N-SiC SIDE LINING - VARIATIONS OF MATERIALS STRUCTURE

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Abstract

The key process in fabrication of Nitride bonded silicon carbide side lining of reduction pots is the reaction between Nitrogen and Silicon. Silicon may react with Nitrogen in solid, liquid and gaseous phase. The reaction is strongly exothermal.

Almost all N-SiC refractory materials of more or less big shapes have the gradients of porosity from middle to the edges. The reason for these gradients may be the overheating of the middle part of shapes, compared to near surface layers, due to the exothermal effect and consequent increased concentration of volatile Silicon. Volatile Silicon tends to move to areas of lower temperature and the gradients of porosity are 1-2 %, but sometimes it may reach 5-7%.

The problems with side lining of reduction pots may be because of the design of the pots, due to the overheating of the bath, yet the structure of N-SiC materials might be also critical.

Introduction

Silicon carbide side lining of Al reduction cell has been known for more than 30 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 is a problem of the future. When inert anodes are implemented, profound research on new side lining materials will be required, and a new material will replace Nitride bonded Silicon Carbide.

Currently there is an accepted SINTEF test for the corrosion resistance of N-SiC [6,7], as well as variations of the test [8,9,10]. Usually the decision on the possibility to use the material in a lining of the cell is based on the corrosion test results.

Elements of N-SiC technology

The shaped blocks from green mixture of silicon carbide and silicon (Fig. 1a) are fired in the atmosphere of Nitrogen at temperatures up to 1440-1450°C. During the firing, silicon reacts with Nitrogen, and the resulting Silicon Nitride fills the space between silicon carbide grains (Fig.1b). The technology of N-SiC is rather complex and depends upon several factors.

The process of the formation of nitride bonded silicon carbide is called "reaction sintering". During reaction sintering the porosity decreases and the strength increases. The conventional sintering of silicon carbide requires 2100-2300°C. Reaction sintering allows a reduction in the temperature to 1400-1450°C. Reaction volume effects are responsible for the diminishing of porosity during the heat treatment of the green shape.

In many aspects the technology of N-SiC comes from the technology of reaction sintered silicon nitride. For this technology it is critical to divide the processes into "solid silicon – gas" reaction, "liquid silicon – gas" reaction and the "volatile silicon
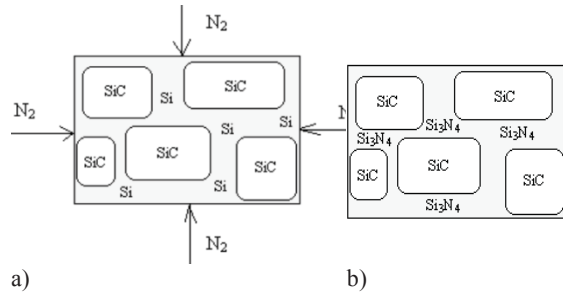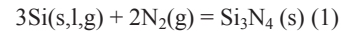

Figure 1. Schematic illustration of N-SiC processing: a) before and in the process of the firing, b) after the firing.

– gas" reaction with following condensation.

$$3Si(s,l,g) + 2N_2(g) = Si_3N_4 (s) \quad (1)$$

The reaction (1) proceeds with a positive volume effect [11]. This means, that 1 mole of silicon nitride occupies the volume 20% larger than the 3 initial moles of silicon. This takes place during the reactions of nitrogen with solid (liquid) silicon and with gaseous silicon. As a result, the porosity of the material decreases. The reaction (1) of nitridation of silicon is strongly exothermic [11,12].

$$\Delta Q (1400^{o}C) = 720 \text{ kJ/mol} \quad (2)$$

In case, that Silicon in the green shape will melt due to the heat of reaction, the reaction will proceed only on the surface of Silicon, and the nitridation process will not proceed. Usually the process of nitridation of Silicon is performed at temperatures below the melting point of Silicon, but the final stages are performed above the melting point of Silicon (the melting point of Silicon is 1410°C). According Honig [13] the partial pressure of Silicon vapors above Silicon at temperature 1337°C (below the melting point of Silicon) is 10-4 torr (0,013 Pa), while at 1472°C (above the melting point of Silicon) it is 10-3 torr (0,13 Pa).

Part of the Silicon Nitride is formed during the reaction of Nitrogen with solid or liquid Silicon (and also due to the diffusion of Nitrogen through Silicon Nitride film), but also some of Silicon Nitride is formed due to the reaction of Nitrogen with Silicon vapors.

