AL27 - Silicon Carbide Sidelining Materials in Reduction Cells: Corrosion Resistance, Service Life and Testing

Oksana Danilova[1], Natalia Ushakova[2] and Andrey Yurkov[3]
1. Head of Laboratory,
2. Head of R&D Center,
3. Adviser,
Voljsky Abrasive Plant, Carborundum Universal, CUMI, India, Voljsky, Russia
3. Mendeleev University of Chemical Technology, Moscow, Russia
Corresponding authors: And-yur@mail.ru; yurkov.a.l@muctr.ru; yurkov.a.l@vabz.ru

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

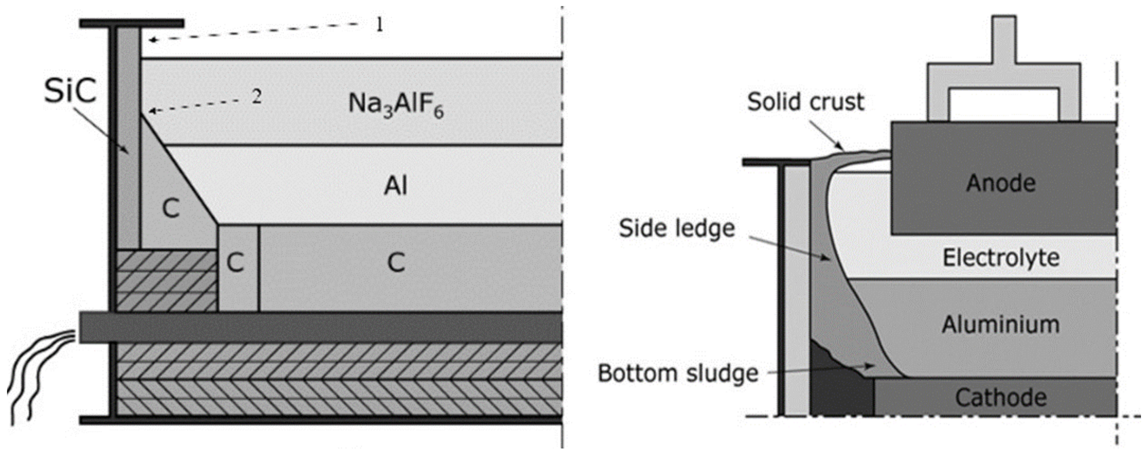
Corrosion phenomena is very complex, and it is necessary to take into account different processes and mechanisms of degradation. Corrosion of the refractories at high temperature-is caused by the gases and liquid which comes in contact with refractories. There is a chemical corrosion of refractories 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

(a) (b) (c)

Figure 2. (a) Si3N4-SiC sidelining after 60 months of service in reduction cell. (b) Si_3N_4-SiC sidelining materials after service in Al reduction cells. A groove in the upper part of side lining. (c) Si3N4-SiC sidelining materials after service in Al reduction cells. Cracking and spalling of side lining in the upper part after the service in the reduction cell for 24 months.

Table 2. Chemical composition of Si_3N_4-SiC materials after service in reduction cells (depicted on Figure 3) - current research and according to [14] (№1).

Number	Composition, mass.%					Service time, months	Comments
	SiC	Si_3N_4	SiO_2	Si	Oxides, including Na_2SiO_3		
1	50.7	16.62	11.1	-	21.58	46	-
2	73.1	15.4	7.3	-	2.2	39	Upper part
3	68.1	18.2	7.2	-	6.5	39	Lower part
4	73.7	23.3	1.65	0.34	0.98	36	Upper part
5	71	25,3	2,3	0.3	1.1	36	Lower part

In the papers [15-17] the authors took a generalized picture of the growth of silica content in Si_3N_4-SiC with time, not giving details and values of time and concentrations. According to them, after some short period the silica content in SiC side lining reaches 7-8 wt.% and remains more or less permanent (the graph on Figure 3) for a certain time.

The exact data on Silica content is Si_3N_4-SiC side lining in industrial reduction cells is limited. Our data, collected at different Al smelters, show on sufficient silica content (Table 2), varying from 1.65 % to 7-11 %. The values, reported by Proshkin [14] and our data are depicted over the graph (Figure 3), taken from papers [15-17].

In Si_3N_4-SiC materials coarse grains of α-silicon carbide are surrounded by small grains of silicon nitride (Figure 4). In as-received materials after nitration the crystals have strict shapes, especially in relatively big α-SiC grains (Figure 4a). It is considered that α-silicon nitride crystallizes in the form of needle like grains (Figure 4b), while β-silicon nitride crystals are more uniform in length and width (Figure 4c).

