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

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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).

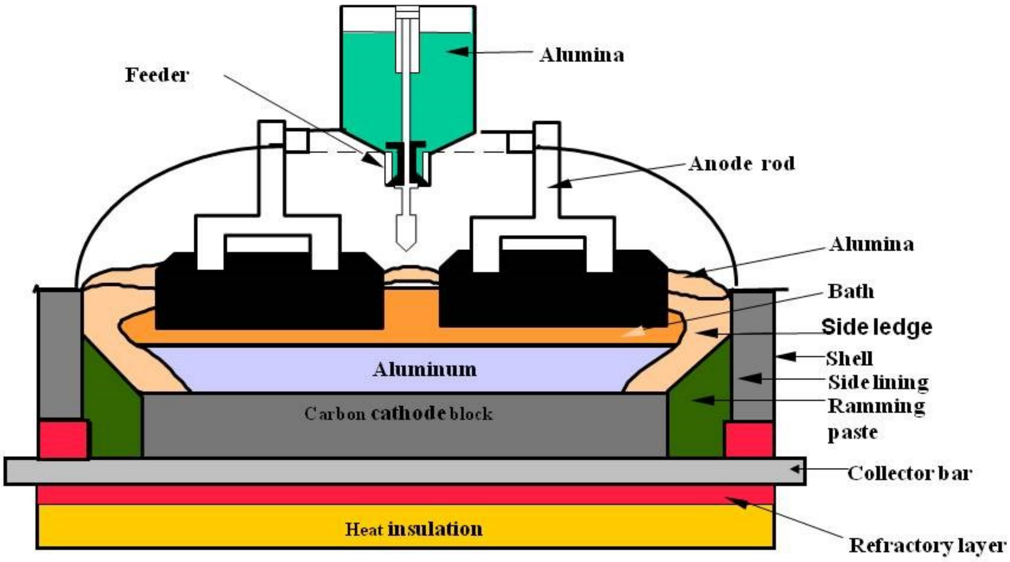

Figure 1. Cross-section of the reduction cell.

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 sheets of window glass. Some of these barriers did not find industrial application. However, steel sheets are still used by some plants

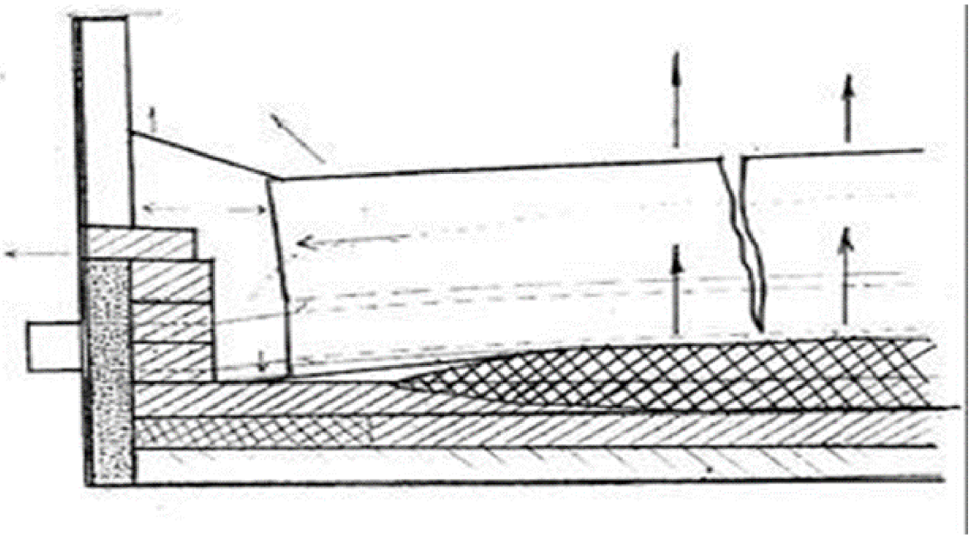

Figure 2. The "Lens" of interaction of infiltrated electrolyte and refractories: Top - schematic view of the cross-section; Bottom - cross-section of the cathode during the dry autopsy.

The following considerations were worked out in the course of a very long and time consuming industrial and laboratory trials with refractory barrier layers of the cathode materials:

- An alumina silica refractory is far from being the optimal material for a refractory barrier. Although some theoretical considerations on the silica/alumina ratio may exist, other variants should be found.
- There is a long history of trials with different barrier materials: 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 layers.

