Oxidation resistance and corrosion resistance of silicon carbide side lining

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Abstract

Si_3N_4-SiC materials have considerable strength, yet in Al reduction cells the decay of SiC side lining takes place due chemical corrosion and oxidation, sometimes accompanied and enhanced by physical erosion. N-SiC lining materials in reduction cells should be corrosive resistant to electrolyte and oxidation resistant. In aluminium reduction cell the upper part of SiC lining is subjected to interaction with oxygen, carbon dioxide and carbon monoxide from air. However other parts, covered with side ledge and near the bus bar windows, also may be oxidized during the service. Probably oxidation resistance and corrosion resistance of Si_3N_4-SiC materials may be governed by different factors. The priority of oxidation resistance and corrosion resistance to cryolite of silicon carbide over silicon nitride leaves many questions. Anyway, silicon nitride and silicon carbide slowly oxidize during the service in N-SiC side lining of reduction cell. The question on priorities of oxidation and corrosion resistance of one over another has aspect not only in the service life time in reduction cell, but also in uncertain optimum of concentrations, slight porosity and concentration gradients.

Keywords: Silicon carbide; silicon nitride; oxidation; corrosion.

1. Introduction

Silicon carbide side lining of aluminium reduction cells has been well known for many years. In the scientific literature, other materials are discussed as potential candidates for side lining elements - SiC based [1, 2, 3, 4] and non-SiC based [5]. However, the change of N-SiC side lining in the construction of aluminium reduction cell for another more resistant material is a problem of the future. Probably, when inert anodes will be implemented, profound research on new side lining materials will be required, and a new material will replace nitride bonded silicon carbide.

Currently there is well-known SINTEF test for the corrosion resistance of N-SiC [6, 7], and it is accepted by many smelters. The procedure of this testing simulates the behaviour of side lining during the first hours of electrolysis. There are the variations of this test for the corrosion resistance [8, 9, 10]. Also there is a corrosion resistance test without application of the electric current [11]. It is performed with preliminary oxidation of N-SiC samples.

Usually the decision on the possibility to use the material in a lining of the cell is based on the corrosion test results.

2. Experimental

Standard industrial N-SiC side lining refractories, produced at VAW Voljsky Abrasive Works, Russian Federation (VAW) were used for the analysis. The properties of materials (porosity, density, strength) were determined using standard methods. The chemical composition of the materials was determined by standard wet chemistry methods (SiC, Si, SiO_2, CaO, Fe_2O_3, Al_2O_3) and by XRD (SiC, Si, SiO_2, Si_3N_4). Nitrogen and oxygen were determined using the LECO method. Silicon oxynitride, Si_2ON_2, α- and β- modifications of silicon nitride were determined by XRD. Structures were analyzed at Nikon Eclipse optical microscope and Tescan X-max SEM with EDX Oxford instruments microprobe analyzer.

3. Results and discussion

Although there are no unique specifications of nitride bonded silicon carbide side lining material for aluminium reduction cells, the composition is more or less standard. Silicon carbide content varies from 72 % to 75%, silicon nitride and silicon oxynitride content is in the range of 15 – 25 %. Silica content, that is supposed to be non-desirable admixture, is usually below 1 % or even below 0.5 % (in reality it is in the range below 0.3 %).

During the service of N-SiC side lining in Al reduction cell, the concentration of silica slowly increases. Unfortunately, there are no well proven data on the increase of silica in the lining with service time. However, this may be explained by the fact, that it is impossible to make such dependence, because there are too many variables. In different parts (Figure 1) (above the melt, under the melt and in the lower part), N-SiC side lining undergoes different transformations.