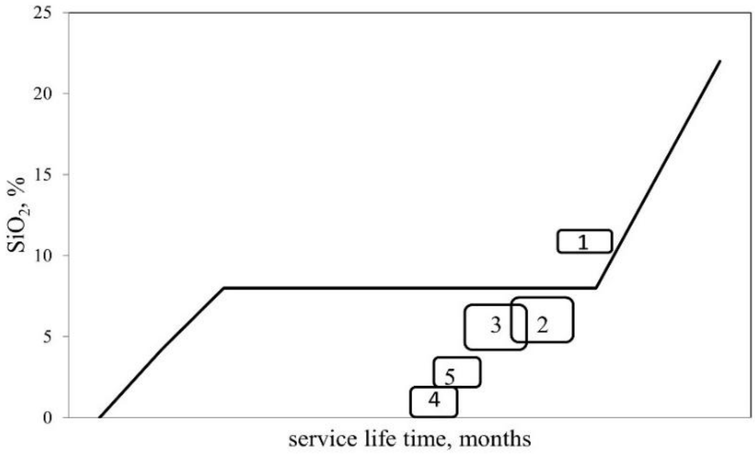


Figure 3. The graph of silica content growth in Si_3N_4-SiC side lining from [14](№1) and our (№№ 2,3,3,5) [15-17] experimental data (concentrations are in Table 2): 1 – after [14], side ledge is poor, side lining is overheated, 2- side ledge is poor, service life time 39 months, upper part, side ledge is poor, service life time 39 months, lower part, 4 - side ledge is good, service life time 36 months, lower part, 5-side ledge is good, service life time 36 months, upper part.

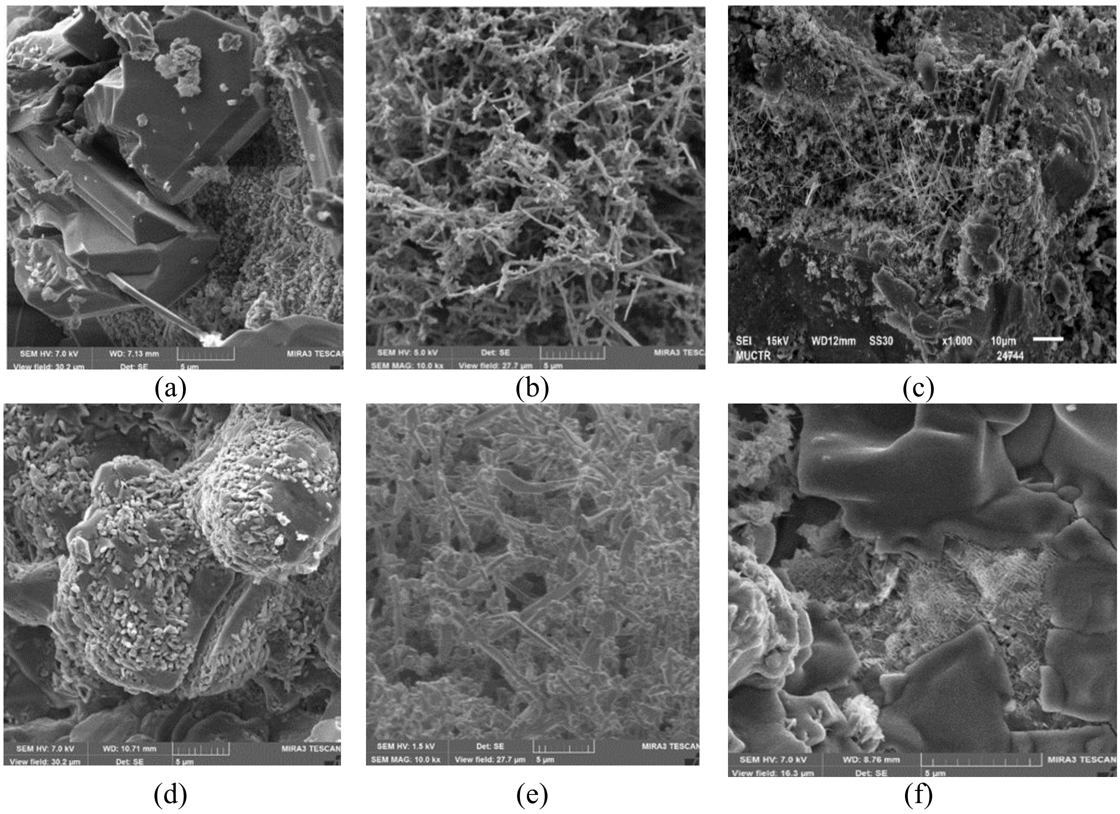


Figure 4. Microstructures of Si_3N_4-SiC materials- (a), (b), (c) – as received, (d) and (e). After service in industrial cell above the level of the bath, (f) – after service in industrial cell below the level of the bath. (a)- α-SiC crystals with some part of β-Si_3N_4 before service; (b) – with predominant α- Si_3N_4 before service. (c) – with α/β- Si_3N_4 +SiC before service. (d) - α-SiC crystals with some part of β-Si_3N_4 after service. (e) - with predominant α- Si_3N_4 after service. (f)- Si_3N_4-SiC material, corroded by liquid cryolite (small grains of crystallized cryolite are between smooth grains of SiC).

