Dissertation Review

Name of the PhD Candidate : Mr Sai Krishna Padamata
Planned Date of Graduation : September, year: 2020

Title of the Dissertation: «Electrolysis of cryolite-alumina melts and suspensions with oxygen evolving electrodes»

At present, almost all primary aluminum is obtained by Hall-Heroult process, which is provided by the consumption of carbon anodes and the emission of a significant amount of greenhouse gases. A radical modification of the Hall-Heroult process is possible when replacing the consumable carbon anodes with non-consumable inert anodes, which do not interact with the electrolyte and the oxygen evolved at the anode. The use of such anodes in combination with aluminum-wetted cathodes makes it possible to significantly decrease the anode-cathode gap in a cell and reduce the energy consumption.

As the PhD Candidate Sai Krishna Padamata rightly notes, today there is no information on the successful use of inert anodes in conventional technology. The main reason for this is the aggressiveness of the cryolite-alumina melt at high temperature. To prevent rapid corrosion of structural materials, it is necessary to reduce the operating temperature. In this regard, there is a need to create and develop a new low-temperature technology. Its main advantages are energy saving, a significant reduction in greenhouse gas emissions and an increase in the cell lifetime. Attempts to develop a low-temperature process for the production of aluminum were focused on the modification of a conventional electrolyte based on sodium cryolite. However, due to the low alumina solubility in such melts, they did not find application in industry. Sai Krishna Padamata suggests another way to solve the problem – to produce aluminum by electrolysis of potassium cryolite electrolyte saturated with alumina in a cell with vertical metal electrodes at temperature as low as 800 ^{o}C.

Information regarding the features of such electrolysis remained extremely scarce, completely undeveloped were the ideas related to mechanism of the cathode and anode processes and the effect of the alumina dissolution. These issues are considered in the present dissertation.

The PhD candidate accomplished a very significant experimental work studying the electrochemical behavior of the Cu-Al anode in the potassium cryolite containing different amount of dispersed alumina, the kinetics of the cathode process when tungsten was used as a cathode, the alumina dissolution and sedimentation rate under the influence of temperature, alumina particle size and phase composition. Finally, he performed the electrolysis in a cell with Cu-Al anode and W cathode with very high current efficiency and the aluminum purity of 99.4%. The results obtained open up prospects for the further development of a novel technology for low-temperature aluminum production.

Mr Sai Krishna Padamata used modern research methods – electrochemical (chronopotentiometry, cyclic voltammetry, electrolysis), metallographic (XRD, SEM), analytical, thermodynamic calculations, etc. by applying the high quality equipment.

The thesis is logically substantiated, written in good English.

A respectable literature review including 124 references has been completed. It should be noted that a lot of problems are raised in this work (inert anodes, dripping cathodes, and the rate of dissolution and sedimentation of alumina, and low-temperature electrolysis). Each of them can represent a scientific project; each has a large number of publications. Accordingly, it is impossible to fully take into account everything. However, it should be noted that some of the references do not directly relate to the research topic. For example, the effect of $AlPO_4$, which is not used in this work, on the liquidus temperature of the KF-AlF_3 system is discussed in some detail [62], while the works studying the liquidus temperature of the KF-AlF_3 with different molar ratios of the components is not reported. Likewise, works devoted to the low-temperature electrolysis in the KF-AlF_3-Al_2O_3 melts, directly related to the topic of the dissertation, are not discussed.

Some shortcomings of manuscript, which, of course, do not detract from its achievements:

1. Is it appropriate to call low-temperature technology alternative if it is based on the same principle as conventional technology?

2. Question to the experimental part - electrolyte preparation (p. 37). It is known that KF is very hygroscopic, how effective is the drying technique that you used? The way of the electrolyte preparation, in which easily sublimated AlF_3 is placed at the bottom of the crucible and KF (with a melting point of 858 °C) is loaded on the top, does not seem very correct. Since the mixture is supposed to overheat to about 900 °C, the required CR of the mixture is likely to change. How was the CR of prepared electrolyte analyzed?

3. (p.68, fig.34) Why in the stationary polarization curves the potential of potassium reduction changes, while its concentration is quite high in all electrolytes?

4. (p.95, table 16) The table “Composition of aluminum…” contains the names of 14 elements with a concentration below 0,01 wt%. What is the accuracy of determining the element concentration by the optical emission spectrometer? Is there a necessity to list all of these elements in the table?

Name of the Dissertation Commission Member : Tkacheva Olga Yurievna

Chair / Function : ……………………………

Date : 05.06.2020

Signature : …………………………… *

** No signature required when submitted per email.*