MICROSTRUCTURAL AND THERMO-MECHANICAL BEHAVIOUR OF SIC REFRACTORIES IN BLAST FURNACE APPLICATION

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ABSTRACT

Silicon Carbide based Refractory materials are commonly used in Blast Furnace of iron making application. They compose part of Lower Stack, lower and upper bosh regions in Blast Furnace. Refractories are subjected to severe thermal gradients, Alkali attack, high oxidation atmospheres, high abrasion and Carbon monoxide attack. These refractories also play important role in converting thermal energy to generate electrical energy as by product as well in formation of protecting layer due to high thermal conductivity.

SiAlON bonded SiC materials are advanced over Nitride bonded SiC (NBSiC). In this paper, advantages of SiAlON bonded SiC over NBSiC are discussed. Microstructures and thermo mechanical properties of NBSiC and SiAlON bonded are investigated in order to understand their behaviour in Blast Furnace application. The resulting microstructure deals with SiC grains bonded with Silicon Nitride and SiAlON phases with a high degree of complexity. Microstructural properties of NBSiC and SiAlON bonded SiC refractory are studied by X-ray diffraction for phase identification and by Scanning Electron Microscope for phase morphology. As these material are used in severe atmospheres of carbon monoxide and alkali, effect of CO-Disintegration and Alkali attack resistance properties also investigated along with long term oxidation. Overall comparison of microstructural and thermo mechanical properties of NBSiC and SiAlON bonded SiC are studied with illustrations of uses in blast furnace application.

Key Words: SiAlON bonded SiC, Nitride bonded SiC, Blast Furnace

INTRODUCTION

Iron making technique is undergoing lot of developments. Intensified smelting measures are followed by many iron makers in the world like High temperature blast and pulverized coal injection, have been adopted in blast furnace (BF). Hence the atmosphere in blast furnace is more severe. Before the application of SiC based refractories, the blast furnace was traditionally lined with dense clay bricks and high alumina bricks which couldn't meet the requirements of new technologies used in Blast Furnace and life span of Blast Furnace was shortened [1]. Prof. Knopicky first used SiC refractory in blast furnace in Belgium. After twenty years, nearly 56% of operated blast furnaces in the world is using SiC brick as lining materials. Different bonds are still investigated in order to increase the quality of the SiC bricks. The development went from oxide to oxynitride bonded bricks and ended in pure nitride bonded and self-bonded SiC bricks. The last two types are currently widely used. The SiAlON bond is the latest and having a 4-phase system [2].

The relationship between that of SiAlON and Si_3N_4 is similar to that between brass and pure copper. In the latter case, copper atoms are replaced by zinc to give a better and stronger alloy than the mother metal. In the case of SiAlON, there is substitution for Si by Al with corresponding atomic replacement of N by O, to satisfy valancy requirements. The resulting 'solution' (SiAlON) has superior properties to the original pure solvent (silicon nitride).

Silicon Nitride

The fundamental structural unit of Si_3N_4 is the Si_3N_4 tetrahedron as shown in Fig.1, which is analogous to the SiO4 structural units in silicates. The tetrahedra are linked together into a rigid three dimensional framework by sharing corners. The Si-N bonds are short and they are very strong. This strong, rigid, compact structure is responsible for many of the important properties of Si_3N_4.

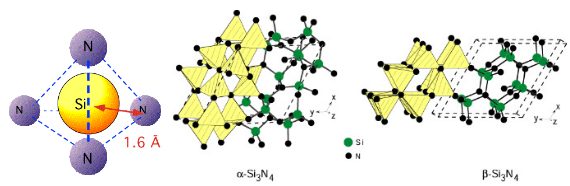

Fig.1: Structural unit of Si_3N_4

Processing of Nitride bonded SiC

The main raw materials used are silicon carbide grains and silicon metal powder. The characteristics of these two materials are listed in Table. 1 and the process steps of fabricating Si_3N_4 – SiC are shown in flow diagram Fig.2.

