MICROSTRUCTURE DESIGN OF A MORE SUSTAINABLE ALUMINA-SPINEL REFRACTORY CASTABLE

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ABSTRACT

Alumina-spinel based refractories are excellent furnace linings due to high refractoriness and superior corrosion and slag penetration resistance. Tabular alumina aggregates have been popularly used in alumina-spinel refractories due to their high purity, high melting point and volume stability at high temperatures. Nevertheless, white fused aggregates were also considered in this work in the quest to propose a new microstructural design for refractory materials with improved thermo-mechanical properties. The influence of white fused alumina aggregates on the castable porosity, physical property, microstructure and thermal shock resistance (TSR) were investigated. Calcium hexaluminate phases (CA_6) were formed along the borders of tabular and white fused alumina aggregates at 1500 °C but in denser layers around white fused aggregates. Residual modulus of elasticity after one and five thermal shocking cycles are comparable for both M-TA and M-WFA castables regardless of original strengths after sintering. Interestingly, residual modulus of rupture for M-WFA castables remains higher than that of M-TA castables after one and five thermal cycles.

INTRODUCTION

Alumina-spinel castables have been long used in several areas of the steelmaking process including ladle lining [1]. Two types of alumina are widely produced for refractory applications comprising tabular alumina (TA) and white fused alumina (WFA). Nevertheless, tabular alumina has been the main alumina aggregates used in alumina-spinel (Al_2O_3-$MgAl_2O_4$) castables. Due to significant amount of closed pores (about 5 vol%.) evenly distributed, tabular alumina is believed to improve thermal shock resistance compared to castables containing white fused alumina [2]. Additionally, tabular alumina consists of elongated, tablet-shaped crystallites with lower open pores than that of white fused alumina grains which are angular shaped [3]. The difference in morphology and particle porosity is mainly due to the different processing routes, that is sintering and electrofusion for tabular and fused alumina respectively. With sodium impurities unevenly distributed and concentrated more at grain boundaries, the deficiency of the large and dense crystallites of white fused alumina in thermomechanical behaviour compared to tabular alumina-based spinel refractories is not well understood. The work reported in this paper seeks to investigate the correlations between microstructural changes and thermomechanical properties of alumina-spinel castables containing tabular (M-TA) and white fused alumina (M-WFA) at high temperatures.

MATERIALS AND EXPERIMENTAL PROCEDURE

Raw materials

Tabular alumina, TA (Almatis, Germany) and White Fused Alumina, WFA (Imerys, Germany) were used as the main alumina aggregates (coarse, medium and fines) in the castables. Calcium aluminate cement (CAC, Secar 71, France) as binder, reactive alumina (P152SB, Alteo, France) and a chemical additive (Peramin AL200, Imerys, France) as dispersant add up to the castable composition.

The characteristics of tabular alumina and white fused alumina aggregates are given in Table 1. The determination of the apparent densities, open porosities and water absorption of the alumina aggregates was done using the Archimedes method.

Tab. 1: Properties of tabular and white fused alumina aggregates.

Property	Tabular Alumina	White Fused Alumina
Apparent porosity, g/cm³	3.6	3.5
Open porosity, %	4.3	9.9
Water absorption, %	1.2	3.7
Shape	Blocky	angular
Al_2O_3, %	99.9	99.8
Na_2O, %	0.3	0.3

Castable preparation

Table 2 shows the two types of alumina-spinel castables prepared: (i) one containing tabular alumina aggregates (TA) and (ii) the other containing white fused alumina aggregates (WFA). Both formulations were cast into prisms of 160x30x30 mm³. Castables were cured (at 20 °C, 100 % RH) for 48 h, dried at 110 °C for 24 h and fired at 5 °C/min up to 1100 °C, 1300 °C and 1500 °C for 6 h.

Tab. 2: Compositions of castables, wt%.

	M-TA	**M-WFA**
Tabular Alumina		
0-6 mm	60	-
White Fused Alumina		
0-5 mm	-	60
Sintered spinel		
0.5-1 mm	9	9
0-0.5 mm	4	4
0-0.09 mm	10	10
Reactive Alumina	11	11
CAC Secar 71	6	6
PCE AL200	+ 0.1	+ 0.1
Water	+ 4.1	+ 4.1

Testing methods

Apparent porosity measurements based on the Archimedes method were performed using water as the immersion liquid. 3-point bending tests were used to measure the modulus of rupture for castables after curing, drying and firing. To interprete the microstructural evolution of the castables fired at 1500 °C, scanning electron microscopy (SEM) studies were carried out with the equipment Quanta FEG 250. Regarding the thermal shock tests, pre-fired samples (1500 °C for 6 h) were subjected to a total of five heating and cooling cycles. Samples were placed in the furnace already heated at 950 °C for 2 h. Afterwards, the samples were removed and air-cooled to room temperature. For each cycle, the damage caused by the thermal cycling was evaluated by elastic modulus measurements (E) *via* frequency resonance at room temperature with the Grindosonic® MK7. Modulus of rupture (MoR) tests were carried out to evaluate the residual strength after thermal cycles.

RESULTS AND DISCUSSION

Castable properties

Lowest and highest porosities in both castables were measured after treatment at 110 °C and 1500 °C respectively. The apparent porosities in M-WFA are higher compared to M-TA castables (see Figure 1). However, there is a slight decrease in porosity in M-TA at 1300 °C. One of the reasons for higher porosities in M-WFA castables can be partly attributed to higher open porosities in white fused alumina aggregates.

