Waste
To
Energy

IMPROVED REFRACTORIES AND SYSTEMS

FOR WASTE TO ENERGY APPLICATIONS

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Abstract

Waste-to-energy (WTE) facilities based on steam generating units (boilers) have proved to be a reliable technology for safe waste disposal and green energy production. The current trend for feedstock diversification in WTE processes and the need for higher energy throughput result in more severe operating conditions, including temperature fluctuations, operation at higher temperatures and higher diversity of chemically aggressive substances. Consequently, safe and efficient operation of WTE boilers requires the use of high performance refractories to protect the metallic wall membranes in most WTE units.

This work presents a comparison between the main current shaped products materials used in WTE facilities, namely oxide-bonded silicon carbide (OSiC) and nitride-bonded silicon carbide (NSiC). A new NSiC quality with enhanced oxidation resistance recently developed is also analyzed. The oxidation and corrosion resistance of these materials are evaluated at lab scale. The results obtained highlight the better performance of NSiC over OSiC products for the protection of the waterwall membrane in WTE applications. This better performance results from the lower permeability of the NSiC materials and the chemical stability of the nitride bonding phase.

SAINT-GOBAIN

1- INTRODUCTION

In waste-to-energy plants, the combustion chamber is an essential part of the system. It is delimited by metallic tubes, arranged vertically and welded together in continuous sections (waterwall membrane). The water circulating in the tubes recovers part of the heat generated by the waste combustion. This process leads to the production of superheated steam, which is then used to supply hot water for district heating and/or feed steam turbines for the generation of electricity.

The relatively high temperatures and chemical composition of flying ashes and flue gases resulting from waste burning produce a highly corrosive atmosphere in the combustion chamber. Consequently, high performance refractories are necessary to protect the waterwall membrane, hence contributing significantly to the safety and efficiency of the installation. The outstanding high-temperature strength properties, thermal conductivity and chemical resistance of silicon carbide (SiC), conjugate, of course, with its affordable price, make this material the preferred choice for the refractory products constituting the protective lining of the waterwall membrane.

Under termal gradient

Typical SiC-based shaped refractories are composed of 3 main phases: SiC grains, with a well-defined and controlled particle size distribution, a binding matrix and pores. The quality of SiC grains is well known to have a huge impact on product performance and reliability. On the other hand, the role of the binding phase in the final material properties is not always highlighted as it should be. Indeed, the nature of the binding phase is also key for product performance. It impacts not only mechanical and thermal properties of the shaped material, but also its oxidation and corrosion resistance. Hence, good oxidation and corrosion resistance of the binding phase itself and low permeability to corrosive fumes and ashes contribute to extend the lifetime of the refractory, and consequently of the metallic parts protected by it. The present work compares the performance of different SiC-based shaped refractories in terms of oxidation and corrosion resistance. Two main material families are considered: SiC grains bonded by oxide matrices (OSiC) and SiC grains bonded by silicon nitride matrices (NSiC). Lab tests are performed to evaluate their resistance to steam oxidation and molten salts attack under under termal gradient.

2- MATERIALS AND METHODS

Four SiC-based shaped refractories are investigated in this study:

- Oxide-bonded SiC quality 1 (denoted OSiC1, Figure 1a), which is widely used in French and Italian WTE plants, among other locations;
- Oxide-bonded SiC quality 2 (denoted OSiC2, Figure 1b), which is used mainly in Spanish WTE plants for the time being;
- Nitride-bonded SiC quality 1 (Refrax PRO®, standard NSiC from the Saint-Gobain portfolio, Figure 1c);
- Nitride-bonded SiC quality 2 (Refrax PLUS®, enhanced NSiC from the Saint-Gobain portfolio recently developed, Figure 1d).

1a) Oxide-bonded SiC quality 1, OSiC1

1b) Oxide-bonded SiC quality 2, OSiC2

1c) Nitride-bonded SiC quality 1, Refrax PRO®

1d) Nitride-bonded SiC quality 2, Refrax PLUS®

Figure 1: Pictures of the samples investigated.

