Laboratory Evaluations of Ceramic Sidelining Materials

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Abstract

Silicon-nitride bonded SiC sidelining materials are today the state of the art in modern prebake aluminium cells. SINTEF started in early1990's procedures for performing relevant test methods and quality evaluations of the different commercial materials available on the market. The test methods developed include both chemical and physical properties. Since then a high number of materials have been evaluated and tested on regular basis. New tests and analysis have been included in the test program to investigate and to understand the degradation mechanism in more detail. Lately we have trials with using computed tomography (CT) as a tool to investigate microstructures, pores and cracks inside the materials. A special test method for chemical resistance is developed and used to measure the degradation in the same chemical conditions as in industrial cells. In this special test cell some materials have also been tested in oxygen atmosphere to investigate the degradation of ceramic materials, for instance with using inert anode technology. In the paper overall test results will be shown and examples on good and bad quality materials will be given.

Keywords: Aluminium electrolysis cells, sidelining materials, tests, analysis, degradation.

1. Background

When the aluminium industry started to increase the amperage to produce more metal and hence increase the productivity, new cell designs were needed. One important part of the new cell designs was reduced sidelining thickness to be able to use anodes with larger dimensions. Therefore, the traditional carbon-based sidelining materials were replaced by ceramic sidelining materials based on SiC. It was found that the best lining with acceptable cost was silicon nitride bonded SiC.

SINTEF started in the middle of the 1990's together with the Norwegian aluminium industry to investigate the performance of SiC, and also to establish tests and analyses in laboratory scale to be able to rank the different materials on the market. The test program is divided into physical and chemical properties. The main challenge was to develop a chemical resistance test with chemical conditions as close as possible to those prevailing in industrial cells. The test set-up was established in 1997. From that year on, we have performed several tests of different commercial materials and in this paper, we will summarize the main findings. The method was published for the first time in 1999 [1] and results from our work have been published regularly [2 - 6].

We do know from industrial autopsies that degradation occurs during the lifetime of the cells. The degradation mechanism and some properties of used sidelining materials are reported earlier [7 - 9]. In some cases, severe degradation has been observed at the level above the bath, as shown in Figure 1 and Figure 2, also after short time of operation. The reason is bad quality sidelining materials as explained later in the paper.

Figure 1. Example on severe degradation due to bad quality sidelining material. Plant A.

Figure 2. Example of severe degradation due to bad quality sidelining material. Plant B.

2. Production Routes of Nitride Bonded SiC

A typical production route for nitride bonded silicon carbide is shown in Figure 3. The raw materials are silicon carbide grains and elementary silicon mixed together with an organic binder, which is pressed to a green block with desired dimensions. The green blocks are going through a drying step before entering the nitridation step in furnaces purged with nitrogen gas to establish the binder phase (silicon nitride). The finished product then consists of SiC (typically 72 - 80 wt%) bonded by a phase of Si_3N_4 (20 - 28 wt%). The dimensions of the blocks vary according to the type of cell and cell design. Normally, the thickness is from 60 to 100 mm.