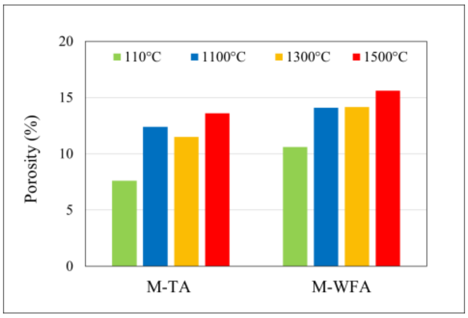

Fig. 1: Apparent porosity of the tabular (M-TA) and white fused (M-WFA) alumina based castables after drying at 110 °C and different firing temperatures.

Modulus of rupture are relatively low and comparable in both M-TA and M-WFA castables up to 1300 °C. At 1500 °C, both castables have high modulus of rupture but more significant in M-TA castables as seen in Figure 2.

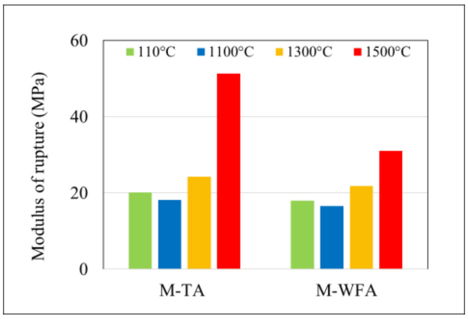

Fig. 2: Modulus of rupture of tabular (M-TA) and white fused (WFA) alumina based castables after drying at 110 °C and different firing temperatures.

Microstructure

SEM images show the presence of hibonite (CA_6) at the borders of the alumina aggregates for both M-TA and M-WFA castables as shown in Figure 3. Despite high open pores in white fused aggregates, WFA aggregates look denser compared to TA aggregates but are embedded in a more porous matrix containing big pores.

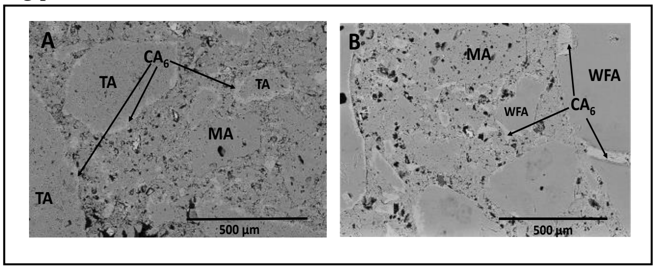

Fig. 3: SEM micrographs of A) tabular and B) white fused alumina-based spinel castables sintered at 1500°C.

However, CA_6 seems to be evenly distributed along the tabular alumina aggregates. In M-WFA castables, CA_6 tends to form on discrete parts on the surface of the aggregate but in denser layers than in M-TA castables.

Thermal Shock

M-TA and M-WFA castables show a gradual loss in modulus of elasticity after thermal shock cycles. The residual modulus of elasticity were comparable for both M-TA and M-WFA castables regardless of original strengths after sintering (see Figure 4 below).

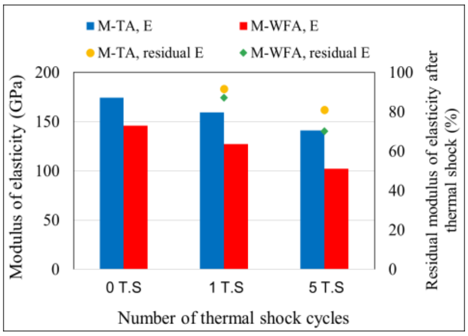

Fig. 4: Modulus of Elasticity of the tabular (M-TA) and white fused (M-WFA) alumina based castables after sintering and thermal shock cycles.

The modulus of rupture after sintering is significantly higher for M-TA than M-WFA castables at 1500°C. Likewise, after the first thermal cycle, M-TA castables experiences a bigger drop in strength compared to M-WFA castables. Surprisingly, the residual modulus of rupture for M-WFA castables remains a little higher than that of M-TA castables after one and five thermal cycles.

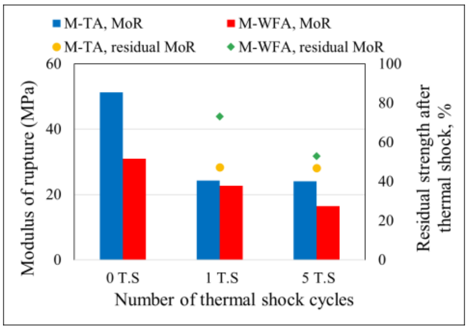

Fig. 5: Modulus of Rupture of the tabular (M-TA) and white fused (WFA) alumina based castables after sintering and thermal shock cycles.

CONCLUSIONS

This work shows the significant influence in castable properties at high temperatures comparing the two types of alumina aggregates. Higher modulus of elasticity and rupture could be related to the less porous and dense microstructure of M-TA castables. Thermal shocking results show a higher elastic modulus and residual elastic modulus in M-TA castables after five thermal cycles. Conversely, M-WFA castables exhibit a lower modulus of rupture but a higher residual modulus of rupture of about 50 % after five thermal cycles.

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