Abstract

The development of inert anodes for aluminium reduction cell has been a challenging issue for industries. The inert anodes use can be environmentally friendly, energy-efficient and economic. It has been previously discussed by the researchers that the inert anodes can only be fully efficient when used in vertical electrode cell along with a wettable cathode in low-temperature melts. Currently, Cu-based alloys have been considered as promising candidates (along with the Fe-Ni alloys) as the inert anodes material in aluminium reduction cells with low-temperature electrolytes. When it comes to the wettable cathode, TiB_2 is widely considered as promising materials although other materials such as carbon, tungsten, graphite are tested to analyse the cathode behaviour of the material in various conditions. The low-temperature alumina suspension electrolytes are considered to reduce the impurities in aluminium produced, so it is important to examine the behaviour of alumina in the melts. Metallic anodes tend to contaminate the produced aluminium with their corrosion products and introducing alumina suspension particles in the electrolyte could resolve this problem by suppressing the convective transfer of corrosion products In this thesis, the anode behaviour of Cu-Al based electrodes, cathode behaviour of tungsten electrode in low-temperature KF-AlF_3 melts are tested. Along with that, the alumina dissolution and sedimentation rate in KF-AlF_3 melts at different conditions are tested.

In the first stage, the tests were conducted to characterize the electrochemical behaviour of CuAl-based anodes (Cu-9Al-5Fe (A1), Cu-10Al (A2), and Cu-10Al-1.7Be (A3)) in KF-AlF_3-Al_2O_3 melts (CR $\left(\frac{Mole\ \%\ KF}{Mole\ \%\ AlF_3}\right) = 1.3$) and suspensions have been made and presented. The effects of the suspension (or melt) properties, the anode composition and the temperature on the electrochemical behaviour of the anode and the kinetics of the oxide layer formation during polarization are studied. Increase in volume fraction led to an appreciable decrease in apparent limiting current density of the oxygen evolution and the metal oxidation. The results obtained suggested the further study shall be conducted on A2 anode. In the second stage, anodic processes on A2 electrode in molten KF-AlF_3-Al_2O_3 (5 wt. %) and suspensions were characterized. Effects of cryolite ratio CR (1.2-1.5), temperature and particle volume fraction ($\varphi = 0 – 0.15$) on the electrochemical behaviour of the anode were demonstrated. The cathode process on tungsten (W) has been examined in melts with CR's (1.3-1.5), The diffusion and mass transfer coefficients for the cathode process (W electrode) were determined. The findings suggest that the melt with CR 1.4 at 800 °C and the particle volume fraction around 0.09 are better parameters to use Cu- 10Al anode.

The effects of the temperature, the particle size and the phase composition of the dispersed material and its volume fraction in the suspension on the dissolution kinetics and the sedimentation velocity are 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 used. The Reynolds numbers for sedimentation have indicated the Stokesian regime. Typical alumina dissolution rates were in the range of 0.028-0.167 $g \cdot kg^{-1} \cdot s^{-1}$, which is close to the values reported previously. Sedimentation velocities were in the range of $(0.05\text{-}3.61) \cdot 10^{-2}$ m/s, which is several times higher than those obtained previously for φ = 0.24-0.32 at 700 °C.

Based on the obtained results, the electrolysis of $1.4KF\text{-}AlF_3\text{-}Al_2O_{3(sat)}$ with Cu-Al anode and W cathode was performed. The purity of the aluminium using optical emission spectrometer was determined. The XRD, SEM-EDX methods were used to study the phases formed on the anode surface. The current efficiency of about 84.41% was attained and produced aluminium had a purity of 99.40%.