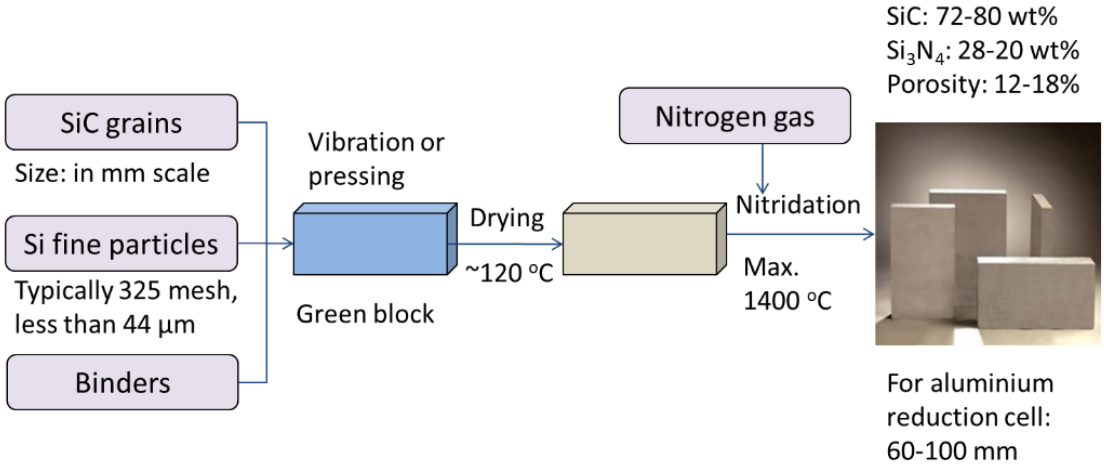

Figure 3. Schematic production route of nitride bonded SiC.

3. Testing of Sidelining Materials

3.1. Sampling Procedures and Relevant Test Methods

The most relevant parameters to be tested and analysed are shown in Table 1.

Table 1. Relevant test methods.

Test Parameter	Standard method	# samples from the block and position
Physical properties:		
Open porosity (%)	ISO 5017	4 (2 outer and 2 inner)
Density (g/cm^3)	ISO 5017	4 (2 outer and 2 inner)
Thermal expansion to 1200 °C (%)	DIN 51045	1
Thermal conductivity to 1000 °C (W/mk)	Laser Flash, NETZSCH LFA 457	2 (outer and inner)
Mechanical properties:		
Cold crushing strength (MPa)	ISO 10059-1	2 (outer and inner)
Bending strength (MPa)	ISO 5014	2 (outer and inner)
Mineralogical / chemistry:		
Total SiC, α-Si_3N_4, β-Si_3N_4, Si_2ON_2, Si (wt%)	XRD Rietveld	2 (outer and inner)
Total oxygen and total nitrogen (wt%)	LECO	2 (outer and inner)
Microstructure:		
Pore size distribution, pore surface area(m^2/g)	Mercury porosimetry	2 (outer and inner)
Structure	SEM and light microscopy	2 (outer and inner)
Special test methods:		
Chemical resistance, polarised 50 h	SINTEF	4 (2 outer and 2 inner)
Oxidation in air at 950 °C for 100 h	SINTEF	2 (outer and inner)

It was observed early in the research that the materials are not homogenous. For this reason, it is of great importance to define and keep track of the sampling position within the block. Normally, all tests and analyses were performed within a 10 mm thick slice cut from the middle of a block, shown in Figure 4 (left frame). A selected number of test methods and their sampling positions are indicted in the right-hand part of the same figure.

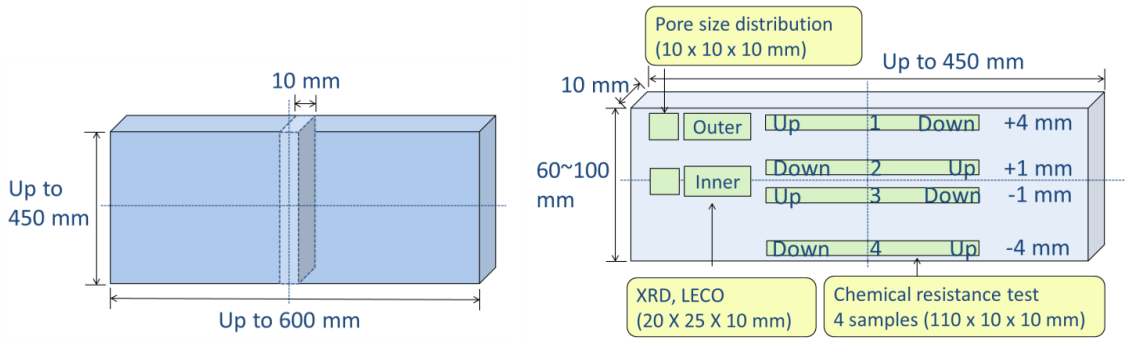

Figure 4. Sampling positions and corresponding test methods (not in scale). The drawing on the right side represents enlargement of the slice shown in the drawing to the left. "Down" denote the sample positions in the chemical resistance test cell.