Tab.1: The characteristics of the raw material

Material	Composition (Wt %)				
	SiC	Si	SiO_2	Al_2O_3	Fe_2O_3
SiC	96.0 – 98.0	1.5		0.25	0.50
Si		98.0 – 99.0		0.24	0.85

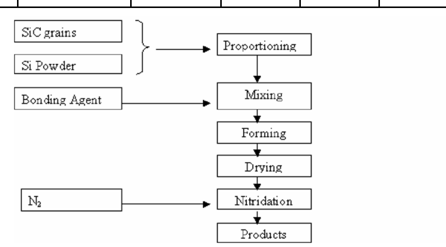

Fig. 2: Flow Diagram of Si_3N_4 – SiC brick making process

SiAlON

β-SiAlON is based upon the atomic arrangement existing in β-Si_3N_4. In this material, Si is substituted by Al with corresponding replacement of N by O. In this way up to two-thirds of the silicon in β- Si_3N_4 replaced by Al without causing a change in structure. The chemical replacement is one of changing Si-N bonds for Al-O bonds. The bond lengths are about the same for the two cases but the Al-O bond strength is significantly higher than that of Si-N. In SiAlON the Al is co-ordinated as AlO4 and not as AlO6 as in alumina (Al2O3). Therefore, in β-SiAlON the Al-O bond strength is 50% stronger than in Al2O3. Thus SiAlON's intrinsically have better properties than both Si_3N_4 and Al2O3.

As a solid solution, the vapour pressure of β-SiAlON is lower than that of Si_3N_4. As a result the SiAlON will form more liquid at a lower temperature. β-SiAlON is thus more easily densified than Si_3N_4 using normal sintering techniques. The lower vapour pressure of SiAlON reduces decomposition at high temperatures so that the SiAlON is thermodynamically more stable than Si_3N_4. The α-SiAlON grains tend to have a small, equiaxed morphology which results in materials which have a lower strength and toughness than β-SiAlON. However, α-SiAlON has a higher hardness than β-SiAlON

SiAlON -bonded SiC refractories have better abrasion, alkali attack resistance and thermal shock resistance than high-alumina or corundum bricks. SiAlON -bonded SiC refractories also having better oxidation resistance and higher strength than carbon products. Thus they are widely applied especially as blast furnace (BF) refractories (a critical and dominating factor in the quality of iron smelting and also the life span of blast furnace). As the matrix in SiAlON –bonded SiC, SiAlON has mostly been prepared using Si, Al, Al_2O_3 and/or Si_3N_4 powders as raw materials using an in situ process of nitradation reaction sintering. In 1979, Lee et at., prepared SiAlON using natural kaolin by carbothermal reduction – nitradation (CRN) reaction. Since then, this method has offered a new technical path to prepare SiAlON based materials economically by carbothermal conversion from natural products and waste material containing Si and/or Al elements.

SiAlON is a continuous solid solution consisting of Si, Al, O and N, as an end member of silicon nitride Si_3N_4 (Z=0), and its chemical formula is written as $Si_{6-z}Al_zO_zN_{8-z}$ (0 < Z < 4.2), as shown in Fig.3.

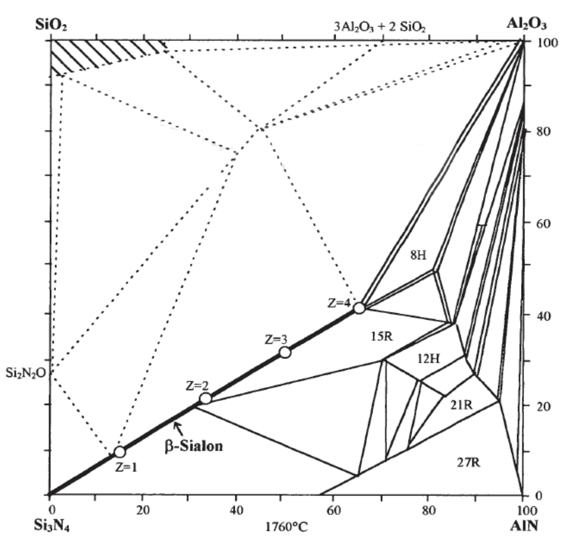

Fig. 3: Phase Diagram of the Si_3N_4 – AlN – Al_2O_3 – SiO_2 system

Processing of SiAlON bonded SiC

The main raw materials used are silicon carbide, silicon metal powder and Alumina. The characteristics of these two materials are listed in Table.2 and the process steps of fabricating SiAlON bonded SiC are shown in flow diagram, Fig. 4.