At oxidation in the upper part of the side lining in Al reduction cell (the structure of material #3, Table 2) silicon nitride crystals lose their crystal shapes and become more rounded (Figure 4c), silicon oxide appears on lumpy silicon carbide crystals (Figure 4d).

2.2 Corrosion of Si_3N_4-SiC Materials in Industrial Al Reduction Cells and "Gas-solid" Reactions

In aluminium reduction cell Si_3N_4-SiC refractory interacts with corrosive gases according to reactions 1-8 (Table 3). Other reactions are possible, here we give the most probable. Silicon carbide transforms to silica, silicon nitride transforms to silica also, although silicon oxynitride may appear, as an intermediate product [10].

Table 3. Volume effects of silicon carbide and silicon nitride reactions.

Number	**Chemical Reactions**	**ΔV/V, %**
1	$SiC + 2\ O_2 = SiO_2 + CO_2$ (g)	112
2	$SiC + 3CO_2 = SiO_2 + 4\ CO$ (g)	112
3	$Si_3N_4 + 7\ O_2 = 3\ SiO_2 + 4\ NO_2$ (g)	80
4	$Si3N_4 + 6\ CO_2 = 3\ SiO_2 + 6\ CO$ (g) $+ 4\ N_2$ (g)	80
5	$SiC + 2\ CO = 3\ C + SiO_2$	+ 308-344%*
6	$SiC + CO2 = 2\ C + SiO_2$	+ 103-124%*
7	$SiC + CO = 2\ C + SiO$	-15%
8	$Si_3N_4 + 6\ CO = 3\ SiO_2 + 6\ C + 2\ N_2$ (g)	-27,90%

*The uncertainty in calculation of the volume effect is in the lack of knowledge, in what crystallographic modifications appear silica (glassy, quartz, crystabalite, etc.) and carbon (graphite or coke).

The major part of reactions proceeds with positive volume effect that means (Table 3), that the reaction products occupy more space, than the reactants. It may play positive role for the prolongation of the service lifetime of refractory, because the appearing silica fills in the pores, diminishing the porosity of materials (Table 1). The diminishing of porosity prevents the penetration of gases and liquids inside refractory.

