

## SiC IN ELECTROLYSIS POTS: AN UPDATE

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### Abstract

The physical and chemical properties, the bond types and the resistance to bath, aluminium, carbon dioxide and air attack of SiC are reviewed, outlining especially the use of non-oxide bonded SiC refractories as sidewall materials for aluminium electrolysis cells. State-of-the-art is nitride-bonded SiC. This type of SiC sidewall lining material is particularly suitable for the operation of modern electrolysis cells equipped with point feeders for automatic alumina feeding to the bath. It is also a key material in upgrading older cells to higher current and anode size.

### Introduction

This update is a continuation of [1, 2] and covers the period 1995 to 2005. The literature explains the required physical and chemical properties: the sidewall needs to

- Resist molten aluminium [3]
- Resist molten bath [3]
- Resist CO<sub>2</sub>/CO and HF vapours [3]
- Have low porosity [4-7]
- Have very high strength [8]
- Have reasonably high thermal conductivity [8, 9]
- Have high bulk density [6]
- Have high electrical resistivity [6, 10]

### Binders

Silicon carbide based refractories can be divided into four kinds of materials according to their bonding phases [11]. These phases include silicon carbide, silicon nitride, silicon oxynitride and SiAlON.

### SiC

According to Skybakmoen et al [3], self-bonded SiC was superior to all other materials tested, but some local and uneven corrosion occurred where the more reactive binding phase was preferentially attacked [10]. The weakest part of the SiC bricks seems to be the binder. SiC-based materials show high oxidation resistance in general by forming of a protective layer of SiO<sub>2</sub>. In the gas/melt interface and in the vapour zone one may expect faster removal of SiO<sub>2</sub> by dissolution; corrosion resistance then depends on the on the base materials.

### SiAlON

Cao et al [12] investigated β-SiAlON/SiC composites in a molten cryolite melt to see how SiC content, corrosion kinetics and mechanism affected corrosion resistance. They found that the corrosive reactions between β-SiAlON/SiC matrix and cryolite are

retarded due to the formation of NaAlSiO<sub>4</sub> with a high viscosity on the surface of β-SiAlON/SiC matrix.

### Si<sub>2</sub>N<sub>2</sub>O

According to Welch [10] some oxynitride species show better short-term resistance, and perform satisfactorily when the anode effect frequency is reduced. However, electrolyte penetration results in partial or total dissolution of the protective oxide formed, resulting in long-term structural degradation. Cheng et al [11] found that Si<sub>2</sub>N<sub>2</sub>O and SiAlON-bonded SiC have less corrosion resistance against cryolite melts than Si<sub>3</sub>N<sub>4</sub> bonded SiC.

### Si<sub>3</sub>N<sub>4</sub>

However, compared with the other binders for silicon carbide refractories, nitrides are the least corroded [13], because they have an extremely high electrical resistance and therefore do not suffer from the electrochemically driven processes. Therefore silicon nitride bonded silicon carbide is the material most used in the primary aluminium industry and counts as state-of-the-art sideling material. According to Skybakmoen [7] the Si<sub>3</sub>N<sub>4</sub> phase is thermodynamically more unstable than the SiC-phase and it has been claimed that the Si<sub>3</sub>N<sub>4</sub> phase is oxidised first in a Si<sub>3</sub>N<sub>4</sub> bonded SiC material.

### Manufacture

The manufacture of Si<sub>3</sub>N<sub>4</sub> bonded SiC has been reviewed several times [7-9, 14, 15]. Si<sub>3</sub>N<sub>4</sub> bonded SiC materials are produced by blending SiC particles (mm size) with fine-grained silicon metal powder and a binder. SiC may have some content of SiO<sub>2</sub>, Si, Fe, and C coming from the production process. The bricks are shaped by pressing/vibration, then dried to remove moisture. The bricks are sintered in furnaces in a flowing nitrogen atmosphere at temperatures of more than 1400°C. During the nitriding process silicon reacts with nitrogen, forming Si<sub>3</sub>N<sub>4</sub> as a binder between the SiC grains. The final product will then consist of of large SiC grains (mm size) with a microporous binder phase of Si<sub>3</sub>N<sub>4</sub>. Typical composition is 72-80 wt.% SiC and 20-28 wt.% Si<sub>3</sub>N<sub>4</sub>. High purity (better than 97%) SiC grains must be used. For shaping the bricks, vibratory presses are recommended so as to avoid stratification.