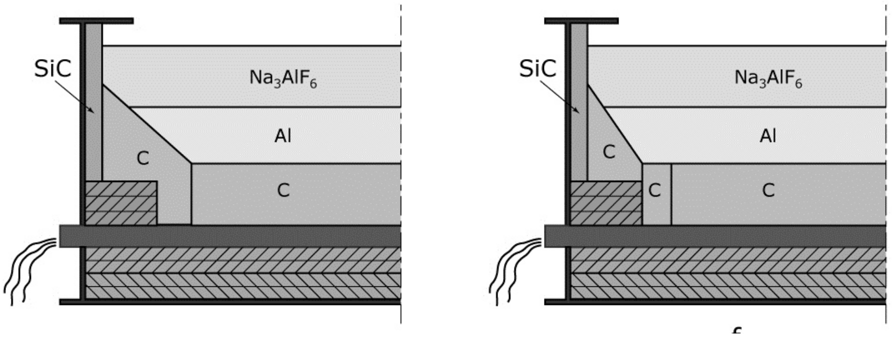
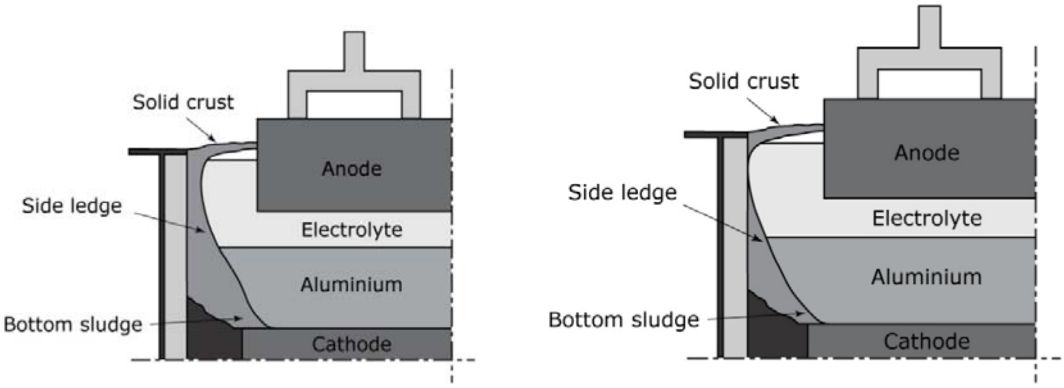


Figure 1. Different zones in SiC side lining.

Another variable is the existence of side ledge (Figure 2), absence of the side ledge and thin side ledge. The consequence is different temperature in one and the same zone of the side lining and different kind of interaction - in case of absence or existence of side ledge.



a) b)

Figure 2. Cross section of the reduction cell: a) with side ledge;b) almost without side ledge in the upper part.

According to [12] the degradation mechanism of SiC side lining is equal for all service conditions and has 3 stages of aging. In the first stage the oxidation is rather rapid and the decay of the thermal conductivity is rather low, in the second stage the stability takes over (when silicon oxide layer is formed), the rate of oxidation is constant, and the second phase lasts for a long period – a number of years. Then (when the silicon oxide content reaches 15 – 20 %) the third phase starts with relatively rapid growth of silicon oxide content. In the end of the third phase the silicon oxide content reaches 28 – 39 %, while the thermal conductivity drops to 5 - 7 W/mK.

Proshkin [13] reported, that in case of overheated side lining the silica content in N-SiC lining may be up to 11.1 %, while carbon dioxide and sulfur compounds (like COS, SO_2 and CS_2) may also play a certain role in deterioration of silicon carbide and silicon nitride to silica or to other compounds.

Our experience shows, that in N-SiC side lining, covered by side ledge the silica content after 36 months may be 2.2 % at the level of the metal and only 2.3 % at the level above the metal (7 - 10 cm from the top of deckplate), while in the block almost without the side ledge with service life time 39 months there is up to 7.5 % of Silica.

Our experience in copper metallurgy [14] gives similar facts – N-SiC material contains 8.22 % of Silica above the melt of copper after exposition 6 months, while under the melt of copper the same material contained from 1.39 % to 3.79 % of silica.

Anyway, the concentration of silica in nitride bonded silicon carbide in side lining of aluminium reduction cells grows slowly.

Question number one (that was already opened by Laucournet [11]) – whether silicon carbide and silicon nitride reacts with components of the electrolyte directly or silicon carbide and silicon nitride oxidize and the resulting silica reacts with the components of electrolyte.

