AL12 - Graphite Foil as a Barrier for the Penetration of Aluminum and Cryolite into Cathode Lining

Andrey Yurkov[1], Artem Malakho[2] and Viktor Avdeev[3]
1. Leading Scientist
2. Head of the Laboratory
3. Head of the Chair
Moscow State Lomonosov University, Chemical Department, Moscow, Russia
Corresponding author: and-yur@mail.ru; andrey.yurkov@tech.chem.msu.ru

Abstract

The barrier refractory materials against the penetration of liquid aluminum and cryolite in the lining of the reduction cell have been used for many years. The tested barrier materials include alumina, carbon ramming paste, red brick, silica brick, aluminous brick, castable low-cement slabs, flat glass, steel sheets, etc. The penetration of cryolite and sodium to the refractory layer often results in appearance of the "lens" of reactants under the carbon bottom blocks. The "lens" will cause bending strains in the carbon cathode blocks, that may lead to cracking. The graphite foil is a promising candidate to be a barrier material against the penetration of molten aluminum and cryolite. The graphite foil has a unique structure that results in unique properties. Molten aluminum does not wet graphite foil. The gas permeability of the graphite foil is extremely low due to high tortuosity of pores. Industrial testing shows, that graphite foil in the lining of the reduction cell acts as a semi-transparent barrier, and the height of the lens under the foil decreases considerably.

Keywords: Aluminum reduction cell, graphite foil barrier, cryolite penetration.

1. Introduction

The constructions of reduction cells have a long history of continuous improvements [1, 2]. Yet, until now the only electro conductive cathode material in the reduction cell is carbon (although a lot of work has been done to implement titanium boride as cathode material).

The refractory layer of the cathode consists of alumina-silica materials. These materials can react with cryolite and sodium that penetrate through carbon cathode blocks. The reactions of cryolite and sodium with refractory layer of the cathode may have negative consequences for the service of the reduction cells [1, 2]. The thermal conductivity of reacted refractory and heat insulation cathode materials increases; that may change the thermal balance and performance of the reduction cells. The volume of the major part of reactions of cryolite with alumina-silica compounds increases, that may cause bottom "heaving" of the carbon cathode blocks, strain and cracking of cathode blocks.

There have been many trials of different barrier materials that were placed between the carbon cathode block and the refractory layer. These barrier materials should prevent or diminish the movement of cryolite and sodium to the refractory layer. Among these tested materials were silica brick, silica powder, alumina brick, alumina powder, red construction brick, mullite brick, window glass, and various combinations of mullite brick and fireclay brick in the upper and lower parts of the refractory layer.

Graphite foil, or compressed thermally expanded graphite (TEG), might be a promising material for such purpose. The goal of this work was to evaluate the specific properties of compressed thermally expanded graphite (graphite foil) as a barrier for the penetration of molten aluminum and cryolite in the refractory layer of the cathode.

2. Refractory Barriers in the Reduction Cell

Carbon cathode blocks with collector bars are installed on a refractory layer that is made of fireclay bricks or dry barrier mixtures (DBMs). The main purpose of the refractory barrier layer is to stop the infiltration of electrolyte – in other words, to be a barrier against the infiltration of electrolyte (Figure 1).

