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The physical and mechanical properties of alumina-based ultralow cement castable refractories

A. Gungor [a,*], O. Celikcioglu [b], S. Sahin [a]

[a] Karabuk University, Engineering Faculty, Metallurgical and Materials Eng. Dept., Karabuk, Turkey
[b] Karabuk Iron & Steel Factories, Karabuk, Turkey

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Abstract

In this study, the effects of the type of alumina on the physical, chemical and mechanical properties of the ultralow cement castable (ULCC) refractories were investigated. Brown fused alumina, tabular alumina and rotary bauxite-based ULCC refractories were prepared by mixing each type of alumina with silicon carbide, carbon, cement, metallic silicon and microsilica. The density, porosity and cold crushing strength (CCS) of the refractory castables were measured after drying at 110 °C for 24 h and firing at 1450 °C for 5 h. The slag penetration resistance of the refractory castables was determined using slag corrosion tests. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffractometry (XRD) were used to characterize the castables. It was found that all three refractory castables had strong slag penetration resistance and that the tabular alumina-based refractory castable had the largest specific cold crushing strength with an acceptable percent of porosity among the refractory castables.

Keywords: Refractory; Alumina; Mechanical Properties; Corrosion

1. Introduction

The development of refractory castables is important due to their increasing applications in the metallurgical, cement and chemical industries [1]. Compared with shaped refractories, the increasing use of unshaped refractories has become common practice, especially in steel-making applications such as the production of steel ladles and the linings of tundishes [2]. The refractory castables have generally complex heterogeneous microstructures and their physical and thermomechanical properties are highly temperature-dependent because of the complex hydration and dehydration processes [3]. Therefore, the service conditions considerably affect the structure and properties of the refractory castables.

In monolithic refractories, calcium aluminate cement (CAC), one of the most widely used binders, promotes initial hardening and mechanical strength before firing [4]. In the early stages of hardening, the CAC dissolves in water and releases calcium, aluminum and hydroxyl ions. After saturating the water, these ions form calcium aluminate hydrates that harden the structure [5,6].

In the last few decades, the service life of alumina based refractory castables has been improved significantly by reducing the cement content. The reason that the cement content is reduced is to prevent the formation of low melting temperature compounds in the presence of lime (CaO) [7]. Modern refractory castables, such as low cement castables (LCC) and ultralow cement castables (ULCC), are complex mixtures of calcium aluminate cement, ultra fine materials, aggregates and admixtures [7,8]. These castables have valuable properties, including a low thermal expansion coefficient, good thermal conductivity, good thermal shock resistance, high resistance to slag and liquid metal corrosion and high strength at low and high temperatures [9–13].

Carbon-containing refractories have been extensively used in steel making industries and their microstructure, properties, slag corrosion resistance and service life have been improved significantly since the 1970s by controlling the carbon content [14]. However, in an oxidizing atmosphere, carbon easily oxidizes above 600 °C and has a negative effect on the porosity,

* Corresponding author. Tel.: +90 3704332021; fax: +90 3704333290.
E-mail address: agungor@karabuk.edu.tr (A. Gungor).

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density and strength of the castables [15]. Therefore, to inhibit or slow down the oxidation reaction and to reduce the porosity, metal or carbide additives, including metallic silicon and silicon carbide as antioxidants, are frequently added to carbon-containing refractories [16,17]. Metallic silicon reacts with carbon to form silicon carbide and/or reduces carbon monoxide to carbon by transforming to silicon dioxide [18]. Silicon carbide is very effective at preventing the oxidation of carbon and at improving the corrosion resistance and mechanical strength of the refractory castables [19,20]. However, it is known that a high silicon carbide content reduces the flowability properties of the casting materials after mixing with water. Therefore, microsilica is frequently added to improve the packing of the particles and the flowability of the castables as well as to decrease the porosity [4]. In addition, microsilica reacts with alumina and forms strong bonds at relatively low and high temperatures [21]. Transformation of the microsilica to mullite improves the mechanical strength.

In this study, the effect of the type of alumina on the physical, chemical and mechanical properties of the ultralow cement castable (ULCC) refractories was investigated.

2. Experimental procedures

2.1. Materials and preparation of ULCC refractories

Brown fused alumina, tabular alumina, rotary bauxite, silicon carbide, carbon, calcium aluminate cement, metallic silicon, and microsilica were used to prepare three different ULCC refractories. The particle size, purity and chemical composition of the raw materials are given in Table 1, and the composition of the ULCC refractories is given in Table 2.