Tab.2: Characteristics of the raw material

Material	Composition (Wt %)				
	SiC	Si	SiO_2	Al_2O_3	Fe_2O_3
SiC	96.0 –	1.5		0.25	0.50
Si		98.0 – 99.0		0.24	0.85
Al_2O_3				>99.0	

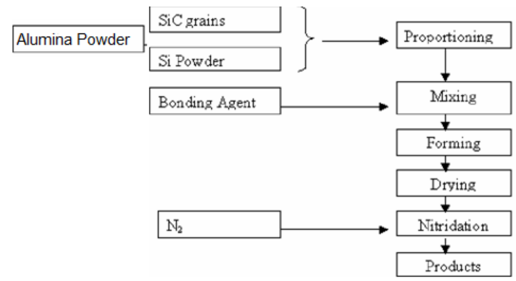

Fig. 4: Flow Diagram of SiAlON – SiC brick making process

SiAlON solid solution may be formed in the matrix of the SiC bricks by the reaction between Si_3N_4 and Al_2O_3 during sintering at elevated temperature.

Si3N4 + Al_2O_3 → β – SiAlON (1)

The strength of the brick increases as bonding force increases between SiC particle by the formation of SiAlON until Z number reaches 2. In SiAlON bonded SiC products, β - SiAlON grains exist as short platelet in between SiC grains [3].

Temperature, Pressure and atmosphere are the critical parameters having large effects on the microstructure and properties of products, so it is very important to control strictly all parameters for obtaining high quality and stable properties of products.

EXPERIMENTAL PROCEDURE

Materials

Based on metal silicon, SiC grains/fines and alumina fines etc. as starting raw material, sample bricks in the size 230 X 114 X 75 mm including Nitride bonded SiC and SiAlON bonded SiC were produced by reaction sintering in N_2. Nitride bonded SiC and SiAlON bonded SiC Samples are analysed for X-ray diffraction for phase identification, CO-Disintegration and Alkali attack resistance and Pore Size Distribution.

RESULTS AND DISCUSSION

RESULTS

Chemical Analysis:

The sample for chemical analysis was crushed to a fine powder (-100µm) in a tungsten
Carbide mortar. Determination of SiC and C by infrared spectroscopy LECO method (ISO 21068 -1+2. Determination of total nitrogen content by DIN 12698. Determination of metallic Silicon by ISO 21068-2. Test results are shown in Table.3 and Table.4.

Tab.3: Chemical analysis of Nitride bonded SiC

Nitride Bonded SiC		
Al_2O_3	0,28	
SiO_2	0,23	Difference
Fe_2O_3	0,18	
TiO_2	0,03	
CaO	0,31	
MgO	0,06	
K2O	0,01	
Na_2O	0,02	
Mn_3O_4	0,01	
Cr_2O_3	0,01	
P_2O_5	0,01	
ZrO_2	0,01	
C-frei	0,07	infrared spectroscopy
SiC	75,49	infrared spectroscopy
Si-met	0,10	ISO 21068-2
α-Si_3N_4	13,13	XRD, DIN 12698
β-Si_3N_4	10,05	XRD, DIN 12698

Tab. 4: Chemical analysis of SiAlON bonded SiC

SiAlON bonded SiC		
Al_2O_3	2,31	
SiO_2	0,26	Difference
Fe_2O_3	0,06	
TiO_2	0,02	
CaO	0,15	
MgO	0,12	
K2O	0,01	
Na_2O	0,02	
Mn_3O_4	<0,01	
Cr_2O_3	<0,01	
P_2O_5	0,01	
ZrO_2	<0,01	
C-frei	0,08	infrared spectroscopy
SiC	70,31	infrared spectroscopy
Si-met	<0,10	ISO 21068-2
α-Si_3N_4	2,57	XRD, DIN 12698
$Si_3Al_3O_3N_5$	17,19	XRD, DIN 12698
$Si_4Al_2O_2N_6$	6,89	XRD, DIN 12698

XRD Phase Analysis:

Mineral analysis by XRD Phase analysis (Fig.5&6: XRD Micrograph) shows the SiAlON bond phase in SiAlON bonded SiC and Silicon Nitride in Nitride bonded SiC, Ref: Table.5 and Table.6.