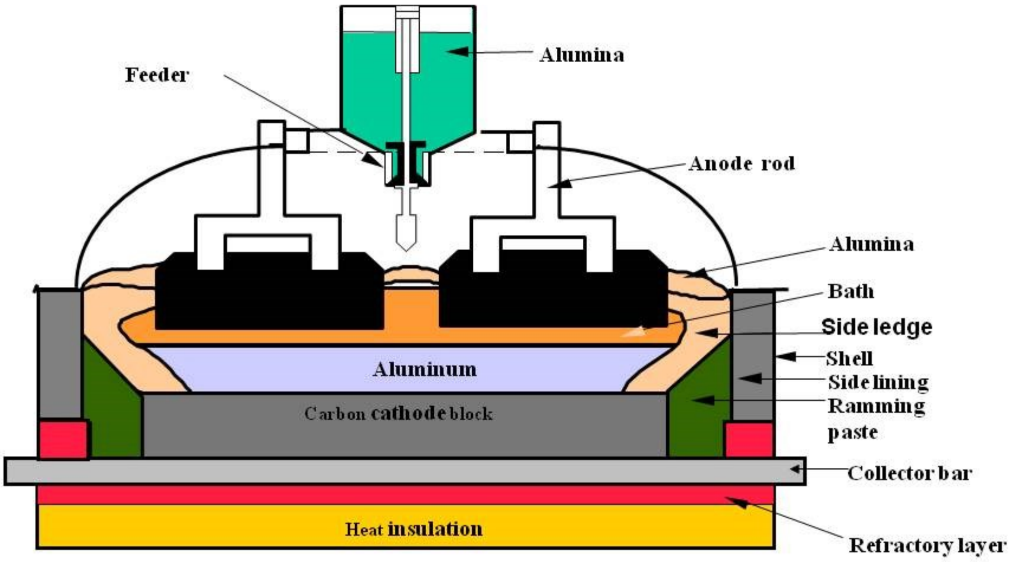

Figure 1. Cross-section of the reduction cell.

The infiltration of electrolyte in the refractory (and then in the thermal insulation) layers has two negative consequences:

1. The thermal conductivity of refractories infiltrated by electrolyte may change by a factor of 3–5, while the thermal conductivity of thermal insulation materials may change by a factor of 10–50 [2, 3, 4]. The heat flow through the bottom of the cell increases, the thermal balance of the reduction cell changes, electrolyte (with alumina) starts to crystallize on the surface of cathode blocks, forming bottom sludge and decreasing the surface of cathode, and there might be changes with the current distribution, current efficiency, and energy consumption.
2. Depending on the circumstances, the "lens" of products of reactions of infiltrated electrolyte and the refractory barrier layer (Figure 2), having a thickness of up to 40–70 mm, may press the carbon cathode blocks from inside the reduction cell, causing bending strains and cracking.

Fireclay bricks (alumina silica bricks, alumina calcium oxide silica bricks, and other silicate bricks) are not optimal barrier materials for aluminum reduction cells. As we have mentioned, cryolite-based electrolyte for aluminum reduction dissolves alumina better than anything else.

From a chemical point of view, effective refractory barriers against the penetration of cryolite might be tin oxide, nickel oxide, compounds of nickel oxide, iron oxide, or zinc oxide (such as spinel $NiFe_2O_4$). These oxides almost do not react with NaF and aluminum fluoride [2, 5]. Yet the cost of these materials, which is 50–100 times higher than firebrick, provides the impetus to find less costly variants of alumina silica materials. Attempts have been made to fabricate barriers between carbon blocks and refractory layers from electrolyte penetration using steel sheets and

6. References

1. Morten Sørlie, Harald F. Øye. *Cathodes in aluminium electrolysis*, 3rd Edition, Dusseldorf, Aluminium-Verlag, 2010, 662 pages.
2. Andrey Yurkov, *Refractories for Aluminum. Electrolysis and Cast House*, 2rd Edition, Springer Publishing House AG, 2017, 267 pages.
3. I. Yakimov, G. Arhipov, A. Pogodaev, A.Shimansky, Physico-chemical investigations of parts of the cathode lining of aluminium reduction cells. *Proceedings of 9th Int. Conference Aluminum of Siberia*, Krasnoyarsk, 2003, 209-213.
4. G. Arhipov, V. Borisov, A. Ivanova, The properties of the lining of aluminium reduction cells. *Novye ogneupory (in Russian),* 2004, (6), 39-45.
5. L. Ivanovsky, V. Lebedev, V. Nekrasov, *Anode processes in molten halogenides (in Russian),* Moscow, Nauka 1983, 268 p.
6. ASTM 577-C-99 Standard test method for the permeability of refractories
7. ISO 8141:1991 Dense shaped refractory products – Determination of permeability to gases.
8. A. Selzard, J.F. Mareche, G. Furdin, Modelling of exfoliated graphite, Progress in materials science, 50 (2005), 93-179.
9. S. Biloe, S. Mauran, Gas flow through highly porous graphite materials, Carbon, 41 (2003), 525-537.
10. A.V. Proshkin et al, Lining of cathode assembly of electrolysis cell for production of aluminum, *Patent* WO 2017/044010, 2015.
11. A.V. Proshkin et al, Cathode lining of the reduction cell for the production of primary aluminum, *Patent* RU 2608942, 2017.
12. A.V. Proshkin, V.V. Pingin, A.G. Sbitnev. Findings of studies of graphite foil as an element in the barrier layer in aluminum reduction cell, *The Proceedings of the Congress "Non-ferrous Metals and Minerals",* Krasnoyarsk, 2018, 453-458.