3.2. Chemical Resistance Test Method

Several methods for measuring and testing of the chemical resistance of the material in question exist, as published earlier [10 - 13]. However, there are no standardized methods. SINTEF started to evaluate several possibilities in the middle of the 1990s, and after 2 - 3 years of development work we ended up with a 50 h polarised test method. The main aim of the test set-up was to simulate the chemical conditions found in industrial environments, to be able to make a quality ranking of commercial materials. The test method is suitable as a basis for improving materials quality, and also to gain better understanding of the degradation mechanism taking place in industrial cells.

The test cell set-up is shown in Figure 5. The initial composition of the bath at the start of the electrolysis is 10 wt% AlF_3 in excess, 5 wt% CaF_2, 7 wt% Al_2O_3, and balance Na_3AlF_6. The temperature is 955 ± 2 °C. The test time is 50 h. After 25 h the anode is changed, and 25 g cryolite and 5 g alumina are added. The anode consumption was measured by weight.

After the test, the crucible with the test pieces is cooled. The graphite lid is removed, and the rest of the test cell is heated up again in an open furnace to enable removal of the test pieces as soon as the bath has melted. Adhering bath is removed mechanically and by washing in an aqueous solution of $AlCl_3$.

The degree of degradation is assessed by the volume loss of the pieces during the test. The volume of the test materials is measured before and after the test, using the ISO 5017 standard.

The estimated volume loss of each piece is then expressed by a scale from 0 to 10 describing the degree of degradation, where 0 is best and 10 is worst.

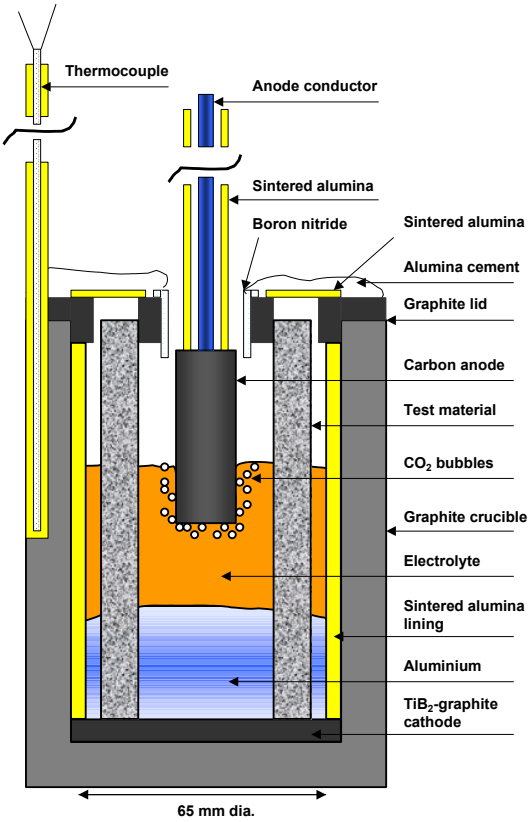

Figure 5. Chemical resistance test cell set-up.

Normally, four samples from different positions in the same block are tested simultaneously. This gives an average level of degradation of the block. However, we can also test samples from different blocks at the same time.

The materials tested normally undergo degradation in the gas phase zone (above the bath), much like observations made in industrial cells. In some cases, the test samples are completely degraded in the gas phase zone. Strongly degraded samples may even show visible degradation in the upper bath level zone. Figure 6 shows a picture of samples after the test. In this case, "good" and "poor" quality samples were tested in two separate experiments.