- Chemical considerations suggest that tin oxide, ferric nickel spinel, zinc oxide, and their variations might be good barrier materials; however, these compounds do not satisfy economic considerations. Also, these compounds are not stable to sodium vapor.
- SiC-based refractories (in the form of preshaped or not previously shaped castables or mortars) look like good candidates as barrier materials.
- Structural considerations suggest limiting the pore size in the refractory material and decreasing the length of the joints between refractory barrier bricks.
- The advantage of Dry Barrier Mixtures (DBM) is the absence of joints, although limiting the pore size in a DBM is impossible.
- The resistance of Low Cement Castables (LCC) to cryolite is superior (according to cup tests) to medium cement SiC castables.
- Alumina silica DBMs and refractory bricks of relatively large shapes, with low permeability and low pore size, provide a service life of reduction cells of 6–7 years, with some cells reaching a service life exceeding 10 years.
- Probably, the best barrier to the penetration of sodium and cryolite in the refractory layer is accurate temperature control of freezing point isotherms in carbon cathode blocks, that limits the electrolyte flow through pores due to the low pore size in carbon cathode blocks.
- Yet the problem of a good barrier against the penetration of cryolite and aluminum still exists, and graphite foil, or compressed thermally expanded graphite looks like a promising barrier material.

3. Thermally Expanded Graphite (TEG), Compressed Thermally Expanded Graphite and Graphite Foil

Graphite foil or compressed thermally expanded graphite is a unique material, it is stable in various aggressive chemical atmospheres. It is a light porous material, yet the gas permeability of this material is extremely low.

Graphite foil is produced from thermally expanded graphite (TEG). There are several stages in processing of compressed thermally expanded graphite (graphite foil), and each stage has influence on the final product.

The acidic anions intrude (Figure 3) between the layers of carbon atoms and form a sort of compounds with carbon atoms. The material is called oxidized graphite. Acidic anions may occupy the space between every layer of carbon atoms (degree of intercalation 1), between every two layers of carbon atoms (degree of intercalation 2) between every three layers of carbon atoms (degree of intercalation 3) and so on. The oxidized graphite is rapidly heated up to 600–1 000 °C, the water and acidic anions start to evaporate, the expansion factor of the process might be 20–40.

The thermally expanded graphite may have the specific surface area from 40 m^2/g to 200 m^2/g. It is produced from intercalated “oxidized” graphite by rapid thermal heating at temperatures 600–1 000 °C, the properties and the composition of the graphite foil are listed in the Table 1. The rapid heating promotes the decay of the intercalated acid compounds between the layers of the graphite lattice and the evaporation, followed by expansion (Figure 4).

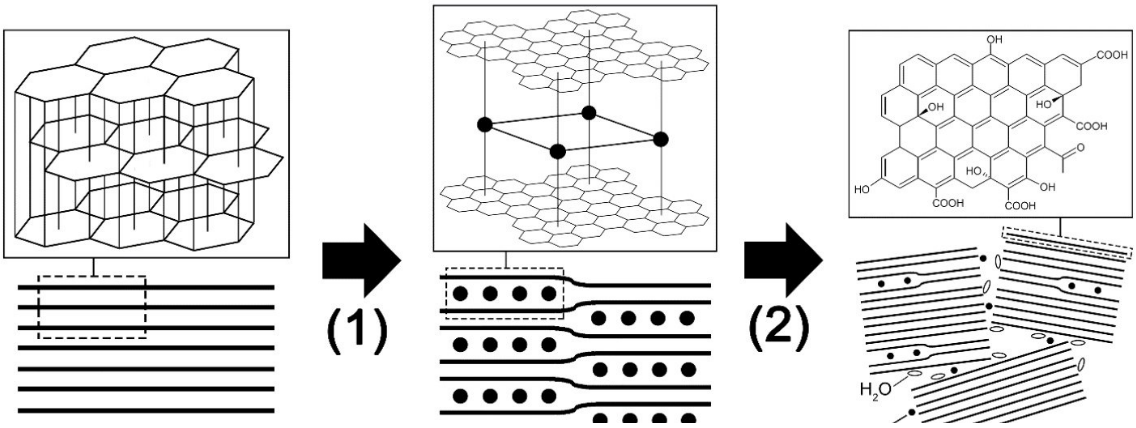

Figure 3. The scheme of processing of the oxidized graphite.