Tab.5: Mineral Content of SiAlON bonded SiC

Mineral Content			
Sample	Main components	Accessories	Traces
SiAlON Bonded SiC	**SiC**	**$Si_3Al_3O_3N_5$**	met. Si
		$Si_4Al_2O_2N_6$	

Tab.6: Mineral Content of Nitride bonded SiC

Mineral Content			
Sample	Main components	Accessories	Traces
Nitride Bonded SiC	**SiC**	**α-Si_3N_4**	met. Si
		β-Si_3N_4	

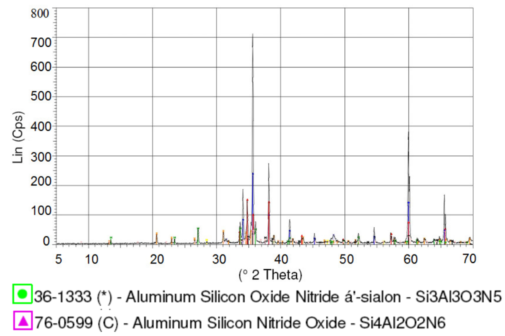

Fig.5: XRD Micrograph of SiAlON bonded SiC

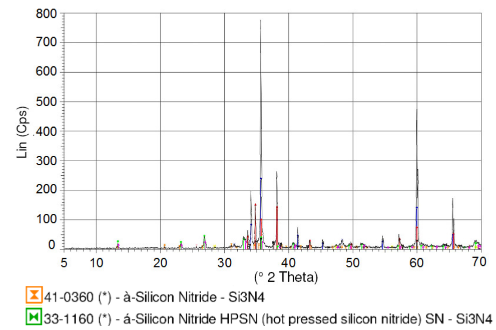

Fig.6: XRD Micrograph of Silicon Nitride bonded SiC

Alkali Test:

Samples of Nitride bonded SiC and SiAlON bonded SiC are buried in technical grade K_2CO_3 and coke breeze. Which was fired at 1000 Deg.C for 3 hours at peak temperature per one cycle. After two cycles of repeated firing samples analysed for Modulus of Rupture (MOR) at room temperature. MOR change shown in Table.7.

Tab.7: Percentage change MOR after alkali test

Sample	MOR Before alkali test (Kg/cm^2)	MOR after alkali test (Kg/cm^2)	Percentage Change (%)
SiAlON bonded SiC	357	353	-1.12
Nitride bonded SiC	323	280	-13.31

Resistance to Carbon Monoxide:

Disintegration of refractories in an atmosphere of carbon monoxide determined with reference to ASTM C 288. Five samples of SiAlON bonded SiC and five samples of Nitride bonded SiC were tested for Carbon monoxide disintegration. CO-disintegration test results of SiAlON bonded SiC and Nitride bonded SiC are shown in Fig. 7 and Fig. 8 respectively.

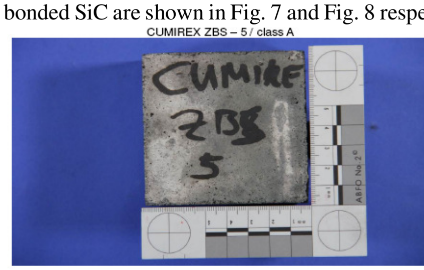

Fig.7: SiAlON bonded SiC Sample after CO disintegration test

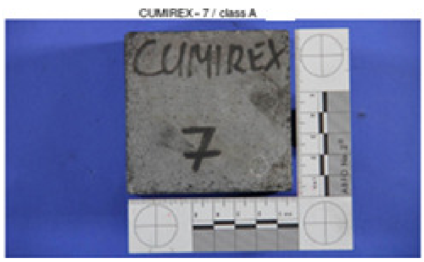

Fig.8: Nitride bonded SiC sample after CO disintegration test

Pore size distribution test:
Mercury intrusion porosimetry test done to evaluate the porosity distribution in SiAlON bonded SiC. Pore size distribution shown in below Fig: 9&10.