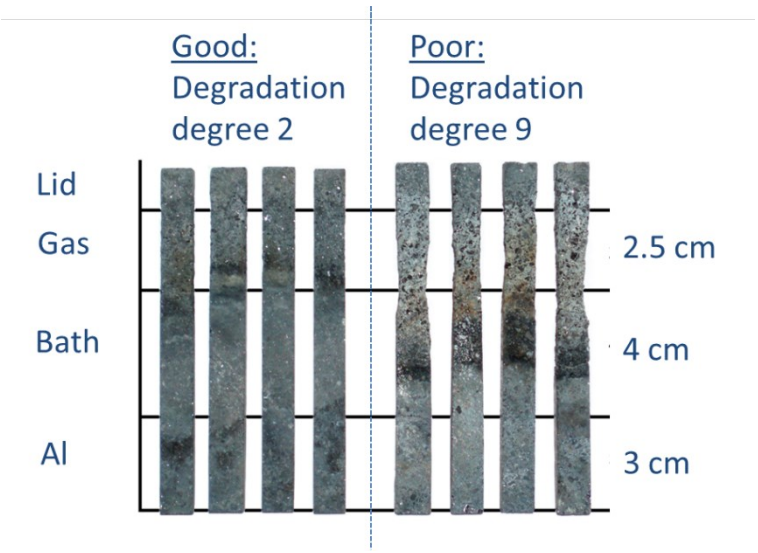

Figure 6. Typical samples after the test. Good (degradation 2) and bad (degradation 9) quality materials.

3.3. Some Statistics from the Chemical Resistance Test

Since 1997, more than 570 samples delivered by about 20 suppliers or electrolysis plants have been tested. The number of samples tested per year is shown in Figure 7.

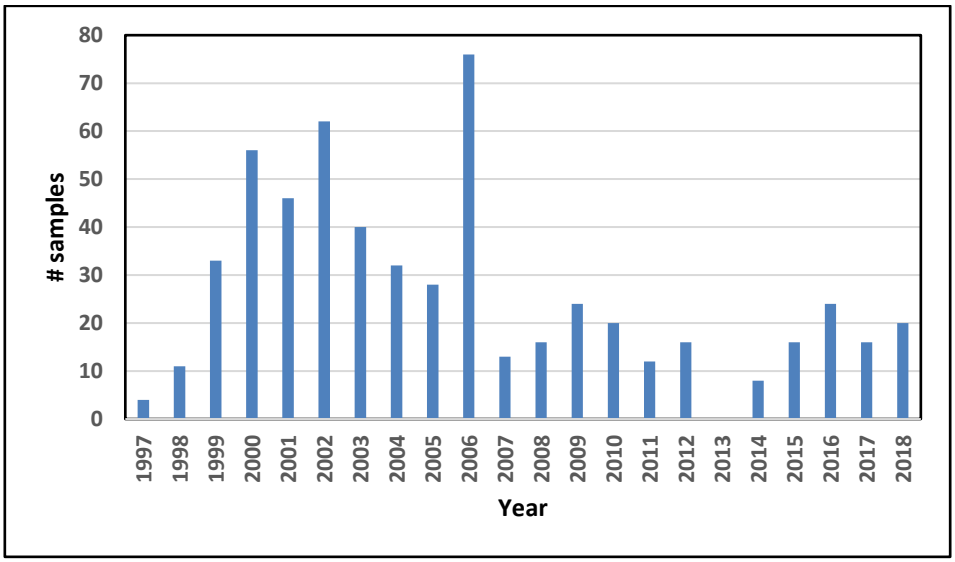

Figure 7. Tested samples in the chemical resistance test cell per year.

As stated above, the materials are not homogenous. As an example, the porosity variations is shown for all samples tested in Figure 8. There are large variations within the positions in the blocks as well as between different types of materials. However, there is no specific time-dependent trend. The average porosity is 15.53±1.67 % varying from 11.24 to 20.45 %. The average value of density is 2.68 ± 0.05 g/cm^3 varying from 2.51 to 2.86 g/cm^3, see Figure 9.

