Electrolysis of cryolite-alumina melts and suspensions with oxygen-evolving electrodes

The method of producing aluminum by electrolytic decomposition of alumina of cryolite dissolved in the melt has been used for more than 130 years, and no alternative has yet been offered. Therefore, studies on the cardinal improvement of the existing hardware and technological scheme are especially important. First of all, we are talking about the use of fusible cryolites based on potassium cryolite and the use of non-consumable anodes and wettable metal cathodes. Then, using a vertical arrangement of electrodes, similarly to a diaphragm-free magnesium electrolyzer, it is possible to significantly increase the productivity of a single unit. Naturally, its working lining should be made of corundum refractories, and to prevent its dissolution, the fluoride melt should be supersaturated with alumina, which involves the use of a suspension.

In the recited work, a thorough analysis of the literature data was made and the correct direction of research was chosen. Thus, the behavior of a tungsten cathode and a bronze anode in a suspension of alumina in acidic potassium cryolite was studied by stationary polarization and cyclic voltammetry. Quantitative characteristics of the dissolution rate of various types of alumina in potassium cryolite were also obtained. They are distinguished by the originality of the study of sedimentation of alumina in saturated melt.

Electrolysis was carried out in laboratory conditions which showed that aluminum can be produced at a tungsten cathode with a high current efficiency, while the specific energy consumption due to an increase in the voltage on the cell increased up to 19.8 kWh/kg at the end of the experiment. Of particular interest are the precision metallographic, x-ray phase and microprobe studies of the passivating layer on the bronze anode, which made it possible to obtain detailed information about its structure, phase and chemical composition.

All studies were performed using modern equipment, and their reliability is not in doubt. The obtained results supplement the available theoretical information about the processes occurring during low-temperature electrolysis of aluminum. We can assume that the author of the dissertation showed himself to be a qualified researcher.

Nevertheless, the reviewer considers it necessary to make the following comments:

1) Was anode gas analysis performed at various current densities at F2?

2) With what instrument, by what method and using what software was the quantitative x-ray phase analysis done? (Table No. 6)

3) During large-scale laboratory electrolysis, 212 g of Al was placed at the bottom of the cell, which was supposed to serve as a trap for the deposited metal, while Fig. 48 shows frozen drops with sizes of 0.1–4 cm; where were they found?

4) For some reason, it was not analyzed for W obtained Al?

5) The existence of an enriched F intermediate layer under the oxide film at the anode may indicate that the passivating film does not possess purely electronic conductivity and is most likely permeable to F-ions of the melt. The fact is that under conditions of industrial electrolysis, even under conditions far from the anodic effect, small amounts of fluorocarbons are present in gases, that is, along with oxygen ions, F ions...
are also oxidized. According to the microanalysis data, F is present over the entire thickness of the film; the mechanism of its migration is not clear and requires further study.

6) The author has no unequivocal opinion on the reasons for the increase in voltage over time on the electrolysis cell.

7) It takes a very long electrolysis to confirm the validity of the equation for the wear of the anode (formula 51), since it can fail much earlier due to physical destruction (delamination), may be this is the main reason for the voltage increase?

These questions do not detract from the importance of the dissertation, but rather indicate the issues that should be given special attention in further research. Based on the foregoing, I believe that Sai Krishna Padamata deserves the desired degree of PhD SibFU.

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