Silicon Carbide Sidelining Materials in Reduction Cells: Corrosion Resistance, Service Life and Testing

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Abstract

There are some aspects in Si_3N_4-SiC refractories for reduction cells that raises certain questions. What shape of the grains of silicon nitride modifications and what type of grain is better? Does silicon nitride appear due to solid-gas or gas-gas reaction of silicon and nitrogen? The balance of α/β modifications of silicon nitride, the occurrence, and the role of Si_2ON_2 are also a matter of scientific interest in processing of Si_3N_4-SiC sidelining material. In aluminium reduction cells, Si_3N_4-SiC composite material is exposed to extremely severe conditions: It is attacked by molten cryolite and molten aluminium, and partly reducing atmosphere with vapors of fluorine compounds. There are three variants of laboratory corrosion test of Si_3N_4-SiC material for the use in aluminium reduction cell. SINTEF test is most popular, then are Luoyang Institute for Refractory Research (LIRR) test, and RUSAL test. These laboratory tests give somewhat different corrosion resistance results that require additional research. The considerations on physical chemistry of corrosion resistance are presented in the paper.

Keywords: Aluminium electrolysis cell cathode sidelining, Silicon carbide-silicon nitride refractory corrosion testing, Service life.

1. Introduction

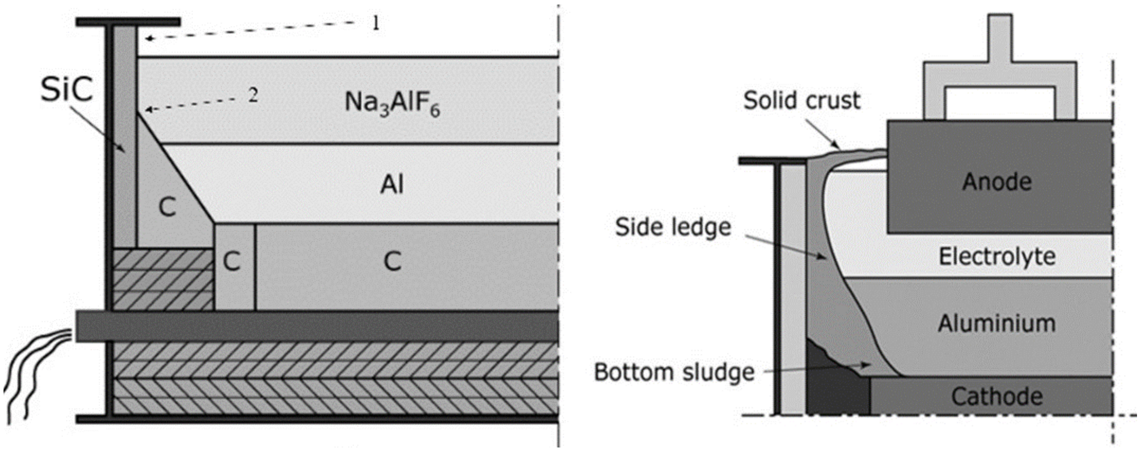
Corrosion phenomena is very complex, and it is necessary to take into account different processes and mechanisms of degradation. Corrosion of the refractories at high temperature-is caused by the gases and liquid which comes in contact with refractories. There is a chemical corrosion of refractories and also corrosion caused by penetration of liquid into pores of refractories. The corrosion of Si_3N_4-SiC in Al reduction cell may be divided into two parts, corrosion by gases and corrosion by liquids.

In aluminum industry the main application of Si_3N_4-SiC material is side lining of aluminum reduction cells [1,2]. Si_3N_4-SiC side wall lining of reduction cells (Figure1) should withstand:

- Chemical interaction with liquid electrolyte (consisting mainly of cryolite Na_3AlF_6 (Figure 2), enhanced by erosion of circulating metal and the electrolyte.
- Oxidation of the upper part of side wall (above the bath) in complex oxidized reduction atmosphere of CO/CO_2 and vapors of fluorine and sodium compounds.
- Mechanical erosion of circulating metal and electrolyte with particles of alumina.

The most important question arises is to know if the gases react first and oxidized the side limning making it more porous and then liquid electrolyte comes in contact and causes corrosion. It's important to know whether corrosion by gases takes place first or by liquid electrolyte.

Usually Si_3N_4-SiC side lining in Al reduction cell is covered with side ledge frozen electrolyte with alumina particles (Figure 1b), but at startup of the cell or in case of overheating of the cell Si_3N_4-SiC material is subjected to direct interaction with molten electrolyte (Figure 1a).



(a) (b)

Figure 1. Typical construction of Al reduction cell: (a) cell without frozen side ledge, 1 – upper part of SiC side lining above the level of electrolyte, 2 – the border between electrolyte and molten aluminum, (b) cell with normal side ledge.

Frozen side ledge (Figure1b) is permeable to gases. The corrosion of Si_3N_4-SiC by O_2, CO, CO_2 in presence of volatile compounds of sodium and fluorine starts from the beginning of operation of the cell (when there is no side ledge), but continue during all service lifetime. In real service the most severe corrosion of Si_3N_4-SiC takes place at the interface of metal and bath, (Figure 1).

The quality of Si_3N_4-SiC materials is critical for the service lifetime of reduction cells, so lab testing is rather popular in Al industry. Rod test is accepted for laboratory corrosion testing of Si_3N_4-SiC materials for application in metallurgy of primary aluminum [3-9]

The aim of the investigation is to generalize the results on oxidation and corrosion phenomena of Si_3N_4-SiC materials from the previous research [10-13], the lab results of other researchers [3-10, 14-17] and the industrial results from the smelters.

2. Results and Discussion

2.1 Corrosion of Si_3N_4-SiC Materials in Industrial Al Reduction Cells.

Normally industrial reduction cells are under operation for 60-84 months, and during this time various changes may occur on macro level (Table 1, Figure 4). Si_3N_4-SiC side lining may partly be dissolute on the border of electrolyte melt (Figure 2a), it may become thinner (Figure 2b), and it may crack (Figure 2c). The latter cases (Figure 2b and c) usually take place with material above the level of liquid electrolyte.

Table 1. The change of porosity and the density of Si3N4-SiC side lining at service in the reduction cell.

Number	Apparent density (initial), g/cm^3	Apparent density (after 180 days), g/cm^3	Open porosity (initial), %	Open porosity (after 180 days), %
1	2.68	2.75	15.8	10.4
2	2.68	2.77	15.6	7.5

corrosion process takes place more quickly, and there is no need for 50 hours exposure. 4 hours of testing, when the tested rods are moving up and down in the molten cryolite, is enough to make some preliminary considerations (Figure 5 c), and after 8 hours the volume losses are sufficient to make conclusions about corrosion resistance of the material (Figure 5 d).

3. Conclusions

The corrosion of Si_3N_4-SiC materials in aluminium reduction cell may proceed by reactions with gases and with liquid substances. A major part of the oxidation reactions of Silicon Carbide and Silicon Nitride proceed with positive volume effect. that means (the reaction products occupy more space, than the reactants. It may play positive role for the prolongation of the service lifetime of refractory. For another thing, that can cause cracking and spalling.

The reactions of Silicon Carbide and Silicon Nitride with molten cryolite proceed via the stage of pre oxidation.

More probably the lab corrosion testing of Si_3N_4-SiC materials to molten cryolite require additional investigations.

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