Dissertation Review Form
-for members of the Dissertation Commission-

Please write a review of the dissertation taking the following criteria into account, where appropriate:

- General remarks
- The significance and status of the dissertation in the field
- The sufficiency and quality of the material
- The adequacy of the methods used
- The validity of results
- The logic of the dissertation's structure
- The knowledge and use of literature in the field
- The project's contribution to the research area
- The author's input into the achievement of the dissertation results
- Language
- The shortcomings of the manuscript

Name of the Ph.D. 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.»

Would you please elaborate upon your review with reference to the criteria as mentioned above in the box below. Please add extra pages if needed

The Dissertation of Sai Krishna Padamata is connected with one of the focal problems of the development of inert anodes for aluminium reduction cell, vertical electrode cell along with a wettable cathode in low-temperature melts. Although the physics of the electrodes in low-temperature is still under investigation, the extraordinary phenomenon of their application is still very scarce, and it needed to be elucidated. Cu-based alloys are considered promising candidates (along with Fe-Ni alloys) as an inert anode's material in aluminium reduction cells with low-temperature electrolytes. Low-temperature alumina suspension electrolytes were found to reduce impurities in aluminium produced, and the behaviour of alumina in the melts was examined. In this research, the anode behaviour of Cu-Al-based electrodes and cathode behaviour of the tungsten electrode in low-temperature KF-AlF_3 melts were tested. The alumina dissolution and sedimentation rate in KF-AlF_3 melts were analyzed at different conditions.

However, successful applications require a controllable generation of low-temperature electrolysis processes with the desired quality of metal that is presently restricted because of limited knowledge on the low-temperature melts. This is why the number of investigations of low-temperature melts appearing in scientific literature is growing almost exponentially at the present time. Against the background of information flow on this topic, the contribution presented in the Dissertation by Sai Krishna Padamata is impressive and adds *considerable novelty into the understanding of the Electrolysis of cryolite-alumina melts and suspensions with oxygen-evolving electrodes.* The following *new observations* and regularities reported by Sai Krishna Padamata can be highlighted:

- This work reports on first observation the development of inert anodes for aluminium reduction cell for industries and the application of the inert anodes for environmental concerns, energy, and cost-efficient. According to a conventional approach, the inert anodes can only be fully efficient when used in vertical electrode cells along with a wettable cathode in low-temperature melts. Thus, Cu-based alloys (along with Fe-Ni alloys) as an inert anodes' material in aluminium reduction cells with low-temperature electrolytes are used in the reduction of impurities in aluminium production, and by examining the behaviour of alumina in the melts. The introduction of the alumina suspension particles in the electrolyte seems to be an excellent way to solve this problem by suppressing the convective transfer of corrosion products.