Experimental

Standard industrial N-SiC side lining refractories 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), the determination of Nitrogen and Oxygen was performed by the LECO method. Silicon Oxynitride Si_2ON_2, α- and β- modifications of Silicon Nitride were determined by XRD. The concentrations obtained by different methods, were similar (within the determination level range).

Results and discussion

The structure of N-SiC refractories is very inhomogeneous - silicon carbide grains are bonded by silicon nitride. Silicon nitride usually is present in both α and β modifications. Silicon carbide is present in α modification; usually producers use 3 grain size fractions, the most coarse fraction being 2-3 mm (Fig.2 a).
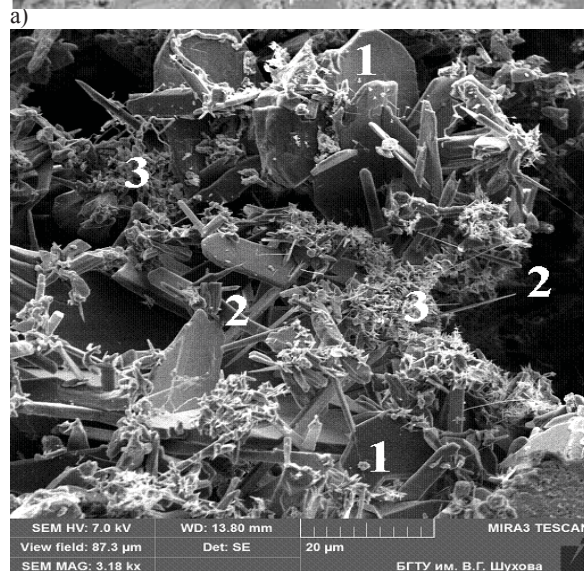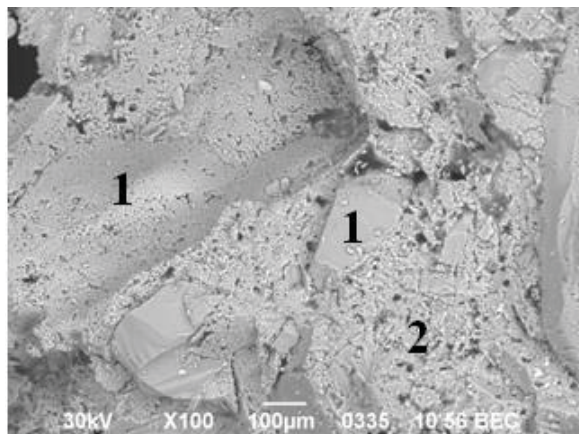

a)

b)

Figure 2. 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

Although in the literature it is mentioned [14,15], 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 have

dimensions up to 2-3 mm, while the dimensions of Silicon Nitride particles are about 10 μm and below. There are also suggestions, that the β-modification of Silicon Nitride is more corrosion resistant to cryolite melt compared with α-modification. Evidence for this suggestion is also difficult to find. 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. The shape of α Si_3N_4 particles is elongated, and include needle-like crystals with l/d>10-20 (Fig. 2 b). They are formed due to the reaction of Silicon vapors with Nitrogen and the following condensation. The specific reaction surface of needle like- and elongated crystals is sufficiently higher, so β-Si_3N_4 might be more corrosion resistant because the surface of reaction of these particles is smaller.

In different N-SiC materials there is different ratio of α/β Si_3N_4 (Table I and II). In some materials the predominant phase is α modification, and in the others – β-modification. Usually there are no materials with 100% of α- or β-modification.

The producers of N-SiC materials and the producers of Aluminium know that in the standard package of tests of N-SiC in the SINTEF institute there is a determination of the porosity at 1 cm from the surface of the block (periphery) and at 2.5 cm from the surface of the block (middle) [6,7]. Usually there is a difference of porosity near the surface of N-SiC blocks and in the middle of the sample.