The refractory castables given in Table 2 were prepared by mixing the raw materials with 6 vol.% water in a Hobart A200 mixer. After mixing, the refractory castables were cast under vibration in pre-greased cube-shaped molds with dimensions of 50 mm × 50 mm × 50 mm. After 3 min of vibration, the refractory castables were left at room temperature for 12 h. The castables were dried at 110 °C for 24 h and fired at 1450 °C for 5 h. During heating of the castables, a 10 °C/min heating rate was used.

After drying and firing the specimens, slag corrosion tests, density, porosity, and CCS measurements as well as structural and chemical analyses of the refractory castables were conducted experimentally.

2.2. Density and porosity measurements

The density and porosity of the refractory castables were measured according to DIN 51065 and DIN 51056 standards, respectively.

The density and porosity of each castable were determined with the following procedure:

1. Measuring the dry weight (M_D): The dry weight of the specimens was measured in grams to the nearest 0.1 g after heating the specimens to 110 °C.

Table 1
The particle size and chemical composition of the raw materials (wt%).

	Brown fused alumina	Tabular alumina	Rotary bauxite	SiC	C	Cement	Si	SiO_2
Particle	0.1–5 mm	0.1–5 mm	0.1–5 mm	<1 μm	<1 μm	1.2 mm	20 μm	<1 μm size
Al_2O_3	96.50	99.31	89.54	–	1.5	69.5–71.5	0.1	
Fe_2O_3	0.03	0.03	1.81	0.2	0.36	0.3	–	–
CaO	0.25	0.02	0.20	–	0.43	27–29	–	–
TiO_2	2.01	0.05	4.10	–	–	0.1	–	–
SiO_2	0.92	0.41	3.12	4.3	2.5	0.8	–	99.7
MgO	–	–	–	–	0.21	0.3	–	–
Na_2O	–	–	–	–	–	0.5	–	–
SiC	–	–	–	95.0	–	–	–	–
C	–	–	–	0.5	95.0	–	–	0.02
Si	–	–	–	–	1.0	–	>99.0	–

Table 2
Chemical compositions of the ULCC refractories (wt%).

	Brown fused alumina	Tabular alumina	Rotary bauxite	SiC	C	Cement	Si	SiO_2
Cast-1	73	–	–	20	4	1	1	1
Cast-2	–	73	–	20	4	1	1	1
Cast-3	–	–	73	20	4	1	1	1

Table 3
Chemical composition of the blast furnace slag (wt%).

SiO_2	CaO	Al_2O_3	MgO	MnO	TiO_2	FeO	S	K_2O	Na_2O
39.7	36.8	9.5	7.0	2.5	1.8	0.6	0.5	1.2	0.4

Table 4
Densities of the ULCC refractories after drying at 110 °C and firing at 1450 °C.

	Density (g/cm^3)		
	110 °C	% Reduction	% Reduction
Cast-1	2.82	–	–
Cast-2	2.65	6.03	4.27
Cast-3	2.56	9.22	9.61

Table 5
Porosity ratios of the ULCC refractories after drying at 110 °C and firing at 1450 °C.

	Porosity (%)		
	110 °C	1450 °C	% Reduction after firing
Cast-1	22.73	19.69	13.37
Cast-2	23.81	21.80	8.44
Cast-3	22.22	21.59	2.83

Table 6
Cold crushing strengths of the ULCC refractories after drying at 110 °C and firing at 1450 °C.

	Cold crushing strength		
	110 °C kg/cm^2	1450 °C kg/cm^2	% Increase after firing
Cast-1	87	517	494.25
Cast-2	71	533	650.70
Cast-3	72	284	294.44

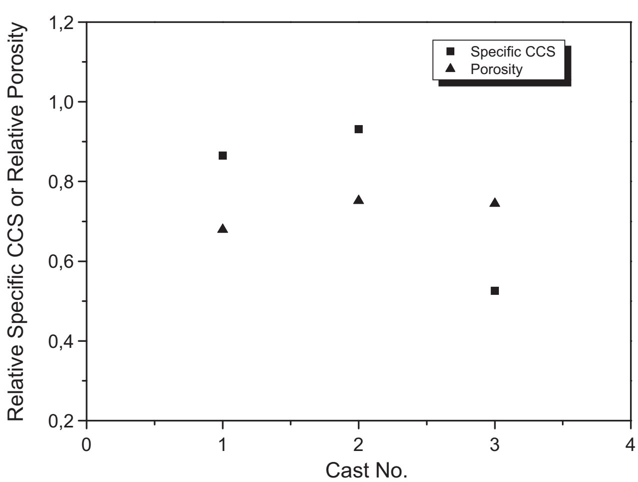

Fig. 1. Relative values of the specific cold crushing strength and the relative porosity of the refractory castables.