In the presence of carbon dioxide and fluorine compounds, Silicon carbide and silicon nitride may react directly with them:

$$2SiC + 2NaAlF_{4(g)} + 2CO_2 = 4SiF_{4(g)} + 2NaAlSiO_4 + 4C \qquad (1)$$

$$2Si_3N_4 + 3NaAlF_{4(g)} + 2CO_2 = 3SiF_{4(g)} + 3NaAlSiO_4 + 6C + 4N_2 \qquad (2)$$

$$2SiC + NaAlF_{4(g)} + 2O_2 = SiF_{4(g)} + NaAlSiO_4 + 4C \qquad (3)$$

Proshkin [13] considers, that due to these reactions during the service the thickness of N-SiC blocks diminishes, and a crack may appear on the blocks.

However silicon nitride and silicon carbide may oxidize by oxygen in air and by carbon dioxide from anode gases

$$SiC + 2O_2 = SiO_2 + CO2\ (g) \qquad (4)$$

$$SiC + 3CO_2 = SiO_2 + 4CO\ (g) \qquad (5)$$

According to [15]

$$SiC + 2CO = SiO_2 + 2C \qquad (6)$$

$$Si3N_4 + 7O_2 = 3SiO_2 + 4NO_2\ (g) \qquad (7)$$

$$Si3N_4 + 6CO_2 = 3\ SiO_2 + 6CO\ (g) + 4N_2\ (g) \qquad (8)$$

According to [15]

$$Si3N_4 + 6CO = 3SiO_2 + 6C + 2N_2\ (g) \qquad (9)$$

And the resulting silicon oxide interacts with the components of the electrolyte

$$9SiO_2 + 4Na_3AlF_6 = 4Na_2SiO_3 + SiF_4(g) + 4AlF_3 \qquad (10)$$

$$3SiO2 + 4NaF\ (l) = SiF_4\ (g) + 2Na_2SiO_3 \qquad (11)$$

The oxidized upper part of side lining probably reacts with fluorine salts and HF in gaseous phase according to reactions:

$$4SiO_2 + 2NaAlF_4(g) = 4SiF_4(g) + 2NaAlSiO_4 \qquad (12)$$

$$4SiO_2 + 4NaAlF_4(g) = SiF_4(g) + 2Na_2SiO_3 + 4AlF_3 \qquad (13)$$

$$3SiO_2 + 4NaF(g) = SiF_4(g) + 2NaSiO_3 \qquad (14)$$

$$SiO_2 + 6HF = H2SiF_6 + 2H_2O \qquad (15)$$

This also may decrease the thickness of the side lining, sometimes forming the crack or different thickness of the side lining (Figure 3)

a) **b)**

Figure 3. N-SiC side lining after the service in Al reduction cell: a) the crack in the upper part of SiC side lining; b) N-SiC side lining, extracted from the cell in course of dry autopsy.