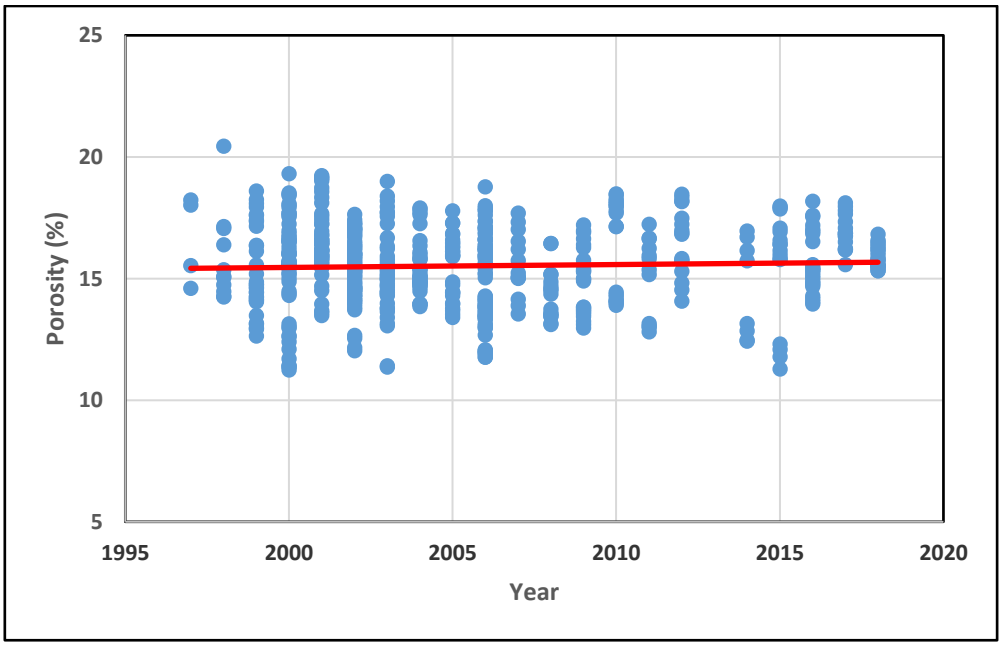

Figure 8. Porosity variations in tested samples as function of time.

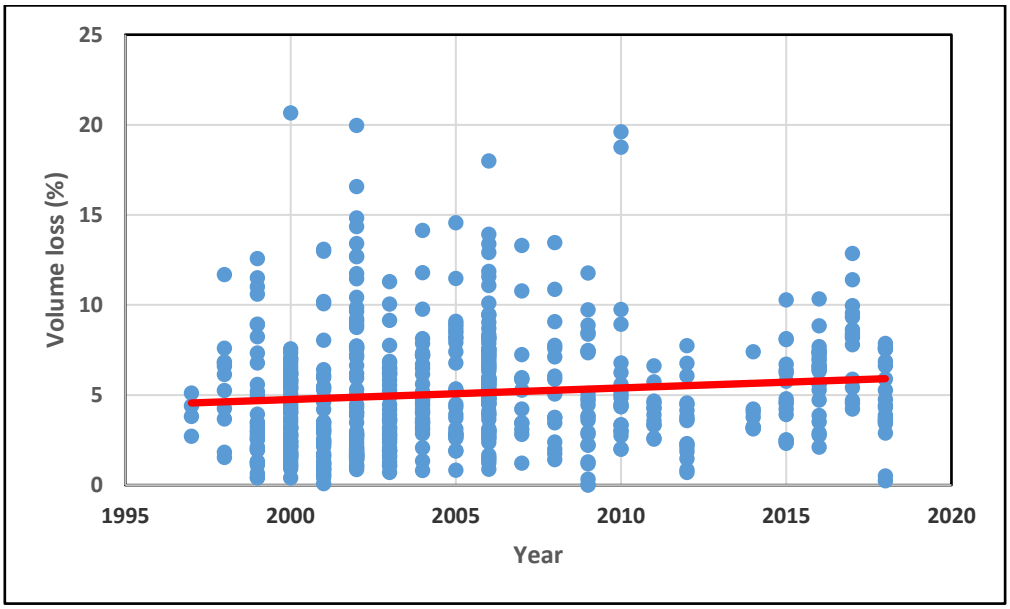

Figure 9. Volume loss in percent of the original weight of all tested samples as function of time.

As seen in Figure 9, the volume loss measured is slightly increasing with time, indicating that the product quality with respect to chemical resistance has not been improved.