Table 1 presents average material properties (3 specimens / tile) of the above mentioned products. SiC content is determined from C content measured by LECO. The crystalline binding phases are determined by XRD. Density and open porosity (OP) are determined by water immersion. Finally, material MOR (modulus of rupture) is evaluated by 3-point bending tests at room temperature. As can be seen, Refrax PRO® and Refrax PLUS® have virtually the same composition and physical properties. Nevertheless, as will be shown later, Refrax PLUS® has enhanced resistance to steam and salts aggression, thanks to significant improvements in material formulation.

Material	**SiC content [%]**	**Binding phase**	**Density [g/cm3]**	**OP [%]**	**MOR [MPa]**
OSiC1	91.1	Cristobalite, mullite	2.64	14.7	48.3
OSiC2	79.3	Cristobalite, corundum, Si2ON2	2.67	14.3	30.8
Refrax PRO®	75.4	Si_3N_4, Si_2ON_2	2.70	14.1	62.3
Refrax PLUS®	76.7	Si_3N_4, Si_2ON_2	2.71	13.7	60.1

Table 1: Basic properties of SiC-based shaped refractories investigated.

In WTE environments, the chemically aggressive compounds are diverse and depend upon the nature of the waste stream (urban, hospital …), the boiler operating conditions, and other factors. Nevertheless, chemical attack by steam, sulphates and chlorides are nearly always observed in this environment.

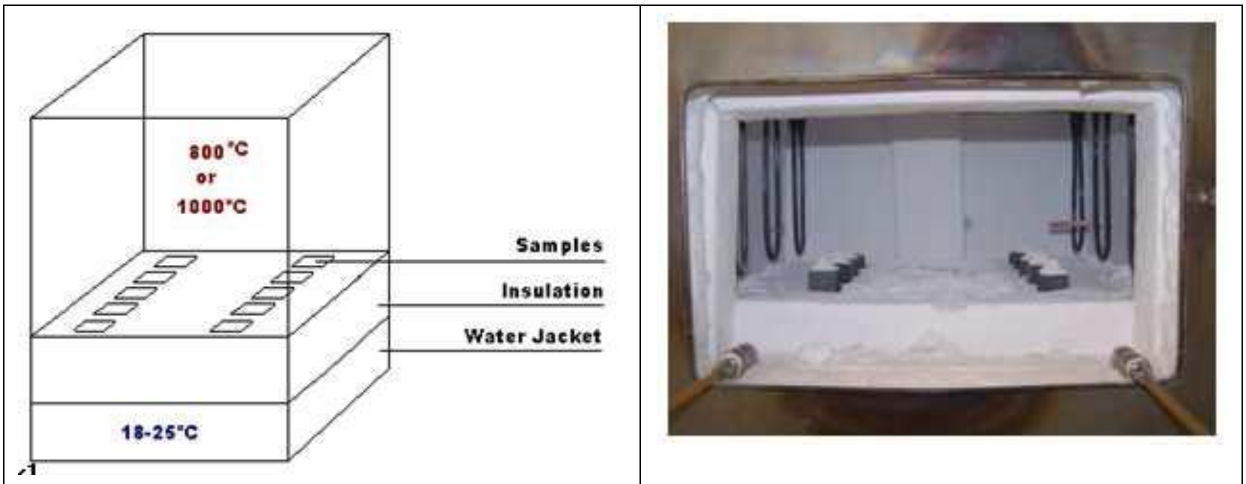
In the present work, lab tests were performed to independently evaluate the resistance of the SiC-based refractories under investigation to steam oxidation and salts oxidation/corrosion. Special attention was given to the volume gain of samples resulting from chemical reactions (e.g. SiC oxidation). Indeed, excessive expansion of refractory parts leads to material failure due to spalling, cracking or rupture under the compressive forces generated by the contact between adjacent tiles. Hence, the lower the volume expansion is, the better will be the material performance in application.

