Investigation of the Frozen Bath Layer under Cold Anodes

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Abstract

Hall-Héroult cell stability is highly affected by anode changing operation. Insertion of a cold anode in a cell will freeze a thick layer of molten cryolite under it. Its thickness, microstructure, and chemical composition vary as a function of time and location in the cell. To better understand the evolution of the frozen layer, mandatory for the validation of numerical models, a measurement campaign was conducted on the anodes having a few hours of operation in the cell. The macrostructure of the selected frozen bath samples has been highlighted using computed tomography while Scanning Electron Microscope (SEM) has been used to qualify its microstructure. An Energy-Dispersive X-Ray Spectroscope (EDS) coupled to the SEM has allowed the qualification of the chemical content. The investigation showed very different macrostructures between samples but also within them. Nevertheless, for all samples, there is a clear distinction between the frozen cryolite and alumina/dusting phases, the latter ones surrounding the cryolite matrix.

Keywords: Cryolite; anode; Computed Tomography; microstructure; anode changing.

1. Introduction

Large scale aluminium production is based on the Hall-Héroult electrolysis process, in which alumina is dissolved in molten cryolitic bath ($Na_3AlF_6 + (AlF_3)_{excess} + CaF_2 + Al_2O_3$) [1]. The electrolysis of dissolved alumina (Al_2O_3), performed using an electrolysis cell [2] (4 - 5 V and typically 200 - 400 kA), is occurring at approximately 960 °C and leads to the carbon consumption of the anode through the global reaction defined in Equation (1). Hence, this electrode needs to be replaced after 25 - 27 days of operation through an anode changing operation. However, the lifespan of the anode may vary by a few days depending of cell technology.

$$2Al_2O_{3\,(\text{dissolved in cryolite})} + 3C_{(anode)} \xrightarrow{12\,e^-} 4Al_{(liquid)} + 3CO_{2\,(\text{gas})} \quad (1)$$

Insertion of a new and cold anode at potroom temperature (~ 25 - 40 °C) in a molten cryolite bath at 960 °C will disturb the stability of the cell in many ways simultaneously [3-5]. From a thermal point of view, upon the insertion the cold anode, few centimeters of cryolitic bath will freeze under it and will melt within the next few hours of operation. Hence, thermal balance will

be affected during this period. In addition, density variation due to cryolite phase change (solidification/fusion) will lead to bath volume changes [6, 7]. Some researchers are now using numerical tools to simulate the anode change to estimate its impact on heat transfer in the electrolysis cell [3 - 5, 8].

The simulation of cryolite phase change underneath and around the anode requires characterization of both liquid and solid bath to be able to validate those models. Recently, Poncsák et al. [9] have studied the impact of the heat flux on the solidification of on unstirred cryolitic bath. They have highlighted the fact that high solidification rate can block diffusion of ions [1, 6, 7] and preserve chemical composition of cryolite. On the other hand, a slower solidification rate will alter bath composition and consequently all its properties. Poncsák et al. [9] also studied two different scenarios of cryolitic bath solidification without electrolysis in a laboratory scale experiment: A transient one where the temperature evolution of the cold anode surface (represented by a cold finger steel probe) is dictated by the bath temperature and a near steady-state one where the finger steel probe surface is stabilized at around 775 °C. The latter case may be more representative of the industrial case considering the large thermal inertia of carbon anodes. The two cases study led to two very different frozen cryolite structures. First, the transient case led to two morphologically distinct solidified bath layers. The first layer, in direct contact with the probe and thus with a high cooling rate, is dense with a relatively homogeneous morphology. The cooling rate of the second layer was lower and led instead to a brittle porous structure. In the second case, i.e. the near steady-state one, similar observations have been made but with lesser morphological variations between the high and low cooling rate zone. The structure and composition of the frozen cryolitic bath are hence highly correlated with the heat transfer occurring near cold surfaces [9 - 11].

As pointed out previously, chemical composition and morphology of frozen cryolitic bath are highly heat flux dependent. Both can affect the frozen cryolite density thus the volume change estimation, which is a very useful parameter in numerical model calibration [8]. However, based on plant observations, at least another phenomenon must be taken into account in the frozen bath apparent density evaluation: gas trapped in the frozen cryolite. Thus, the objective of this work is to analyze morphology of frozen bath sample taken from industrial anode after few hours of operation to get insights of the influence of operational conditions on frozen bath chemical composition and apparent density. The origin of the gas trapped is still under investigation and will not be discussed here.

2. Material and Method

Solidified bath samples were taken from anodes after only few hours of operation at Alcoa Deschambault smelting plant, Quebec, Canada (ADQ) . Frozen bath morphology highly depends of the anodes history, such as anode initial temperature, position in the cell, surface integrity, cell stability, etc. All those parameters can affect the heat flux and bath composition near the newly inserted anodes. Also, the dusting events in the cell can also influence the samples' morphology. Knowing all this, two very different samples from different anodes and operating time of those anodes, have been chosen and are presented in Figure 1. Sample A was chosen based on the fact that its structure seems to be relatively homogeneous with a minimum of porosity (from outside observation). On the other hand, Sample B was selected based on its very porous structure and its near constant thickness. In both cases, the sample surface in contact with the anode has been damaged while removing the sample.

Macroscopic morphological analysis has been performed using a X-ray tomograph, (Siemens Somatom Sensation 64) located at the INRS-ETE in Quebec city. This tomograph has been used in previous studies on carbon anode characterization and all details can be found in [12, 13]. In summary, X-ray computed tomography (CT) allows 3D density analysis without damaging the

4. Conclusion

Two bath samples that froze under newly inserted anode have been investigated with computed tomography and SEM/EDS method to highlight the difference with laboratory observations. The two samples were mainly chosen based on their very different morphologies. In both cases, the computed tomography reveals the large amount of big pores. The origin of those large pores is still under investigation. It may be assumed that they are related to unidentified gas movement mechanisms (e.g. expelling of dissolved gas from the bath during the freezing process). Except for those large pores, morphology of Sample B seems to suit the experimental observations of Poncsák et al. [9] regarding the effect of the cooling rate on the frozen cryolitic bath morphology. However, the Sample A morphology differs largely from laboratory observations and highlights the difference between laboratory and *in situ* experiments. This was mainly shown on the SEM/EDS analyses where undissolved alumina and carbon dust were found in samples. Finally, all these observations reveal the importance of taking into account the presence of gases, which led to the formation of large pores in the frozen bath samples and thus may affect the volume estimation of the frozen ledge underneath the anodes.

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