

Impact of the Solidification Rate on the Chemical Composition of Frozen Cryolite Bath

S. Poncsák¹, L. I. Kiss², S. Guérard³, J. F. Bilodeau³

1. Research professor at Université du Québec à Chicoutimi

2. Professor and director of GRIPS at Université du Québec à Chicoutimi

3. Researchers at ARDC, Rio Tinto Aluminium

Corresponding author: sponcsak@uqac.ca

Abstract



Solidification of cryolite-based bath takes place at different rates along the sideledge, around alumina rafts and new anodes. The solidification rate has a significant impact on the structure and the chemical composition that determine the thermal conductivity and thus the thickness of sideledge or the duration of the existence of the temporary frozen bath layers in other cases. Unfortunately, samples that can be collected in industrial cells are formed under unknown, spatially and temporally varying conditions. For this reason, frozen bath samples were created under different heat flux conditions in well-controlled laboratory environment using the so-called cold finger technique. The samples were analyzed by X-ray Diffractometer (XRD) and Scanning Electron Microscope (MEB) in Back Scattering (BS) mode in order to obtain spatial distribution of chemical composition. Results were correlated with structural analysis. XRD confirmed our earlier hypothesis of recrystallization of cryolite to chiolite under medium heat flux regime. Lower α -alumina, and higher γ -alumina content in the samples obtained with very high heating rate suggest that fast cooling reduces γ - α conversion. In accordance with the expectation, SEM-BS revealed significant variation of Na/Al ratio in the transient sample.

Keywords: Aluminum electrolysis; frozen ledge; cold-finger; chemical composition; cooling rate.

1. Introduction

Solidification of cryolite-based bath takes place with different rates at sideledge, alumina rafts, new anodes or any other cold objects inserted into the molten electrolyte for different operations or measurement campaigns. The structure of the solidified phase (number of the nucleation sites and pores, the size, the orientation and the structure of the different crystals, the proportion of the amorphous phases), as well as the difference between the chemical compositions of molten and frozen bath depend on the cooling heat flux or in other words, on the cooling velocity. In fact, the cooling rate has a huge impact on the relative velocities of nucleation versus crystal growth [1] and on the probability of the entrapment of liquid pockets by fast growing crystals [1, 2]. Normally, the diffusion of ions is promoted during the solidification by the high melting point of pure cryolite [3 - 5], however, an elevated rate of solidification can block this movement.

The structure and the chemical composition determine the thermal conductivity and thus either the thickness of sideledge or the duration of the existence of temporary frozen bath layers around cold objects.

Some information can be found about the structure and the chemical composition of frozen bath in sideledge [2 - 8] and in the crust [1, 9] using samples taken from industrial cells. However, those samples were formed under unknown and varying conditions. To resolve this problem, the authors of this paper created frozen bath samples under different heat flux conditions in well controlled laboratory environment in order to study the variation of the chemical composition

and structure with the cooling rate. Results about the structure obtained with Scanning Electron Microscope (*SEM*) with Secondary Electron Imaging (*SEI*) mode were published earlier [10]. This paper presents chemical composition data correlated with structure, heat flux and solidification rate. The two latter were computed with an in-house developed mathematical model using measured temperature histories as input.

2. Methodology

2.1.1 Solidified bath samples produced using cold finger technique

Solidified bath samples were produced in a well controlled laboratory cell using the so-called cold finger technique. Namely, cold brick-shaped blocks (probes) were inserted into an unstirred synthetic cryolite based molten bath with known composition. Both the composition and the superheat of the bath corresponded to those used in many RTA plants. The quantity of the bath was high enough to avoid any significant perturbation of bulk liquid temperature by the insertion of the probe itself. In the absence of electrolysis, the absorption of heat during the insertion of the probe and the loss toward the environment were compensated by the same heating furnace that melted the bath. Samples were cut from the middle of the large surfaces of the blocks in order to minimize the end effect. On the external surface, there were some easily removable, round shaped, dark colored impurity particles, which were removed and thus not included in the chemical analysis [10].

The solidified bath samples were produced under both transient and near steady-state conditions, including strongly varying ($28 - 2200 \text{ kW/m}^2$) and relatively constant, low heat fluxes ($28 - 100 \text{ kW/m}^2$) respectively. For brevity, in the following we call the first technique “transient”, the second “steady-state”. Table 1 summarizes the main characteristics of the two scenarios. More details are presented in an earlier published paper [10].

Table 1. Main characteristics of the transient and near steady-state production of samples

	Transient	Steady state
Probe	solid (full) block 12.5 x 11 x 2.54 cm	hollow with inner channels 12.5 x 11 x 2.54 cm with a wall thickness of 6.35 mm
Initial temperature	preheated to $\sim 150 \text{ }^\circ\text{C}$ in order to remove humidity	preheated to $\sim 150 \text{ }^\circ\text{C}$ in order to remove humidity and then preheated to the bath temperature in the molten bath
Sample producing process	insertion of cold probe to the bath in order to obtain the thickest possible crust	insertion of cold probe into the molten bath, then waiting until the transient crust is completely re-melted and the temperature of the probe stabilizes close to the bulk temperature; near steady-state crust is formed by the circulation of dried and compressed cold air in the channels of the probe with constant flow rate
Duration of insertion	3 minutes this time was estimated by our mathematical model[11]	~ 30 minutes probes were removed when the temperature became constant inside the probe

Carbon steel and stainless steel were chosen to build the transient and steady-state probes respectively due to their relatively good mechanical and chemical resistance to high temperature

- The earlier presented hypothesis that medium solidification rate promotes the recrystallization of cryolite to chiolite (exsolution) due to the presence of acidic liquid pockets entrapped by growing crystals, was confirmed by XRD.
- The contact between the molten bath and the steel probe forms some FeO that is entrapped mainly in a thin, generally darker layer, close to the probe.

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