Steam oxidation tests were carried out at the Saint-Gobain Research Centre of Cavaillon (SG- CREE, France) at 1000°C for 500h with a steam rate of 32 kg/h/m^3 (ASTM C863) inside an alumina reactor. The test specimens were bars of 65×25×25 mm^3 cut from the tiles shown in Figure 1. Three bar specimens per material quality were tested. Measurements of bars weight, volume, density and porosity were performed after 100h, 250h and 500h of testing. Chemical analyses of the samples were carried out before and after the test.

Regarding the salts corrosion/oxidation test, a specific experimental apparatus was developed at SG-CREE in order to generate thermal gradients within the specimens. Figure 2 presents a schematic drawing and a picture of the furnace with the specimens prepared for the test. The specimens were bars of 65×25×25 mm^3 inserted into a ceramic fiber insulation block, with one extremity exposed to the furnace and the other one in contact with a water jacket.

Temperature measurements were carried out by installing thermocouples within bar specimens. The temperatures obtained in the bar specimens cold and hot sides at furnace temperatures of 800°C and 1000°C were 600°C-720°C and 720°C-920°C, respectively. These temperature ranges reproduce quite well the typical thermal conditions to which refractory tiles are subjected in real WTE boilers.

The tests were performed with the following protocol: 200h at 800°C followed by 200h at 1000°C. The amount of salts put on the top of each bar specimen was 2.0 g (see Figure 2). Three bar specimens per material quality were tested. Measurements of bars weight, volume, density and porosity as well as chemical analyses were performed before and after the test. The specimens were carefully cleaned to remove the molten salts stuck to them prior to volume measurements after the test.



a) Furnace schematic | b) samples in the furnace with salts

Figure 2: Salts corrosion/oxidation test configuration

The salt mixture used to oxidize and corrode the specimens is presented in Table 2. It is similar to the mixture used in [1], which was defined from the analysis of slags sampled different incinerators. The melting of this mixture, evaluated by camera observation at SG CREE during temperature ramp up, was seen to take place between 600°C and 800°C.

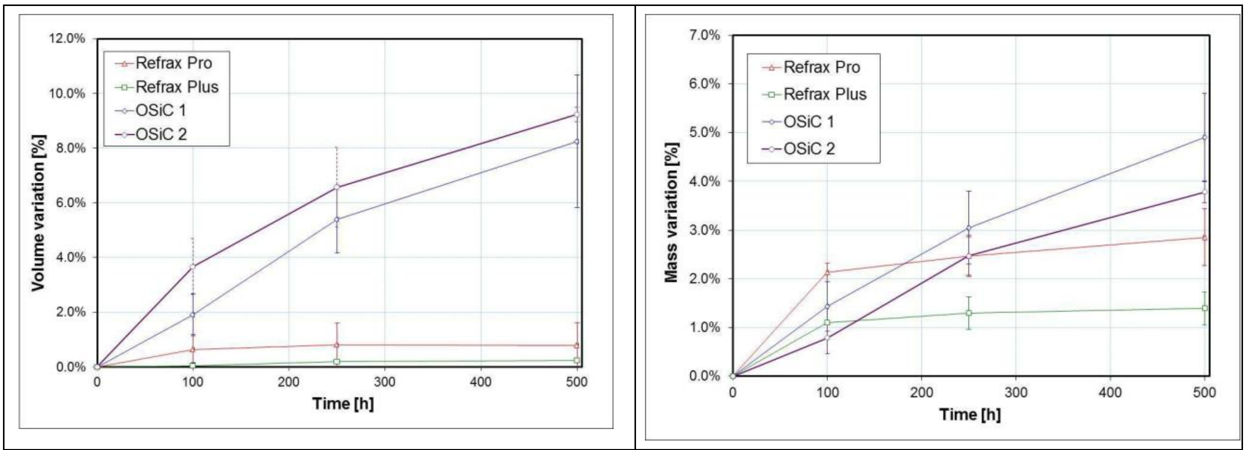
Component s	Weight mass %
KCl	10
NaCl	10
K_2SO_4	35
Na_2SO_4	10
$CaSO_4$	35