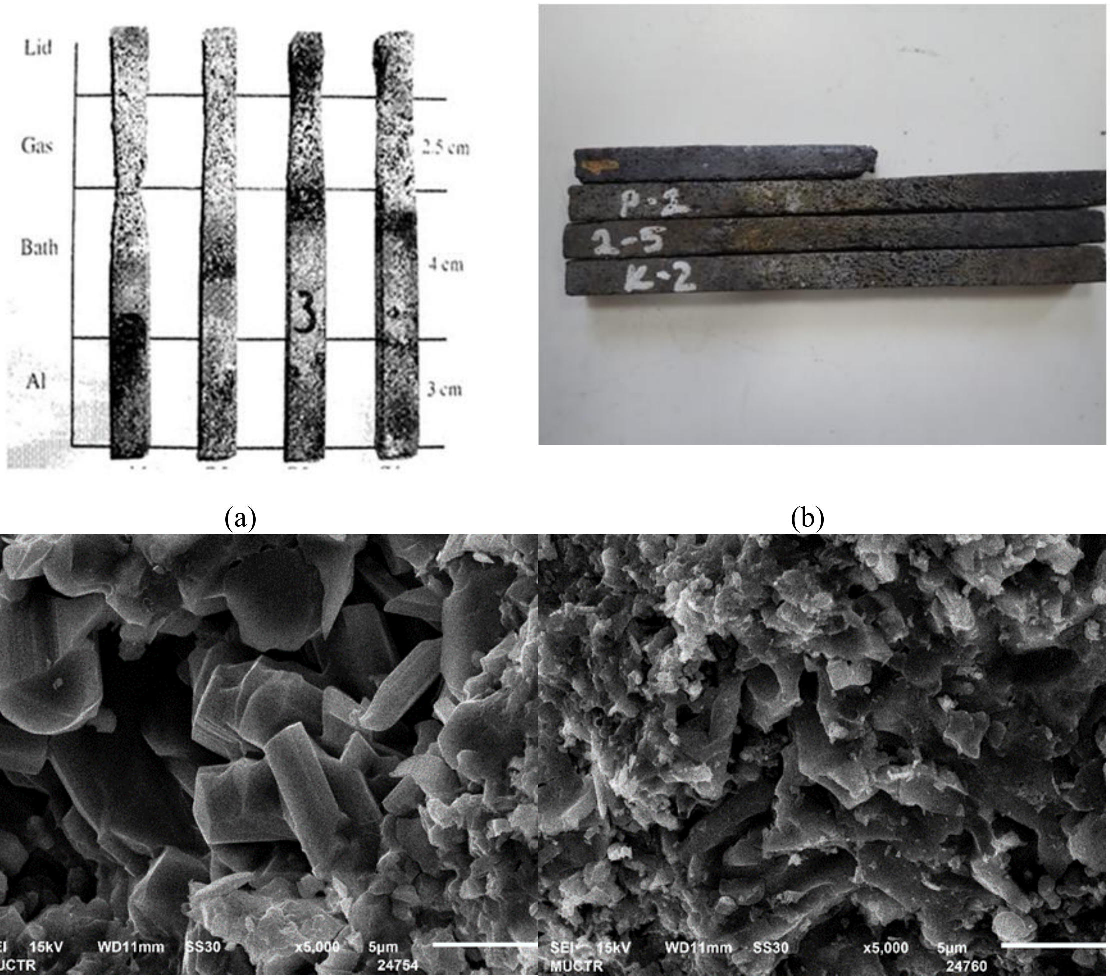
For another thing, the positive volume effect of reactions means, that appearing reaction products will occupy the free space in pores and may cause mechanical tensions in materials that can cause cracking and spalling (Figure 2c) [11-12].

In course of the interaction of silicon nitride (the microstructure of material from Figure 4a) with molten cryolite silicon nitride crystals disappear, and silicon carbide crystals are becoming smooth and round shaped (Figure 4f, Figure 5c and d).

2.3 Laboratory Corrosion Testing of Si_3N_4-SiC Materials

There are three variants of laboratory corrosion test of Si_3N_4-SiC material for the use in aluminum reduction cell. SINTEF test (the test of Norwegian Institute SINTEF) is most popular [3-4], then are LIRR test [6-8] (the test of Luoyang Institute for Refractory Research LIRR), and RUSAL test [14] (the test, invented in Engineering Technological Center of Russian Aluminum (RUSAL, Krasnoyarsk). Probably it is necessary to mention corrosion test of Laucournet [5].

In all tests the Si_3N_4-SiC rods are immersed in the corrosion liquid, and the criteria is a volume loss of the rods after testing. All the tests are 'dynamical', it means, that the corrosive liquid moves around the tested samples.



(a) (b)

(c) (d)

Figure 5. Si_3N_4-SiC rods after corrosion testing, according to SINTEF variant (a) [18,19], according to RUSAL variant [9], microstructures of Si_3N_4-SiC materials according to RUSAL variant (c, d), (c) after testing for 4 hours, (d) after testing for 8 hours.

SINTEF test [3-4,18-19] is known world-wide, it copies the process of industrial reduction in detail. The samples of the tested Si_3N_4-SiC material (Figure 5 a) are dipped in the molten cryolite, alumina powder dissolves in cryolite, and electrolysis proceed. During 50 hours of reduction process Si_3N_4-SiC rods lose the volume above the level of the bath (electrolyte), lose the volume on the border of the bath and air. Below the level of bath, the volume loss also takes place. According to [18-19], the volume loss may be from 2 % to 20 %.

The principal difference of LIRR and SINTEF tests is in additional flowing CO_2 above the melt, while the tested samples are rotating. In RUSAL test there is no electrolysis, tested Si_3N_4-SiC rods are moving up and down in the molten cryolite, so there was no strict border between Si_3N_4-SiC material, oxidized at air and Si_3N_4-SiC material, immersed in cryolite.

Unfortunately, these laboratory tests give somewhat different corrosion resistance results that require additional research. We investigated the structure of Si_3N_4-SiC materials after lab testing after RUSAL variant of testing (Figure 5 b). It is possible to say, that in such conditions the 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.

4. Acknowledgments.

Authors are grateful to Dr. Aleksandr Proshkin, Andrey Sbitnev and Elena Marakushina from Engineering Technical Center, RUSAL, Krasnoyarsk for support in corrosion testing and consultations. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors. The authors declare that they have no conflict of interest.

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