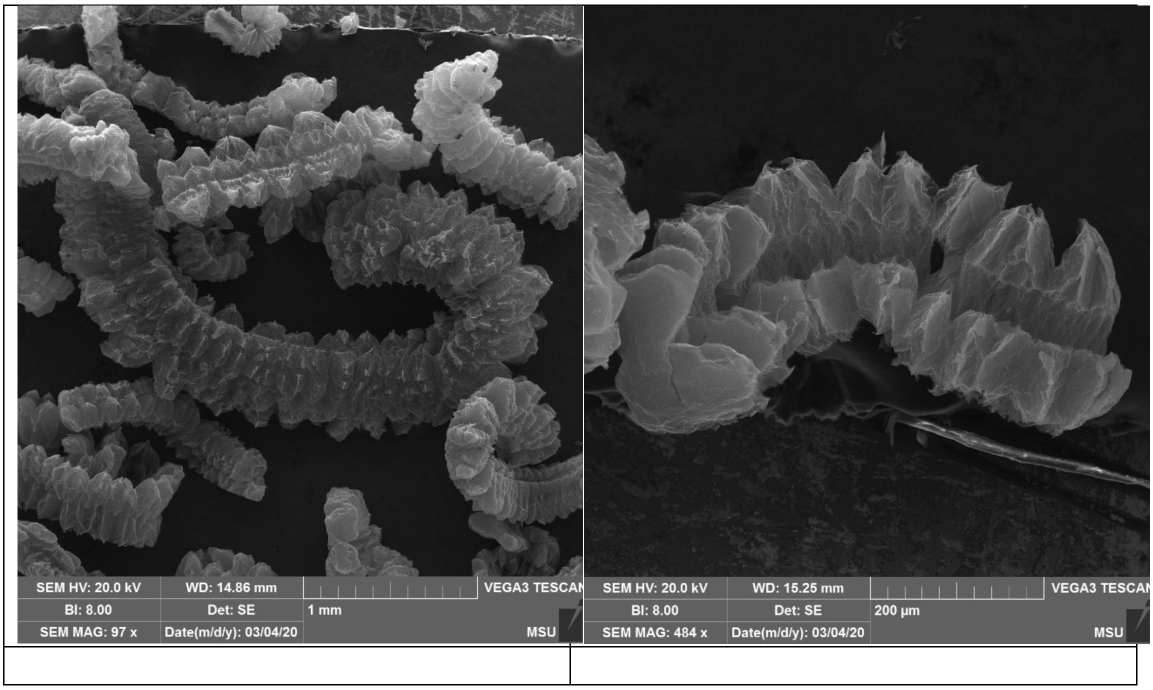

Figure 4. The microstructures of thermally expanded graphite.

Table 1. Properties and the composition of the graphite foil.

Parameter	
Carbon, %	> 98 %
Ash, %	< 2 %
Sulfur, ppm	< 100
Chlorine, ppm	< 50
Tensile strength, MPa	> 5.3
Compressibility, %	> 45
Recoverability, %	> 0.8
Weight loss (670 °C), %/h	< 4

Graphite foil, or compressed thermally expanded graphite is a porous material with pretty big internal surface area. It is produced by pressing or by rolling. There are different grades of graphite foil, having density from 0.5 g/cm^3 to 1.8 g/cm^3 (Figure 5). The most conventional type of graphite foil has density of 1.0 g/cm^3.