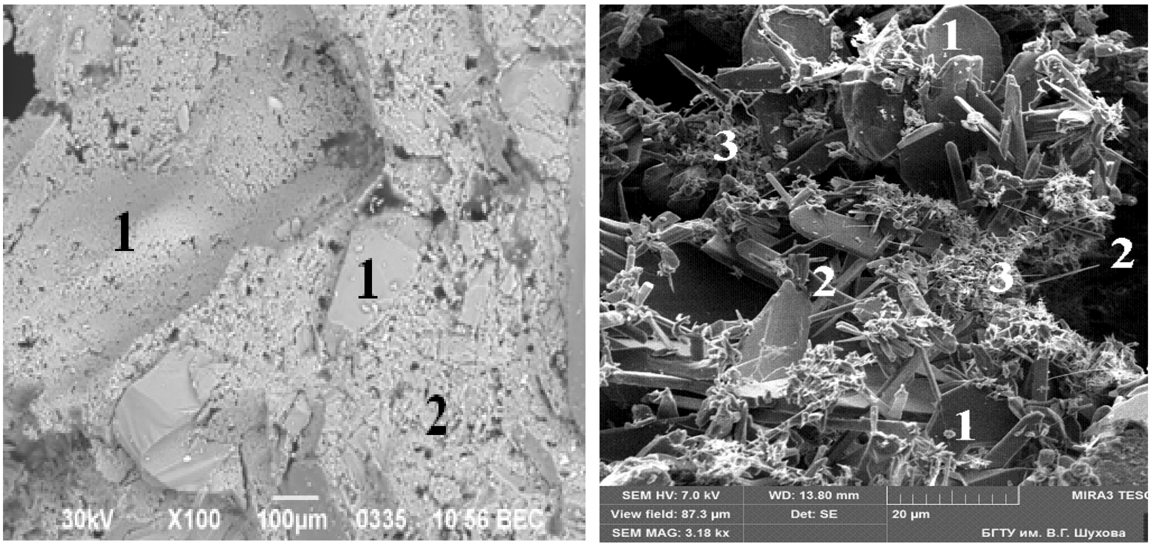
As it is known, at the start-up of the cell the side lining is subjected to direct contact with electrolyte (Figure1 1), and the frozen side ledge is formed only after a month or two (Figure 2). In practice there is no shut downs of the reduction cells at start-up due to the side lining. It means, that during certain period of time N-SiC material can withstand the direct interaction of electrolyte without visual changes in thickness and colour.

Experience shows, that the shut-downs of the cells due to side lining can occur after 36 - 48 months. Although the information on silica content growth is not sufficient, the limited data show a fair amount silica, varying from 2.2 to 7 - 11 %.

In the investigation [11] the samples of N-SiC materials were pre-oxidized in dry air and steam at different temperatures. The authors recorded weight gain and the growth of oxygen content in the samples. In some samples the oxygen content increased up to 7.5 % at oxidation during 100 hours. Yet the authors did not find distinctive correlation between the weight gain during oxidation and the weight loss after dissolution of oxidized samples in electrolyte. Probably the analysis of the results with the emphasis on the changes in the chemical composition of N-SiC materials might give some additional information.

The other question, that appears in literature is – what is more resistant to oxidation and corrosion by electrolite – silicon nitride or silicon carbide. Also the priority of corrosion and oxidation resistance of β-silicon nitride over α-silicon nitride is discussed o0casionally. In the literature it is mentioned [16, 17], that the silicon nitride phase is less corrosion resistant to the cryolite melt compared to silicon carbide phase, details of the specific experiments are difficult to find in the literature. The kinetics of the reaction plays a role, as silicon carbide grains in N-SiC composites have dimensions up to 2 - 3 mm, while the dimensions of silicon nitride particles are about 10 µm and less.