The average value of degree of degradation is shown in Figure 10. Per day, the average volume loss is 5.12±3.31 % (573 samples). This corresponds to degree of degradation 6 on the scale from 0-10 where 0 is best quality materials with respect to chemical resistance. Whether the degradation degree is 3 or 7 is probably not so important in practice; it is most important to avoid the inferior qualities with a degree of degradation above 8.

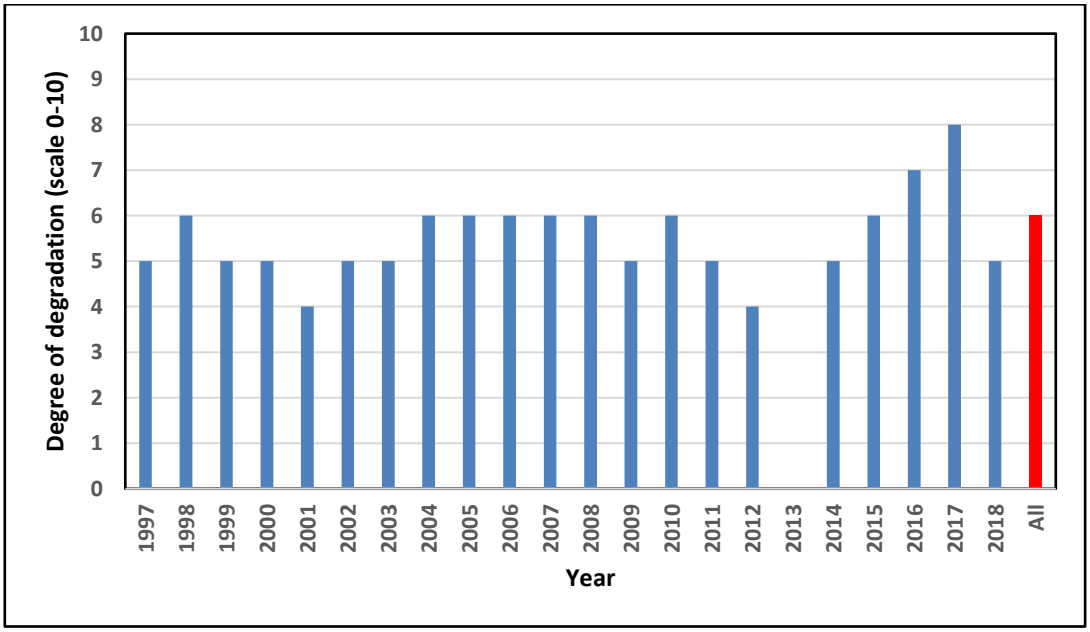

Figure 10. Average degree of degradation per year.

3.4. Samples with Low Degree of Nitridation

The most critical step in the production of nitride bonded SiC is the nitridation, where Si metal react with nitrogen gas to silicon nitride. Attaining complete reaction requires control on the supply of nitrogen gas, temperature, and holding time.

In some cases, we observe high levels of free Si inside the blocks. However, it is not easy to observe this with non-destructive methods, since the outer surface often is well nitrated. A low degree of nitration is also difficult to discover visually on a cut surface. To be able to check this, it is necessary to perform porosity/density, LECO and XRD analysis from the outer and inner parts of the block. A slice from a block is shown in Figure 11. It looks visually normal. The porosity and density from the outer and inner parts are shown in Table 2. The LECO and XRD results are shown in Table 3 for the same samples.

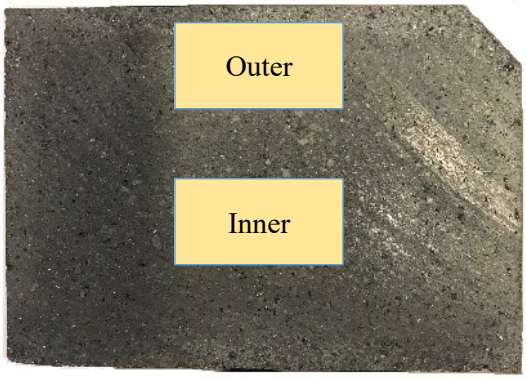

Figure 11. Slice cut from a block with samples positions (samples size 25 x 20 x 10 mm).