Table 2: Corroding salts mixture

3- RESULTS AND DISCUSSION

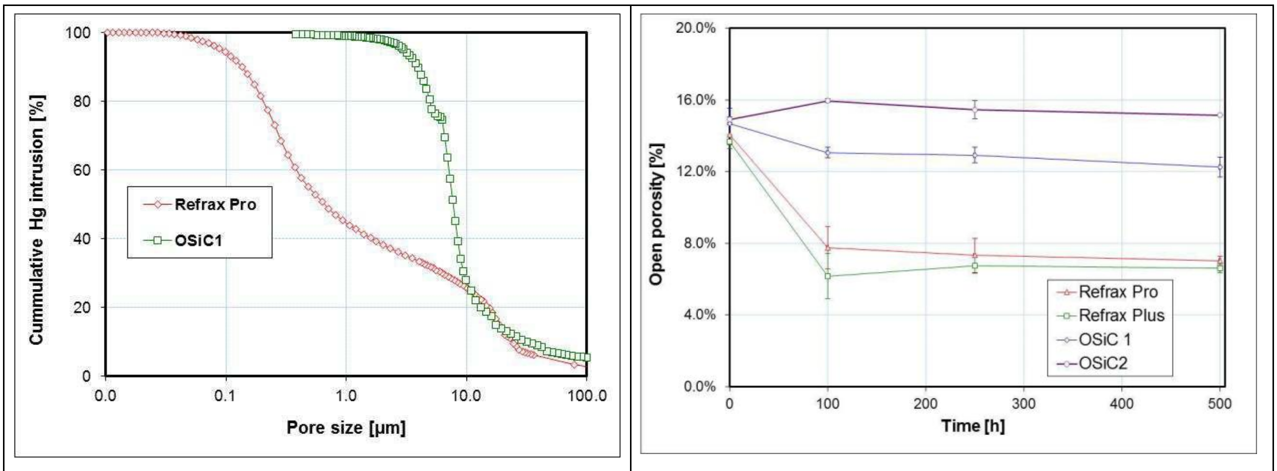
Figure 3 presents the measured volume expansion and mass gain evolutions during steam oxidation testing. All material qualities exhibit the well-known parabolic oxidation behaviour of SiC-based materials [2, 3]. This trend is considerably more pronounced for the nitride- bonded SiC materials. The formation of a protective silica scale on SiC grains and, in case of nitride-bonded SiC samples, over the Si_3N_4 matrix reduces the oxidation kinetics. Further material oxidation is controlled by the diffusion of oxygen across this scale.

It can be seen that the oxide-bonded SiC materials show considerably higher volume expansion than the nitride-bonded SiC qualities. The mass gain is also higher, but not to the same extent. Several aspects can be highlighted to explain these results. One of the most important concerns the material permeability. Thanks to the reaction bonding firing process, the nitridation of silicon induces the formation of a relatively fine, and hence low permeable, matrix for nitride-bonded SiC materials. Besides, the partial oxidation of the Si_3N_4 phase under oxidizing atmosphere leads to a more important reduction in open porosity than oxide- bonded SiC materials. Figure 4 shows the initial pore size distribution of materials OSiC1 and Refrax PRO®, as well as the evolution of open porosity of all tested materials during steam oxidation testing. The lower material permeability of nitride bonded SiC refractories thanks to their finer pore size distributions and lower open porosity better protects not only the material itself from chemical attack, but also the metallic parts underneath. Refrax PLUS® is seen to present the lowest mass gain and volume expansion, hence the best resistance against steam oxidation among the materials tested. This recently developed nitride-bonded SiC material has microstructure morphology very similar to Refrax PRO®. Hence, its better performance is not only explained by the lower material permeability to aggressive species. Refrax PLUS® chemical composition was engineered to reduce the oxygen diffusion across the silica scale formed over SiC and Si3N4 phases and hence slow down the the oxidation kinetics.



