zaikov Yu. P. Carbon electrode for electrochemical studies in electrolyte-alumina melts at  $700\text{--}960 \text{ }^\circ\text{C}$ . *Rus J Electrochemistry.* 2012;48: 1141. DOI: 10.1134/S1023193512120117.
6. Livingstone S. *Rhenium, Rhodium, Palladium, Osmium, Iridium and Platinum.* Pergamon, Oxford, 1975.

7. Dewing E. W., Van der Kouwe E. Anodic phenomena in cryolite-alumina melts. *Th. J. Electrochem. Soc.* 1977;124: 58.
8. Bard A. J., Faulkner L. R. *Electrochemical Methods: Fundamentals and Applications*. 2<sup>nd</sup> ed. N.Y.: John Wiley & Sons Inc. 2001, 833 p.