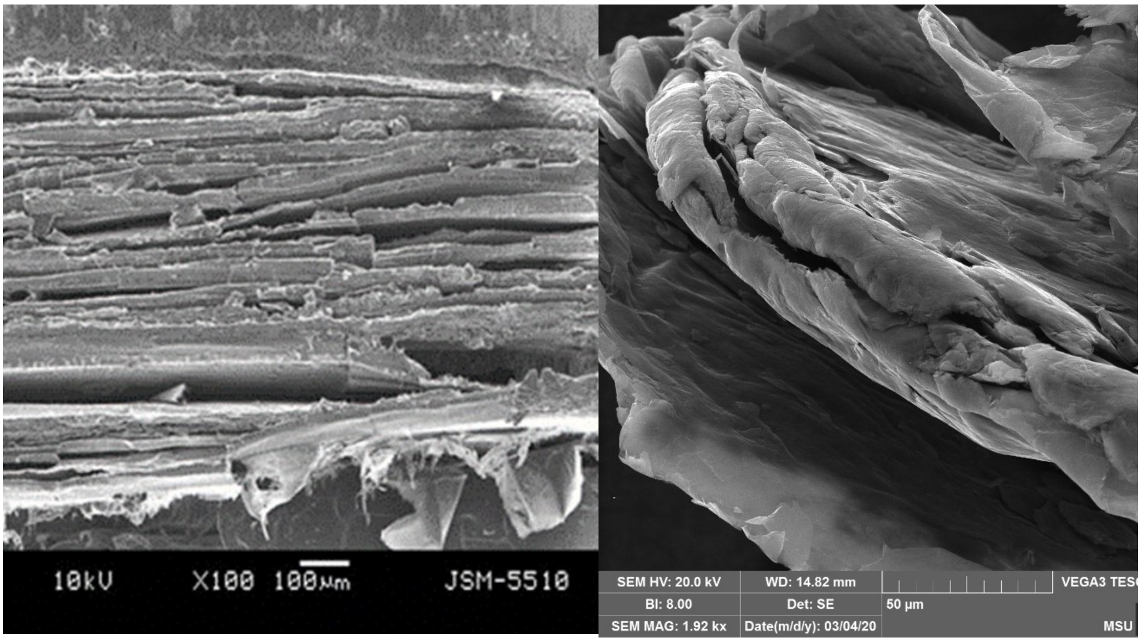

Figure 5. The structure of the graphite foil at different magnifications.

The properties of the graphite foil depend on the properties of the intercalated graphite and the properties of the thermally expanded graphite. The strength of the graphite foil mainly depends on its density (Figure 6). We cannot call the graphite foil a strong material. However, it can recover after loading; to some extent the graphite foil can be bent, and its rupture strength is 4–10 MPa. Such strength characteristics allow people in charge to unroll the rolls of foil on the surface of refractories.

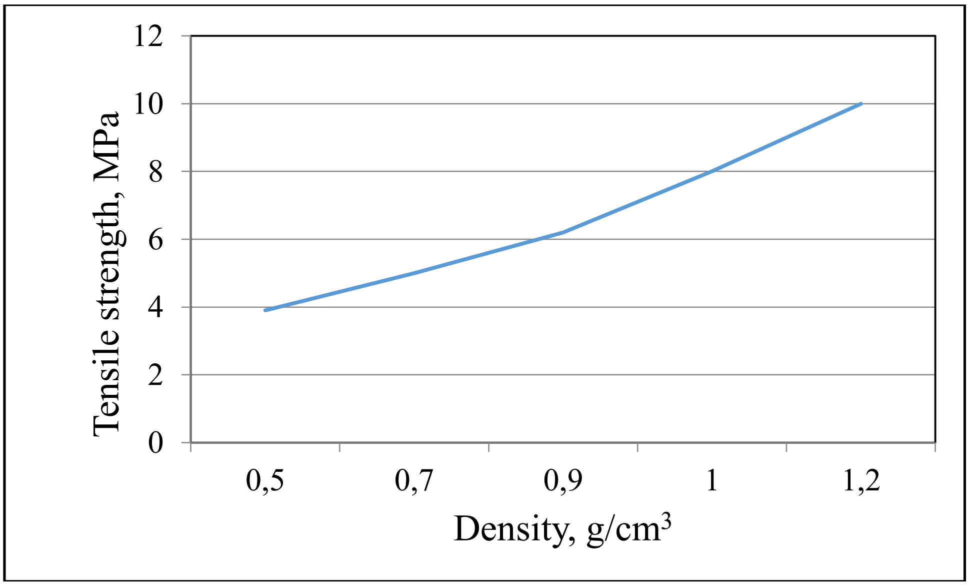

Figure 6. The tensile strength of the graphite foil.

The graphite foil is a porous material (Table 2). Open porosity of the graphite foil is a function of the density, while the closed porosity remains more or less constant. The inner specific surface of the graphite foil also strongly depends on the density. It diminishes from 45–50 m^2/g (in TEG) to

16–18 m^2/g in graphite foil with density 1.4–1.8 g/cm^3 (Figure 7). Yet the material remains porous, and the inner surface area exceeds the values found in conventional porous materials.

Table 2. The porosity and density of the graphite foil.