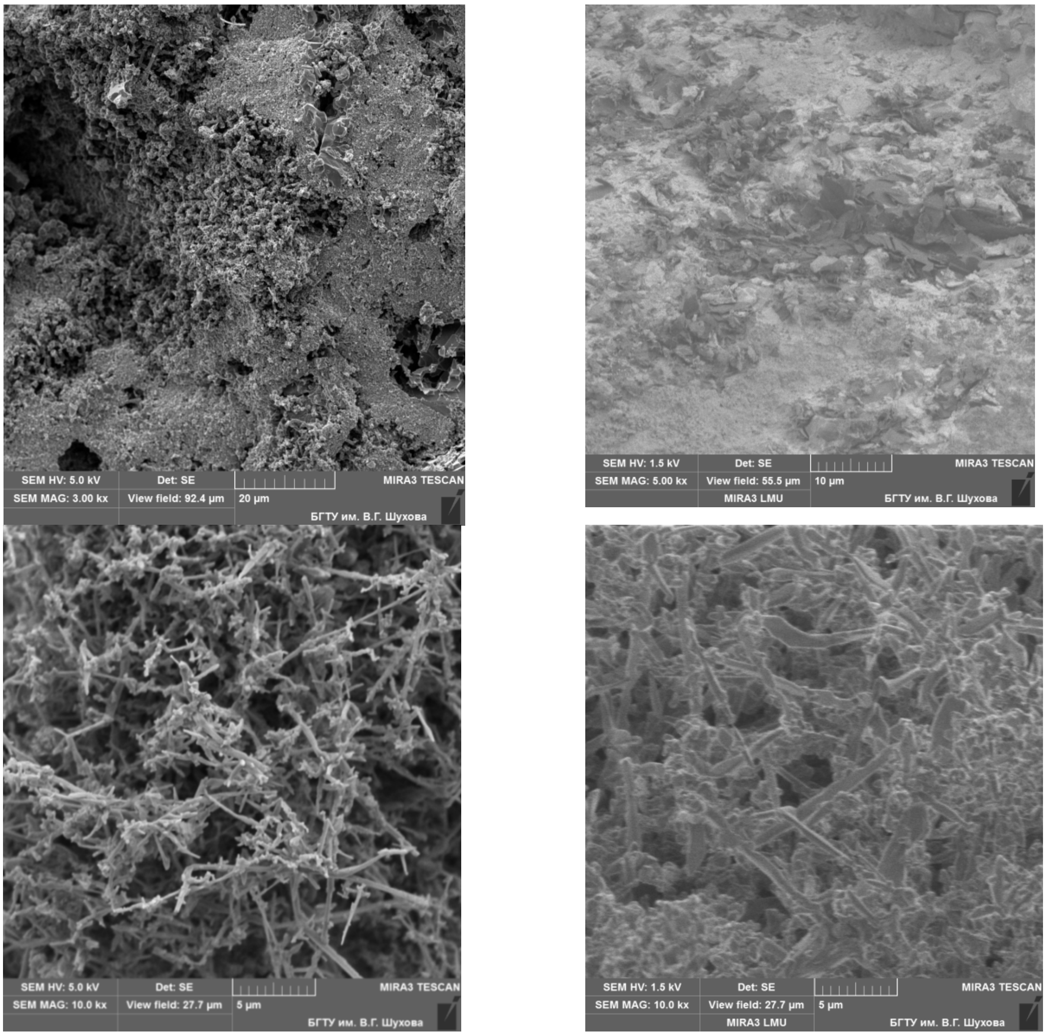
There are also suggestions, that the β-modification of silicon nitride is more corrosive resistant to cryolite melt comparing with α-modification [16, 17].



a) **b)**

Figure 4. Typical structure of N-SiC refractory: a) at low magnification: 1- SiC, 2- Si_3N_4; b) at high magnification: 1- SiC, 2 – α-Si_3N_4, 3 – β-Si_3N_4.

We did not manage to find evidence for this suggestion. Usually the shape of β-Si_3N_4 particles is close to isometric or tends to be short prismatic with l/d from 1 to 2 - 2.5 (Figure 4b). The shape of α Si_3N_4 particles is elongated, and include needle-like crystals with l/d > 10 - 20. They are formed due to the reaction of silicon vapours with nitrogen and the following condensation. The specific reaction surface of needle like and elongated crystals is sufficiently high, so β-Si_3N_4 might be more corrosion resistant because the surface of reaction of these particles is smaller. During the oxidation process the open porosity of N-SiC materials diminish to 2 – 4 % [19]. Our experiments (Figure 5) show similar results.