- In this research, the author tested the anode behaviour of Cu-Al-based electrodes, and the cathode behaviour of the tungsten electrode in low-temperature KF-AlF_3 melts, and he also analyzed the alumina dissolution, and sedimentation rate in KF-AlF_3 melts at different conditions. In the first stage, the tests were conducted to characterize the electrochemical behaviour of Cu-Al-based anodes. The effects of the temperature, the particle size, the phase composition of the dispersed material, and its volume fraction in the suspension on the dissolution kinetics, as well as the sedimentation velocity, were studied.
- A part of this work was devoted to experimental verification of the anodic behaviour of Cu-Al based electrode in low temperature melts at different conditions like alumina volume fraction, CR value, and the temperature was investigated along with the cathode process on W electrode in low temperature melts using cyclic voltammetry and chronopotentiometry techniques. This is the experimental model pretending to highlight the effects of the electrode process in KF-AlF_3-Al_2O_3 melts. (comprehensive overview of the experimental procedure and techniques, as well as explanations of the, is given in Chapter 3 of the Dissertation). This part of the work is performed in a classical approach by application of three-electrode cell, as shown in figure 11 was used to perform the experimental studies. High purity graphite crucible was also used to contain KF-AlF_3-Al_2O_3 (5wt. %) melt. The crucible also acted as a counter electrode. The Al/AlF_3 reference electrode was utilized, which was connected to the measuring device using a tungsten rod. The reference electrode had a porous BN tube containing the liquid aluminium and KF-AlF_3 melt. Autolab PGSTAT302n potentiostat equipped with a 20A booster and controlled by NOVA 2.1.2 software was used to carry out the Electrolysis. Electrolysis was conducted using the Chrono potentiometric method. Stationary polarization was performed for 0.005 to 1.5 A/cm^2 current densities, where the recording was made with 30 μs of current interruption time after a 120s current passage to determine the ohmic voltage drop (IR). Cyclic voltammetry was performed at 0.05 V/s scan rate to examine the possible anodic reactions. Some outstanding results have been obtained describing the Stationary state polarization describes reasonably the polarization in melts (φ=0) occurring with cell voltage U between 2.5 and 3.1 V for all the anode composition. The voltage was changed due to the oxide layer formation and the changes in its structure and composition. The voltage was altered due to the oxide layer formation and the changes in its structure and composition. The stationary galvanostatic polarization curves (figure 17) were recorded in melts (φ=0) and suspensions with φ=0.12 and 0.15. The time to reach the quasi-stationary state was about 100 seconds.

In the non-stationary study at a low sweep rate of 0.05 V/s (figure 18), the anode A1 has an unexpected highest current density as the alloy of this composition is more prone to passivation due to the formation of dielectric oxides. Thus, the presence of significant transport difficulties that may be created by the presence of a concentrated suspension. The aforementioned high current density confirms the possibility of the anode oxidation product dissolution.

- In XRD studies, Cyclic voltammetry was performed on anodes at 700 and 800 °C in melts saturated with alumina at CR = 1.2 -1.5. Records from Voltammograms were carried out to reveal the response of anode with the change in potential at 0.05 V/s. In this subpart, the reversible potentials and the stationary potentials at i=0.4 A cm^{-2} are obtained through the galvanostatic process for 1.2≤CR≤1.5 (Fig. 22). Consequently, an increase in the CR results in the more negative of the anodic potential and evolution of oxygen at low current densities.
- The results, which are extremely important for the understanding of experimental studies were also carried out in Stationary galvanostatic polarization of Cu-Al anode over several melts with different cryolite ratios from 1.2 to 1.5 at 700, 750 and 800 °C to study the kinetic parameters of oxygen evolution. Therefore, the anodic current density i_a, and the anodic potential E_a (vs. Al reference electrode) were recorded during the experiment. The obtained polarization curves are presented in figure 23.

  For the purpose of finding the total overvoltage, it has been demonstrated the relationship between the decomposition to the activation and the concentration components. And, the linear section on the graph was considered as an activation component of the overvoltage. It was extrapolated to higher values of *i*. The rest part was considered as the concentration component. The obtained results for CR=1.2 and T=750 and 800 °C are presented in figure 24. The experimental values of the concentration overvoltage $\eta_{conc}(exp.)$ were estimated and were compared with the values calculated according to the Eq. (23), from which the limiting current density was also found.

  In the cathode process in the $KF-AlF_3-Al_2O_3$ system part, the experiments were performed at 800°C melts with CR (1.2-1.5). The electrochemical behaviour is investigated using cyclic voltammetry and chronopotentiometry. The processes were tested in the melts with CR values of 1.3, 1.4, and 1.5, and the potential sweep rates (ν) was between 0.01 and 0.2 $V.s^{-1}$. The cathode peaks associated with the aluminium reduction **(Al)** depending on the potential sweep rate and CR values were observed between -0.125 and -0.240 V (vs. Al) for all the CR values. Typical cyclic voltammograms (CV) obtained on W in $KF-AlF_3$ melts at 800°C are shown in figure 31.