These materials have to develop the right amount of nitride with the least residual silicon metal and other contaminants like oxygen and aluminium phases. Good control of the nitriding process is therefore crucial. The physical properties are also important, as excessive porosity is detrimental to thermal conductivity and to oxidation resistance.

Wu [15] proposed a reverse reaction sintering process. In this process the Si<sub>3</sub>N<sub>4</sub> is firstly converted into reactive oxides, then react sintered. The new sintering process is accomplished by the reactive sintering of newly formed Si<sub>2</sub>N<sub>2</sub>O or SiO<sub>2</sub> phases. The

products have excellent physical and chemical properties due to their dense structure and to in-situ formed oxides or sub-oxides which fully fill the boundary between  $\text{Si}_3\text{N}_4$  and SiC particles.

### Oxidation resistance

As demonstrated by Jorge et al [16], oxidation resistance is the critical parameter for the performance of silicon nitride bonded SiC in aluminium reduction cells. A non-oxide  $\text{Si}_3\text{N}_4$  can be oxidized in a relatively reductive atmosphere (such as CO) [17] to form silica that will easily be corroded by cryolite. According to Ivey [8] unprotected SiC therefore oxidizes rapidly in the temperature range of 800-1150°C. As Welch [10] reported, the ignition temperature for the binder face can be as low as 200°C. For low oxygen supply rates, this results in preferential oxidation and powdering of the material, creating both cavities and markedly changed thermal resistance. The oxidation resistance of SiC is a function not only of the bond system, but also of porosity and pore size.

However, in materials based on SiC and exposed to the gas phase, Hagen et al [18] observed a protective layer of sodium aluminosilicate fluoride glass. Enhanced corrosion resistance results from the tendency of silicon to form viscous oxyfluoride glasses, which kinetically retard both the oxidation and dissolution of the oxidised product.

### Wear mechanism

According to Andersen et al [19] the wear mechanism of  $\text{Si}_3\text{N}_4$  bonded SiC bricks seems to combine attack by Na, HF, oxidation and moisture. Below bath level, oxidation and sodium play a major role, but bricks there deteriorate least. At bath level the attack is severe. Above bath level the bricks disintegrate, but reaction products are almost absent. Here HF vapour seems to transform the oxidation products into volatile fluorides and other gases.

The main attack agents of cell materials in general are cryolite, liquid aluminium,  $\text{NaAlF}_4$ , CO and  $\text{CO}_2$ . Instead sodium hydroxide was found in SiC and therefore it appears that sodium metal or sodium oxide combined with moisture causes chemical attack. HF gas probably also causes chemical attack. Only at the bath level were Na-Al-silicates.

Bath acidity greatly influences chemical resistance. Corrosion increases with increasing cryolite ratio (increasing sodium content in the bath). Skybakmoen and co-workers [7] propose the following reaction sequence:

- Sodium penetration
- Oxidation to  $\text{Na}_2\text{O}$  and formation of  $\text{Na}_2\text{O} \cdot x\text{SiO}_2$
- Swelling/descaling/dissolution of the reaction products
- New reaction cycle

This reaction cycle is assumed to be especially damaging for materials with high oxygen content.

The older the SiC block, the faster it oxidates and loses its thermal conductivity. Jorge et al. [9] distinguish different steps:

The first step involves oxidation without any infiltration but with a fast drop in thermal conductivity of the  $\text{Si}_3\text{N}_4$  bonded SiC material.

The second step involves continuous infiltration, wear and a slight decrease of thermal conductivity. Thus at ultimate failure, the average thermal conductivity had dropped by approximately 38%.

When combined with joint openings and air gaps, the drop of thermal conductivity leads to a higher hot face temperature and to a less stable frozen ledge. Thus, the sidewall material is more often directly exposed to molten and gaseous bath components. These gaseous components and even the molten bath may penetrate to directly attack the steel shell. The subsequent metal exfoliation creates an insulating layer that dramatically increases the risk of a tap-out of the pots.

### Inert anodes

Nitride-bonded silicon carbide sideling was also tested with oxygen evolving anodes [7]. The test result shows clearly that a significantly higher degree of corrosion occurs under  $\text{O}_2$  atmosphere than under  $\text{CO}_2$  atmosphere. The Gibbs energy of reaction is higher in the case of  $\text{O}_2$  because of its higher oxidizing potential. According to Wang et al. [20] the oxidation resistance shows little difference at 850°C and 750°C, but is much worse at 950°C. According to the testing of dynamic corrosion by the bath at 950°C, the corrosion of silicon carbide bricks speeds up obviously.