Table 2. Porosity and density.

Sample	Density (g/cm^3)	Open porosity (%)
Outer	2.75 ± 0.01	12.90 ± 0.09
Inner	2.60 ± 0.01	15.82 ± 0.11

Table 3. LECO and XRD analyses.

Sample	LECO (wt%)		XRD Rietveld (wt%)						
	O	N	SiC	α-Si_3N_4	β-Si_3N_4	α/β	Si_2ON_2	Si	Sum Si_3N_4
Outer	0.96 ± 0.01	8.11 ± 0.09	80.88	12.41	3.99	3.11	2.11	0.60	16.40
Inner	0.80 ± 0.02	2.45 ± 0.34	85.83	2.19	0.42	5.17	1.65	9.91	2.62

In spite of nearly normal values of porosity and density, the analysis showed in the central part a high value of free Si (9.9 %) in the central part and a low value of total nitrogen (2.45 %). This means low degree of nitridation, and hence, poor quality. This could not have been detected without cutting and analyzing the block.

Computed tomography (CT) was used to investigate a slice with 10 mm thickness to be able to detect the microstructure. A picture of the slice is shown in Figure 12. It is observed a different microstructure in the central part of the block indicating low grade of nitridation. It is denser at the surfaces than in the middle.

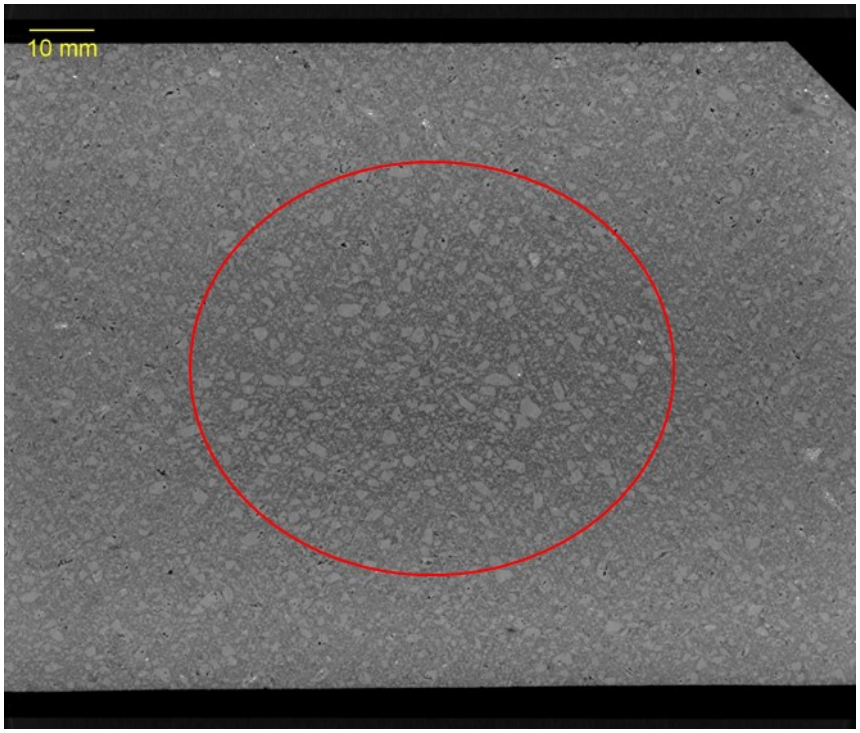

Figure 12. CT scan of slice with low grade nitridation in the middle part of the block (within red circle).

3.5. Tests of Dense SiC

In order to evaluate alternative ceramic sidelining materials, pure and dense SiC was tested. The samples tested had low porosity (< 0.1 %) and high density (3.15 g/cm^3). Pictures of the samples after the test is shown in Figure 13. As seen the degradation is almost not visible and the degree of degradation was nearby between 0 - 1.