a) Volume expansion	b) Mass gain

Figure 3: Volume expansion and mass gain induced by steam oxidation



a) Pore size distribution measured by Hg intrusion for fresh materials	b) Open porosity evolution during steam oxidation testing

Figure 4: Comparison between OSiC and NSiC microstructure characteristics (initial pore size distribution and open porosity evolution during steam oxidation)

Table 3 presents the evolution of the main chemical elements of the investigated materials, namely C, O, N, Si and Al, before and after steam oxidation. Si and Al were measured by X- Ray Fluorescence and C, O and N by LECO equipment. Only one specimen per material quality had these elements measured before and after steam oxidation. C content gives a direct indication of the SiC content in the materials. The increase in O content reflects the oxidation extent of the different material phases (basically the formation of silica from SiC, Si_3N_4 and Si_2ON_2). It can be seen that the reduction of SiC content is drastically stronger for OSiC than for NSiC materials. This is accompanied by a significantly higher increase in O content for OSiC than for NSiC specimens. For instance, SiC diminishes from 92% to 73% for OSiC1 and from 84% to 62% for OSiC2, whereas for Refrax PRO® the reduction is from 75% to 71% and for Refrax PLUS® from 76% to 72.

	OSiC1		OSiC2		Refrax PRO®		Refrax PLUS®	
	Befor e	After	Befor e	After	Befor e	After	Befor e	After
Al (wt%)	1.0	1.1	6.7	7.3	0.7	0.6	0.8	0.7
Si (wt%)	67.3	64.1	55.8	54.8	67.1	66.8	66.5	66.4
C (wt%)	27.6	21.8	25.1	18.4	22.6	21.3	22.9	21.5
O (wt%)	3.5	11.7	9.6	17.4	2.9	6.2	1.8	5.0
N (wt%)	-	-	0.6	0.2	8.0	5.1	8.7	6.3

Table 3: Evolution of main chemical elements of tested materials before and after steam oxidation for 500h at 1000°C

Table 4 presents the average volume expansion and standard deviation after salts corrosion test for the materials investigated. As for steam oxidation, the NSiC samples, especially Refrax PLUS®, are seen to undergo considerably lower volume expansion than OSiC qualities. Concerning the resistance to salts aggression, NSiC refractories present the additional advantage of having a significantly more resistant matrix than OSiC qualities. Indeed, the Si_3N_4 phase is much more stable than silica/alumina in contact with salts, as the latter can easily react to form aluminosilicate compounds with alkalis or even suffer chemical etching due to slags basicity. Si_3N_4 is also inherently more resistant to salts than SiC [4].

OSiC1	OSiC2	Refrax PRO®	Refrax PLUS®
0.7% ± 0.3%	2.8% ± 0.1%	0.3% ± 0.1%	0.1% ± 0.1%

Table 4: Volume expansion induced by salts corrosion test

4- CONCLUSIONS

The present work investigates the resistance of oxide-bonded (OSiC) and nitride-bonded (NSiC) SiC refractories to steam oxidation and salts oxidation/corrosion under thermal gradient. Results show that NSiC, especially the recently developed Refrax PLUS® quality, is much more stable chemically under typical WTE aggressive environments and undergoes significantly less volume expansion than the OSiC refractories investigated. Consequently, they are able to provide longer and more effective protection to waterwall membranes in incineration facilities. The better performance of NSiC results, among other factors, from its lower permeability to aggressive species and to the higher chemical stability of the nitride binding phase compared to silica/alumina binding phases. For Refrax PLUS® specifically, its composition also provides a higher resistance to oxidizing atmospheres thanks to the formation of protective silica scale with reduced oxygen diffusion properties.

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