The difference in porosity between the surface and in the middle may be 0,5-1%, but the difference can be 10-13% near the surface and up to 16-18% in the middle (Fig.3). Usually the porosity in the middle is higher, but there are occasional exceptions.
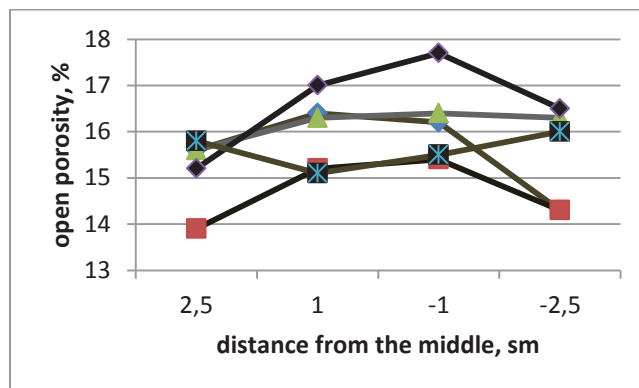

Figure 3. Porosity gradients in N-SiC refractories

Usually there is a gradient of Silicon Nitride concentrations near the surface and in the middle. The difference may be from 0,5 % to 5-7%.

In the technology of reaction sintering of Silicon Nitride and in technology of N-SiC it is known that if the amount of silicon is high, there might be uncontrolled overheating, and the temperature of the samples and the products might be higher than the temperature in the furnace [16,17]. According to [17] the difference in the temperature in the middle of the Si disk with radius 5 cm and near the edge may be up to 50-60°C due to the exothermic effect (while the temperature in the furnace was 1350-1370°C). In industrial technology of N-SiC such factors as the rate of heating, the width of the blocks, the grain size composition and the porosity might be essential for the reaction (1) in a gaseous phase.

The gradients of porosity in N-SiC materials do not originate from the processing of the green shapes and are explained by two reasons:
1. The evaporation of some of the Silicon from the zone with the maximum temperature and the diffusion of Silicon vapor to the zone of lower concentrations, that is to the periphery of the shapes – with following reaction in the gaseous phase. The Silicon Nitride produced is condensing in the pores on the surfaces of existing particles.
2. The reaction (1) goes with a positive volume effect. One mole of reaction product Silicon Nitride occupies a volume 20% larger that the three initial moles of Silicon. This coincides with the reactions of Nitrogen with solid (liquid) Silicon and with gaseous Silicon. As a result, the porosity decreases.

Mol volume of Silicon

V_{Si} = Mol weight/real density = 28/23 = 12,17

Mol volume of Silicon Nitride

V_{Si3N4} = Mol weight/real density = 140/3,19 = 43,89.

Volume effect

$$\Delta V/V = V\ (Si_3N_4)/\ 3\ V\ (Si) = 43,89/\ (3*12,17)= 1,2 \qquad (4)$$

During the reaction sintering of Silicon Nitride and N-SiC material there is no shrinkage, which explains why the volume effect of the reaction can be compared with the reduction of the porosity during sintering. Also there is a fact that the real weight gain at the reaction sintering of N-SiC is from 60 to 80-85% lower, than the theoretical weight gain. This proves the suggestion that Silicon vapor tends to diffuse to the areas with lower concentration of Silicon vapor. The other part of Silicon leaves the material.

The problem is, that the major part of Silicon evaporates in the middle (to some extent it is a proof, that the temperature in the middle is higher), while Silicon Nitride condenses at periphery, that results in a porosity gradient.

There are two approaches to the fabrication of N-SiC refractories for the side lining. The technology of refractories gives the possibility to vary the density of the green shape in a certain range. This range is not big and is about 2-5%. For example, at different pressing regimes, the different grain size compositions of Silicon Carbide and Silicon mixtures gives the possibility to vary the green shape porosity in the range from 15 to 20%. However that might be critical for the process of the Nitridization of the Silicon. During reaction sintering of the N-SiC, the process of the Nitridization of the Silicon is occurring at the same time as the process of sintering and forming of the structure and properties of the material.

In Table I there are the properties and the composition of N-SiC material, having the porosity of the green shape 17-19%.

In the Table II there are the properties and the composition of N-SiC material with the porosity of the green shape 13-15%. Though the concentration of free silicon was almost the same, the gradient of concentration of Silicon Nitride was considerably higher than the sample with a higher porosity in the green state.

Table I. Porosity and composition of N-SiC near the surface and in the middle (the porosity of the green shape is 17-19%, the width of the green shape is 70 mm)

	Near surface	middle
SiC,%	76,8	78,8
Si_3N_4,%	24,4	22,7
$\alpha/(\alpha+\beta)$	0,49	0,46
α, %	12,0	10,4
β, %	12,4	12,3
Si free,%	0,2	0,1
SiO_2	-	-
$(Al_2O_3+ Fe_2O_3+ CaO)$,%	1,3	1,28
Fe_2O_3, %	0,94	1,0
Porosity, %	16,6	16,2

Generally, for specific temperature regimes, in the width of the blocks there is a certain "barrier" level of porosity (and pore size). After reaching it, the gradient of porosity in sintered materials may exceed 2-3%, reaching 10% near the surface and 17-18% in the middle, while the gradients of Silicon Nitride and Silicon Carbide concentrations near the surface and in the center may exceed 3-5%. The α/β modifications of Silicon Nitride ratio near the surface and in the middle differ also.