Index	**Density (geometrical), g/cm^3**	**Relative density, %**	**Open porosity, %**
GF-0.5	0.5	0.25	70–76
GF-0.8	0.8	0.30	64–70
GF-1	1.0	0.40	53–59
GF-1.2	1.2	0.47	48–54
GF-1.4	1.4	0.54	41–47
GF-1.6	1.6	0.59	35–41
GF-1.8	1.8	0.66	37–33

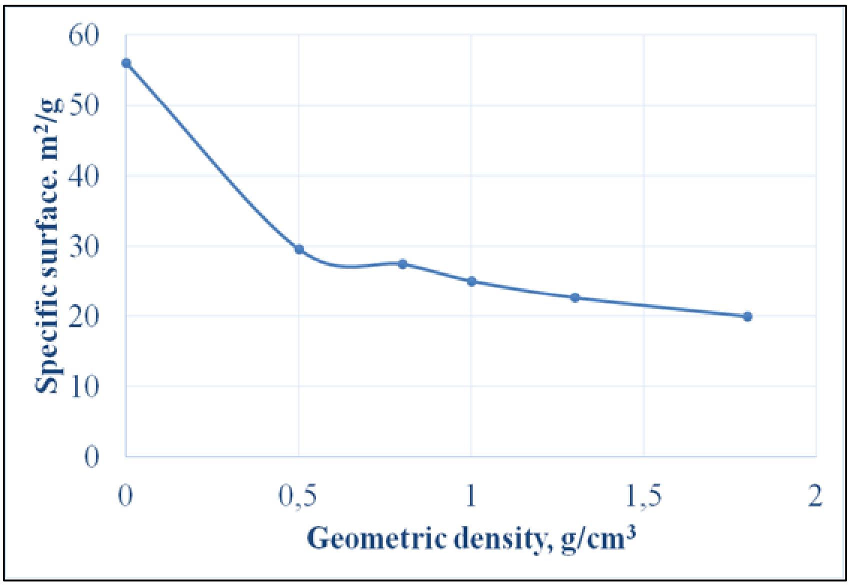

Figure 7. The dependence of the inner specific surface on the density of the graphite foil.

The determination of the pore size in porous materials is not an easy problem, and this statement is absolutely applicable to graphite foil. The upper limit of the pore size measurement by nitrogen adsorption method is 100–130 nm (0.1–0.13 µm). As for the lower limit, it is possible to estimate to diameter of pores up to 2–5 nm (0.002–0.005 µm). On the contrary, there is almost no upper limit for the determination of pore sizes by mercury porosimetry. The starting value of mercury pressure is only 0.0036 MPa, which correspond to diameters above 3 µm. The determination of pore size distribution by mercury porosimetry and by nitrogen adsorption (Figure 8) give a more or less representative picture.

Maximum volume of mercury is intruded in pressure range 0.965–5.51 MPa in the foil with density 0.5 g/cm^3 which correspond to pores with diameter 350–1000 nm (0.35–1.0 µm). The pore size, determined by mercury porosimetry, vary from 1 µm for the foil 0.5 g/cm^3 to 0.05 µm for the foil 1.8 g/cm^3.

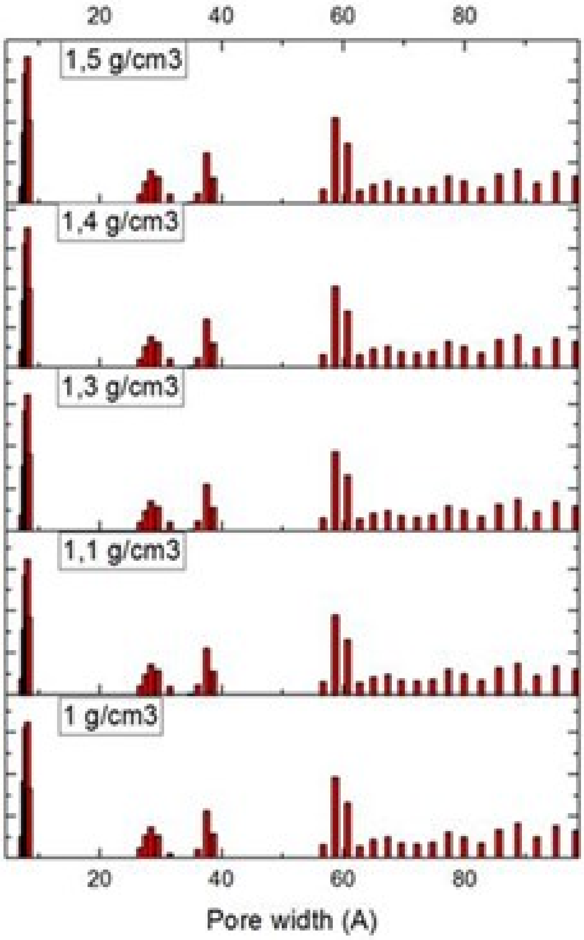

Figure 8. Pore size distribution in the graphite foil with different densities according to nitrogen adsorption.