- In Chapter 4, Mr. Sai Krishna Padamata goal was to provide a complete understanding of the dissolution rate and sedimentation of alumina in $KFAlF_3$ melts and suspensions. The effects of the temperature, particle size and phase composition of the dispersed material and its volume fraction in the suspension on the dissolution kinetics and the sedimentation velocity were studied. The experiments were carried out over the melts with cryolite ratios 1.3 and 1.5 in the range of 750 - 850 °C. Three different types of aluminium oxide were also used, and the electrolytes were synthesized at 900 °C from the dried individual chemically pure (p.a.) salts KF and AlF3. Drying lasted for 4 hours at 400 °C. For dissolution and sedimentation studies, three types of materials were chosen.
- The studies in this Chapter have shown the effect of temperature on the dissolution kinetics at different concentrations of O^{2-} ions are presented in figure 39. The findings state that in terms of dissolution rate, the increase in temperature is preferable as well as using alumina with small particles and electrolytes with higher cryolite ratios.

  The influence of the temperature on the sedimentation kinetics of the suspension based on $1.3KF\text{-}AlF_3$ melt with volume fractions φ=0.1 was also given in figure 45 shows that the suspensions were stable or quasi-stable at *φ* values of 0.25, 0.20 and 0.10 with SGA, $\alpha\text{-}Al_2O_3$ and MA alumina respectively. The critical effect on the stability is influenced by the particle size and the density of the particles. The sedimentation velocity and the Reynolds number, have shown to highly rely on the temperature, alumina volume fraction, and properties.

Upon reading this Dissertation, the *remarks arose*, which mostly concern the dissolution rate, sedimentation, and behaviour of alumina in KF-AlF3 melts. As a whole, the description alumina melts, and suspensions with oxygen are extremely interesting. The original reading paper mentioned above gives the same opinion. Derivation of the parametric decay expression lacks clarity, while the explanation of the physical-mechanical mechanism is not convincing. It is stated that the influence of the dispersed phase volume fraction and the anode material on the current-voltage characteristics at stationary and non-stationary polarization, the phase composition of the oxide layer, and the features of the formation of the oxide layer on the surface of the material were studied. It was found that an increase in alumina volume fraction leads to an appreciable decrease in apparent limiting current density of the oxygen evolution and the metal oxidation as well. It also leads to the drastic increase in the resistance due to several reasons: the accumulation of anode oxidation products and bubbles in the anode layer, the growth of oxide layer, the structural changes, and the decrease in the active surface area.

The most abundant compounds in all oxide layers are Cu_2O and $CuAlO_2$. The 90Cu-10Al anode, the aluminium oxide suspension based on the $KF-AlF_3-Al_2O_3$ system with a volume fraction no more than 0.12 (with five μm Al_2O_3) at a temperature of at least 750 °C are recommended for further studies. The author of this Dissertation confirms pertinence of his technique that the aluminium reduction can be performed using 90Cu-Al anode and wettable tungsten cathode at CR 1.4 and T 800 °C. High purity aluminium can be produced using SGA and adequately protected current leads. Remarkable is comparing the obtained results, data based on the physicochemical properties of KF-AlF3 melts, the current density in anodes (A1-A3), the concentration of overvoltage, and cyclic voltammetry records allow excellent agreement. Although more studies are needed to further verify these models on other materials and conditions, the performed successful attempt indicates that this new model can become an excellent alternative method to produce aluminium.

Summarizing, the candidate for a Ph.D. degree has performed a large amount of insightful research and obtained new original results, which broaden our understanding of the physical mechanisms of the Electrolysis of cryolite -alumina melts and suspension with oxygen-evolving electrodes. The Dissertation work has been performed at a high scientific level. All crucial results presented in the Dissertation are published in peer-review journals. Judging by the Dissertation, the candidate Sai Krishna Padamata merits the Ph.D. Degree.

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