### Chemical/oxidation test cells

A laboratory test cell for measuring the chemical/oxidation resistance for SiC-based materials was developed by Skybakmoen et al. [7] Their test cell exposed the materials to all corrosive environments: liquid aluminium, cryolite melt, its vapours (mainly  $\text{NaAlF}_4$ ) and  $\text{CO}_2/\text{CO}$  from the anode. The tested materials normally undergo corrosion in the gas phase (zone above bath) much like that observed in industrial cells. Strongly corroded samples even showed visible corrosion in the upper bath level zone. In some cases the test samples were completely corroded in the gas zone.

However, a more realistic test to study the chemical attack on  $\text{Si}_3\text{N}_4$ -bonded SiC sidewall bricks in an electrolysis cell system should involve Na-metal together with oxygen, moisture, and NaF in a temperature range between 300 and 1000°C [19]. The  $\text{Si}_3\text{N}_4$ -bonded SiC brick is not resistant to the combination of moisture, Na-metal, HF and oxidation. The combination of these agents is one of the most aggressive environments for oxides, especially for  $\text{SiO}_2$ .

### Solutions for electrolysis pots

Nitride-bonded SiC is now used in cell construction in more than 30 plants worldwide and in thousands of electrolysis cells ranging in amperage from 30 – 350 kA [8, 21]. The major reasons for the extensive use of SiC are to

- prevent air burn
- increase productivity
- extend pot life.

The excellent corrosion resistance of nitride bonded SiC, combined with its extremely high strength and reasonably high thermal conductivity allow an increase in amperage and anode size while in most cases also extending cell life. The ability to use thinner shapes and to provide extra protection in the event of loss of frozen ledge favours SiC in this application.

To maximise benefits from nitride-bonded SiC refractories in aluminium cell construction, it is necessary to examine the economics and heat balance [22]. Heat balance is important not only for the best operation of the cell but also to maximise the life of nitride-bonded SiC sidewalls as well.

Clearly, care must be taken in designing sidewalls in order to maximise the benefits of nitride-bonded SiC refractories.

Using nitride-bonded SiC slabs in electrolysis pots [23 - 25], Refrax® Arc was developed by [16, 26]. This silicon nitride-bonded silicon carbide offers improved oxidation and cryolite resistance. Improved cryolite resistance may have a real influence on the functional characteristics of the sidewall, i.e. the thermal conductivity at any time and the corrosion resistance when the frozen ledge disappears.

These authors developed another improved silicon nitride-bonded silicon carbide material, Sicfrax [9], which offers regular performance in the target range of index: oxidation gain below 2% and corrosion index below 35% according to the cryolite test on pre-oxidised samples of blocks up to 100 mm thick.

Curtis et al. [27] proposed the use of a composite carbon-silicon carbide sidewall block cathode. The composite block provides the opportunity to extend the potlife of cells operating with conventional carbon sidewalls, or it can offer excellent cost saving while maintaining the desired operational results in cells using full size silicon carbide bricks. The composite block consists of a calcined anthracite carbon block, of nitride-bonded silicon carbide and of a glue or carbonaceous cement. The advantage of the silicon carbide layer is to provide excellent resistance to erosion and oxidation of the sidewall lining, while the carbon provides the added flexibility in design and specification in case the blocks need machining.

Combined side wall protector blocks were proposed by Zienkiewicz [28] to replace the ramming paste of the big joints in aluminium reduction cells. He perfected a new manufacturing technique to form the new combined sidewall protector blocks using a proprietary technique to bond silicon carbide material to a preformed carbon block containing variable graphite additions. The combined sidewall protector block can be manufactured in block sizes of up to 800 mm x 500 mm maximum, this limit corresponding to the allowable weight for manual handling and installation.

### Conclusions

Without protection a sideling made of silicon nitride bonded silicon carbide is – under severe test conditions – chemically not stable and will corrode, the binder matrix being the weak component.

When considering revamping aluminium electrolysis cells using nitride-bonded SiC it is important to profit from their excellent corrosion resistance, extremely high strength, and reasonably high thermal conductivity to increase amperage and anode size while also extending cell life.

Using silicon nitride-bonded silicon carbide as sideling material when using inert anodes is problematic, as the sideling will be corroded, because the Gibbs energy of reaction and the oxidizing potential are higher in the case of oxygen.

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