The combination of mercury porosimetry and nitrogen absorption gives very interesting results of the pore size distribution. The main, "characteristic" pore dimension depends on the density of the graphite foil, and this pore size changes from 1 000 nm (1 μm) in the foil GF-05 to 47–50 nm (0.047–0.05 μm) in the foil GF-1.8.

However, the measurement of the pore size distribution according to nitrogen absorption (BET), that gives good results in measurement of fine pores, shows very similar results suggesting that the fine pore structure remains constant.

The gas permeability of the graphite foil is surprisingly low – it is in the range of 10^{-5}–10^{-6} μm^2, that is on the threshold of the measurement sensitivity of the gas permeability according to ASTM-C-577 [6]. We tried to find in the literature values of the gas permeability of graphite foil by ASTM-C-577 or ISO 8141:1991 [7]. The only information was in the paper [8] with indication, that the measurement was fulfilled close to the measurement limit. In order to measure the permeability to gases of compressed expanded graphite and the graphite foil, usually people employ other types of measuring devices [8] and other units.

According to our measurements, the permeability of nitrogen was 1.1×10^{10} mol/m^{2}sPa for the graphite foil with density 1.0 g/cm^3, while for the graphite foil with density 1.2 g/cm^3 the value was 0.11×10^{10} mol/m^{2}sPa.

4. The Application of the Graphite Foil Barriers in the Reduction Cells

The leading aluminum companies started the trials on the application of graphite foil, as a barrier material, in the reduction cells from the beginning of the century. The contact angle of molten aluminum on the graphite foil is 120–140°, that is absolute non wetting.

If we speak about the wetting of graphite foil by criolyte, the picture is more peculiar. To some extent molten cryolite wets the surface of the graphite foil. Compressed expanded graphite (graphite foil) is a porous material, however the dimensions of the pores in the graphite foil (Figure 7) are extremely low, comparing with other materials of the cathode (Table 3). The same may be said about the gas permeability. The gas permeability of the graphite foil is very low, comparing with the values of gas permeability of the fireclay brick and nitride bonded silicon carbide [2].

Table 3. Dimensions of pores and gas permeability of materials.

	Fireclay brick	**N-SiC**	**Graphite foil**
Pore diameter, µm	Up to 20–30	0.1–0.3	< 0.01
Gas permeability, µm^2	0.5–3	0.1–0.2	$10^{-5} – 10^{-6}$

There are patents on the application of the graphite foil in the refractory layer of the cathode of the reduction cell [10, 11].

According to Proshkin [12] graphite foil stops aluminium and due to ultrafine pore structure diminishes the flow of the bath. Laboratory tests had shown absolute non-wetting of the foil by molten aluminum. The dry autopsies [12] had shown, that the barrier graphite foil stops the leakage of aluminum melt in the refractory layer.

Graphite foil does not stop the flow of the bath absolutely, yet due to its unique small gas permeability, it diminishes the flow, and after 5 years the height of the lens (the products of interaction of alumin-asilica refractory and cryolite) was below 40 mm.

Industrial trials might be very essential in order to estimate the density of the graphite foil, that will be the best barrier for the penetration of cryolite and sodium in the refractory and heat insulation layers of the cathode. Different variants of modification of the structure and the composition of graphite foils might be also of interest.

5. Conclusions

The problem of a barrier against the penetration of cryolite and aluminum in the refractory and heat insulation part of the cathode of the reduction cell remains actual.

Graphite foil or compressed thermally expanded graphite is a light porous material, yet the gas permeability of this material is extremely low due to its unique porous structure. Depending on the density, the pore size of the foil might be 0.05–0.5 µm.

The graphite foil barrier material stops the penetration in the refractory part of the reduction cell of the aluminum melt and is a good semi-transparent barrier for the penetration of cryolite.

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