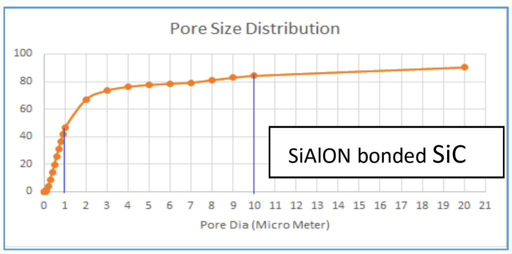

Fig. 9: Pore Size Distribution of SiAlON bonded SiC

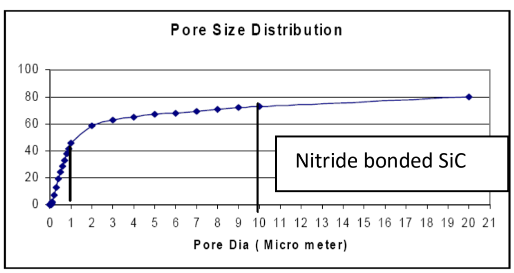

Fig. 10: Pore Size Distribution of Nitride bonded SiC

DISCUSSION

Silicon nitride-bonded silicon carbide refractories invariably contain a small amount of oxygen which is carried on the Surfaces of the reactant powders and is present as silica in the refractory product. The free silica has a detrimental effect on high temperature properties, particularly the alkali resistance of silicon nitride-bonded silicon carbide. This problems is addressed according to SiAlON bond phase, e.g., β' –SiAlON. SiAlON bonding offers the potential for, improved alkali resistance, compared to silicon nitride CO-Disintegration and pore size distribution test results of both nitride bonded SiC and SiAlON bonded SiC shows ideal for application for blast furnace. The critical requirements of different zones of Blast furnace like Tuyere Bowls, Bosh, Mantle or Belly and Lower Stack was mentioned and SiAlON bonded SiC refractory brick properties towards mentioned requirements are discussed below

Tuyere Bowls
SiAlON bonded SiC in addition to resisting hot air and steam oxidation, it resists the tremendous erosion and corrosion, which is caused by molten iron slag attack. Thermal conductivity of the SiAlON bonded SiC brick is sufficiently high to freeze and hold a slag coating in this area.

Bosh
Bosh zone, Slag and molten iron dribbled down as the blast furnace mass descends. Erosion and abrasion of Refractories are very severe. Here Modulus of Rupture (MOR), generally equated by refractory engineers as a good indication of high temperature abrasion resistance. Here the SiAlON bonded SiC brick meets overall requirement of high MOR and alkali attack resistance.

Mantle or Belly
In the belly region of blast furnace, conditions are extremely severe. There is a change of direction in the descending charge causes tremendous abrasion. Carbon monoxide and alkali attack is more severe because there is less slag coating for protection. Occasional violent thermal shock occurs with burden shifts. The hot modulus of rupture of SiAlON bonded SiC brick is most significant in this region

Lower Stack
In lower stack, problems are carbon monoxide reduction, abrasion, alkali vapors, zinc and aluminum penetration and oxidation from carbon dioxide at temperatures as high as 820^{O}C. Also, as burden shift, thermal shock can be extreme in the lower stack. There is a minimal amount of slag. SiAlON bonded SiC brick is having the ability to combat Thermal Shock. Key properties here are high hot modulus of rupture, high conductivity, low coefficient of thermal expansion, extremely good porosity distribution.

CONCLUSIONS

SiAlON bonded SiC refractory bricks are developed based on theoretical superiority over Nitride bonded SiC.

SiAlON bonded SiC shown superiority towards alkali attack resistance over Nitride bonded SiC.

Characterized critical properties of SiAlON bonded in comparison with Nitride bonded SiC and SiAlON bonded SiC refractories are most suitable refractories towards blast furnace application.

Unique SiAlON bonded SiC properties are suitable towards application requirements of Tuyere bowls, Bosh, Mantle or Belly and Lower Stack zone of blast furnace.

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