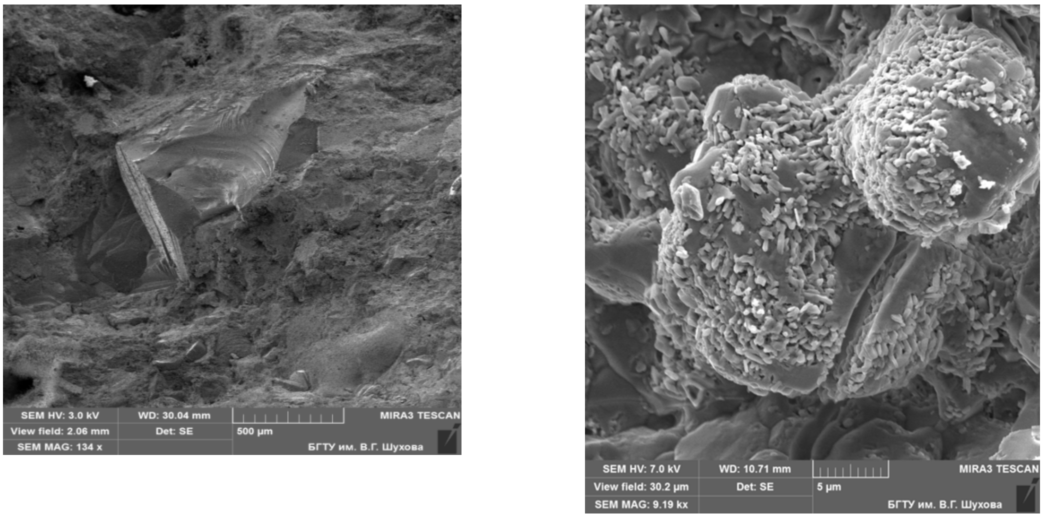


Figure 5. The images of the structure of β-Si_3N_4, α-Si_3N_4 and grains of SiC in N-SiC material: left column - before oxidation; right column - after oxidation.

Tonessen and coworkers [18 - 20] performed experiments with testing oxidation resistance of N-SiC materials in a steam according to ASTM-863 [21] and they consider, that silicon nitride plays an important role in the oxidation resistance of N-SiC materials. According to Tonnesen, silicon nitride is not a simple “weak” phase of the composition. Complex Si-O-N phase, that may appear at certain conditions during oxidation or may be present in the material after processing, is oxidation resistant and not subjected to transformation to crystobalite or to other volume changes.

According to Tonnesen [18 - 20] and Laucournet [11] the permeability of N-SiC materials play an important role in oxidation resistance. Laucournet [11] registered direct relation between the oxidation rate, measured after preliminary oxidation step and the dissolution behaviour, observed in cryolite bath. It is more likely, that the permeability is determined by grains and crystals of appearing during synthesis modifications of silicon nitride. Fine crystals of silicon nitride form the pore structure of N-SiC material with very low pore size distribution (Figure 6) and permeability, that may promote good oxidation resistance.

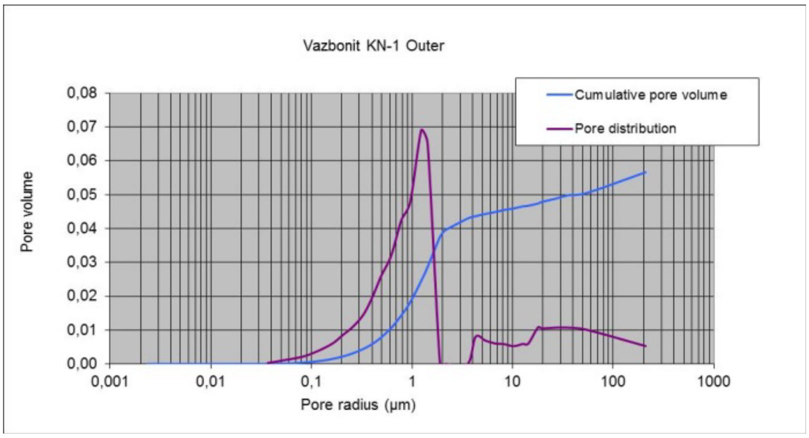


Figure 6. Pore size distribution in N-SiC material.

4. Conclusions

Several kinds of interactions take place between N-SiC refractory material during the service in aluminium reduction cells.

The questions on priority of the direct reactions of silicon carbide and silicon nitride with the constituents of electrolyte in liquid and vapour phase over the oxidation reactions of silicon carbide and silicon nitride with the following reactions of appearing silicon oxide with the components of electrolyte and following dissolution of the products in electrolyte has not only theoretical value.

Microstructure of N-SiC material may have considerable influence on oxidation resistance, especially with respect to gas permeability and pore size distribution.

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