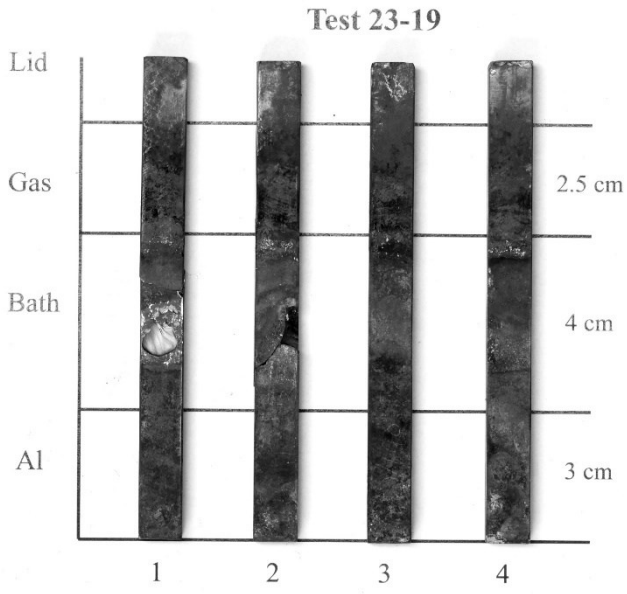

Figure 13. Dense SiC after the 50-h test.

3.6. Samples Tested with Oxygen Atmosphere

In the test cell the carbon anode can be replaced with an inert anode. It will then be produced oxygen instead of carbon dioxide. We tested some ceramic materials under these conditions to make a limited screening of possible lining materials for use with inert anode technology. A Pt anode with same cylindrical dimensions as the graphite anode was used. The test was performed under the same test conditions as for the graphite anode. Two commercial Si_3N_4-SiC materials, here named E and F, were taken out from the same block close to each other and tested under both CO_2 and O_2 atmospheres. Pictures showing the samples after the tests are placed in Figure 14.

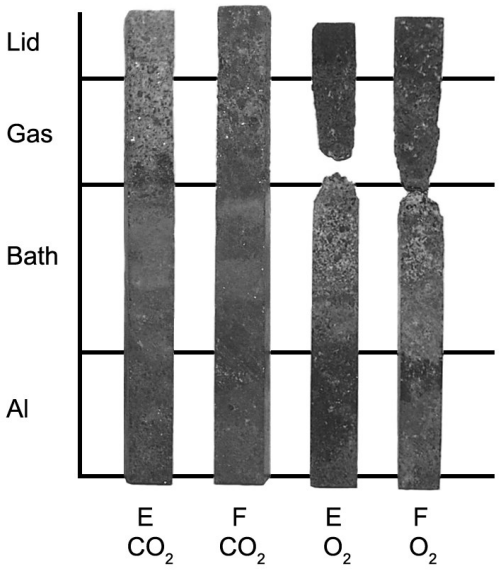

Figure 14. Test samples after test under CO_2 and O_2 atmospheres. Commercial materials named E and F.

We see clearly that the oxidation and degradation is considerable higher in oxygen atmosphere (degree 10) than in CO_2 atmosphere (degree 1 - 2). The binder is more oxidized. The results indicate that the materials are not suited for use with inert anodes.

4. Conclusions

The overall results can be summarized as follows:

- Nitride bonded SiC materials are not homogenous. Sample positions need to be defined before analysis and tests.
- The average degree of degradation is 6 on a scale from 0 to 10, where 0 is the best quality.
- The material quality has not been improved since the late 1990's.
- Poor nitridation in the middle of the block may cause severe degradation in industrial cells after short time of operation. High levels of free Si need to be detected by LECO and XRD analysis, since it cannot be observed by visual inspection.
- Computed tomography (CT) may become a new tool to detect cracks and porosity variations as well as the size of the SiC grains.
- Nitride bonded SiC degrade more in oxygen atmosphere than in CO_2 atmosphere.
- Pure dense SiC shows excellent behavior and no degradation.

The binder phase is the weak part of the material and the microstructure and phase composition is of great importance.

Degradation will occur mainly in periods with unstable sideledge. Hence, the best protection will be stable operation conditions and a stable sideledge that protect the materials.

5. References

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