Review

on PHD thesis "ELECTROLYSIS OF CRYOLITE-ALUMINA MELTS AND SUSPENSIONS WITH OXYGEN EVOLVING ELECTRODES" by Sai Krishna Padamata

Discussed thesis is devoted to the problem of the development of inert anode technology in the primary aluminum production. The topic of an inert anode is the focus for more than 50 years. There is no need to substantiate its relevance, since the main benefit is to improve the environmental consequences of production. This is especially important to note that the current scale of the aluminum production all over the world is about 65 million tons per year, and thus it concerns the ecology of the planet.

The inert anode technology involves many questions. The thesis focuses on only one of them, in particular, reducing impurities or increasing the purity of the final aluminum. This problem manifested itself already at the stage of semi-industrial tests, when it became clear that the anode material in the electrolysis passes into the melt and then is collected in the final product – metallic aluminum. The concentration of impurities reaches a value when aluminum practically loses its grade.

The idea of conducting electrolysis in a suspension consisting of an electrolyte and alumina is investigated as a solution to the problem. The proposal was suggested in 1991 by Theodore R. Beck with co-authors in an American patent. It is assumed that the melt saturated with alumina dissolves the anode corrosion products to a lesser extent. However, to date, the idea has not been implemented, since it requires a large amount of basic research. This dissertation contributes to the basic knowledge on the electrolysis of saturated by alumina cryolite melts.

To achieve this goal, the author formulated a list of tasks: (1) to determine the influence of alloy composition on the anodic process of Cu-Al based anode in KF-AlF_3-Al_2O_3 electrolyte; (2) to understand the influence of alumina volume fraction in suspension on the behavior of Cu-Al based anode; (3) to assess the influence of cryolite ratio (CR), the temperature on the anodic process in suspensions; (4) to determine the cathode process on tungsten in KF-AlF3 melts at different CR (1.2-1.5); (5) to determine the sedimentation and dissolution rates of aluminium oxide in KF-AlF_3-Al_2O_3 electrolyte at different CR's (1.3-1.5) and temperatures (750-850°C).
The solution of the set tasks was achieved through the implementation of appropriate research. As a consequence, the following experimental results were obtained.

The current-voltage cell characteristics and anode degradation depending on the alumina volume fraction were studied. It appeared the increasing alumina particles content in melts led to decrease current density, anode oxidation and increase in the cell resistance. The corrosion products have changed from $CuAlO_2$ to Cu_2O; oxygen evolution decreased. The optimized particle volume fraction (φ) of 0.09 was determined.

The rate of the cathode process was optimal between -0.125 and -0.240 V and increased with the decreasing CR's and increasing Al_2O_3 (wt.%). The processes in melts were quasi-reversible with CR 1.3 and 1.5. The effects of temperature, particle size and phase composition of the dispersed alumina were studied. Determined alumina dissolution rates were in the range of 0.028-0.167 g·kg-1s-1. The increase in CR led to an increase in the alumina dissolution rate. The mechanically activated alumina dissolved faster. Two alumina particle sedimentation regimes in suspension were distinguished (low and fast). The measured Reynolds number (0.02 - 0.54)·indicated the Stokesian regime of sedimentation with velocities in the range (0.05-3.61)·10-2 m/s. The regimes of sedimentation stability were found for different type of alumina.

On the base of experimental results there were made some conclusions. Application of mechanically activated alumina with fine particles and electrolytes with a higher CR at 800 °C are the preferred solutions for development of the suspensions electrolysis technology. The CR should be 1.3-1.4 due to the limitations imposed by the cathodic process. The sedimentation stability could be achieved at φ=0.10...0.15. The electrolysis of 1.4KF-AlF_3-Al_2O_3(sat) with Cu-Al anode and W cathode was stated to be the solution to obtain cathode aluminium purity of about 99.40% and the main impurities are Fe, Si and Cu. The current efficiency of the

electrolysis was about 84.41%. The anode was working without any geometry damage and the wear rate was determined to be 0.08 cm/year. The specific energy consumption was around 14.5 kWh/kg Al (4hours) and 19.8 kWh/ kg Al for the last 6 hours.

So, the obtained results correspond to the stated goal and formulated tasks.

The list of published works on the topic of the dissertation consists of 5 papers and seems more than convincing.

There are some notes concerning the thesis preparation.

1. The dissertation repeatedly mentions the fact that the solubility of alumina increases with increasing CR. However, the author does not discuss the reasons for this circumstance, nor does he attempt to test electrolytes with CRs above 2 or even close to 3 (K_3AlF_6).
2. The equations (9) - (11) use an AlF5-2 particle, which formally corresponds to melts with CR = 2. At the same time, melts with CR from 1.3 to 1.5 are not discussed in these relations. What anions should be present in such melts?
3. It is not clear what is the sense in discussing completely unrealistic equations presented in Table 5, when aluminum ions oxidize metallic copper or iron?
4. In figure 19 there is no scale (degrees) on the abscissa axis. Instead of the term XRD radiographs, an X-Ray powder pattern should be used.
5. Sometimes figure captions do not provide the full content of the picture, for example, fig. 8.

Acquaintance with the results presented in the thesis allows reviewer to conclude that the work performed is a completed scientific work, which meets the requirements for dissertations, executed for the degree of PHD. It allows to be sure that the author of the work, Sai Krishna Padamata, is worthy of the required scientific degree.

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