There are two slightly different materials for the side lining: with more or less equal properties in the middle and near the surface and with the gradients of porosity and the concentrations of Silicon Nitride and Silicon Carbide.

Table II Porosity and composition of N-SiC near the surface and in the middle (the porosity of the green shape is 13-15%, the width of the green shape is 70 mm)

	Near surface	middle
SiC, %	71,5	78,5
Si_3N_4, %	26,0	17,9
$\alpha/(\alpha+\beta)$	0,32	0,41
α, %	8,3	7,26
β, %	17,7	19,6
Si free, %	0,26	0,23
SiO_2	-	-
$(Al_2O_3+ Fe_2O_3+ CaO)$,%	1,3	1,28
Fe_2O_3, %	0,94	1,0
Porosity,%	10,8	13,1

According to SINTEF testing there is no averaging of the corrosion resistance results in the middle and near the surface. There is no direct correlation between the corrosion resistance (according to SINTEF method) and the concentration of Silicon Nitride, or concentration of β-modification and porosity [6,7]. However some correlation between the corrosion resistance and the porosity may exist.

Further investigation of these correlations with regard to the corrosion resistance to the cryolite of the middle and the near surface area, and the oxidation resistance of the upper part of the block (that are not exposed to the cryolite melt) are required.

It is not easy to predict what is better for the long service life time of the side lining – homogenous structure of the gradients of

porosity and low porosity of the near surface of the block, that can be exposed to the cryolite.
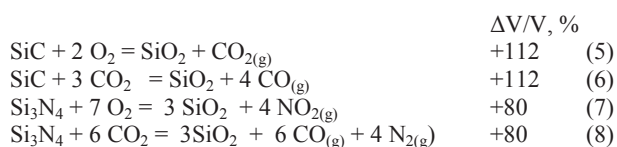
Usually the side lining of the reduction cell is not a critical element of the reduction cell from the point of view of the service life time. The side lining does not usually interact directly with the cryolite and Aluminium because of the frozen side ledge. The exceptions are the start-up period, some process disturbances during operation and the uncertainties in the construction of the reduction cell.

The side ledge might disappear due to the melt overheating that, in its turn, may be the consequence of the problems with the quality of Alumina, with the quality of the anodes, or problems of the reduction technology.

The side ledge might not appear, especially near the studs, in case of high velocity of the melt in the cell due to magneto hydro dynamic instabilities.

In all described cases the quality of the side lining material might become critical.

The upper part of side lining does not contact the melt of cryolite, but it still can be the cause the of failure of the cell. Silicon Carbide and Silicon Nitride are oxidation resistant materials. In normal conditions the temperatures $700\text{-}800^{o}C$ are not critical for the service. In presence of alkali and Fluorine vapors the oxidation reaction is faster. The reactions (5-8) proceed with producing a volume increase:.

	$\Delta V/V$, %	
$SiC + 2\ O_2 = SiO_2 + CO_{2(g)}$	+112	(5)
$SiC + 3\ CO_2 = SiO_2 + 4\ CO_{(g)}$	+112	(6)
$Si_3N_4 + 7\ O_2 = 3\ SiO_2 + 4\ NO_{2(g)}$	+80	(7)
$Si_3N_4 + 6\ CO_2 = 3SiO_2 + 6\ CO_{(g)} + 4\ N_{2(g)}$	+80	(8)

Conclusions

The processing of N-SiC refractory materials differ from the processing of conventional refractories. In N-SiC material the porosity decrease takes place due to the positive volume effect of the reaction of silicon and nitrogen..

Due to the exothermal effect of the reaction, the temperature in the middle of the shapes may be $50\text{-}60^{o}C$ higher than at the surface. The temperature can increase above the melting point of the Silicon leading to gradients of porosity and silicon nitride concentration.

The porosity of the green shape may influence the porosity gradients from the near surface area to the middle of the finished N-SiC material. The same may be said about the gradients of silicon nitride in the material.

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