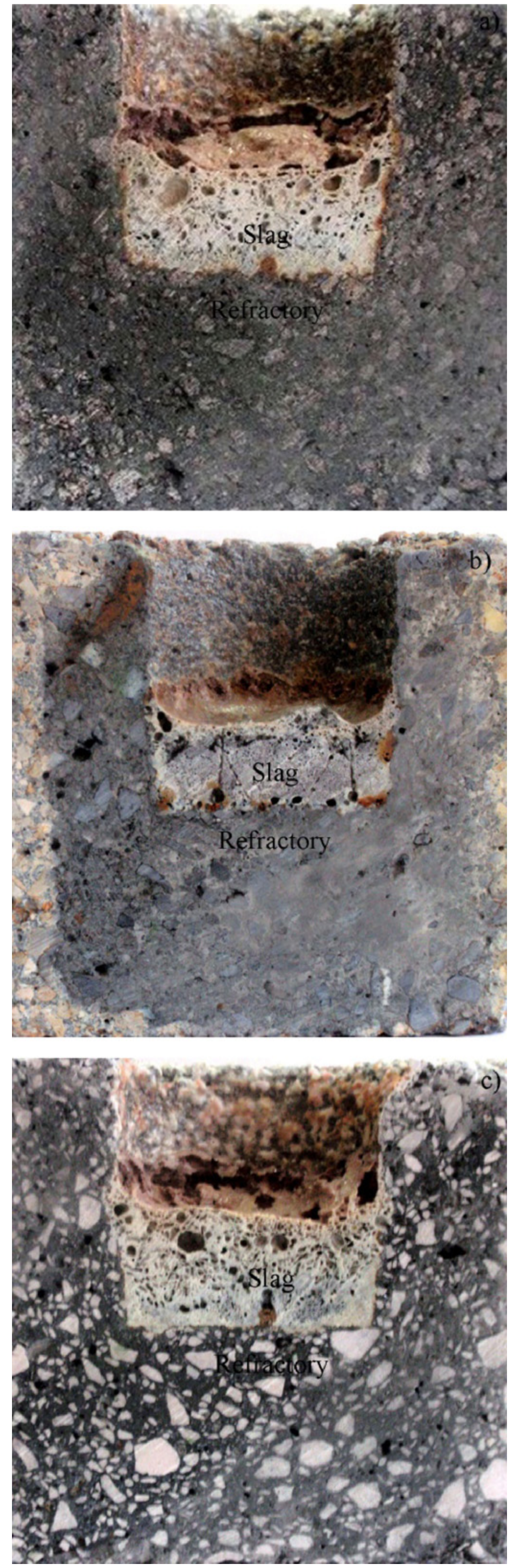

Fig. 2. Images of the refractory castables after slag corrosion tests: (a) cross section of cast-1, (b) cross section of cast-2 and (c) cross section of cast-3.

2. Measuring the saturated (wet) weight (M_W): The specimens were kept in boiling water for 3 h and then cooled to room temperature. Afterwards, the surfaces of the specimens were dried lightly with cotton cloth, and the saturated weight was measured in grams by weighing in air to the nearest 0.1 g.

3. Measuring the suspended weight (M_S): The suspended weight of the specimens was determined to the nearest 0.1 g after boiling and while suspended in water.

According to the DIN 51056 standard, the volume of the open pores (porosity, %) in the castables was determined using the following equation:

$$\text{Porosity}\ (\%) = \frac{M_W - M_D}{M_W - M_S} * 100$$

According to the DIN 51065 standard, the bulk density of the castables was determined using the following equation:

$$d_b = \frac{M_D}{M_W - M_S} * \rho_{water}$$

d_b: bulk density (g/cm^3)
ρ_{water}: density of water (g/cm^3).

2.3. Cold crushing strength

The CCS of the castables was determined according to the DIN 51067 standard using an Atom Technique compression machine having a 200-ton capacity. The following equation was used to determine the CCS of the castables:

$$\sigma_{ccs} = \frac{F_{max}}{A_o}$$

σ_{ccs}: cold crushing strength (kg/cm^2)
F_{max}: force at the fracture (kg)
A_o: surface area (cm^2).

2.4. Slag corrosion tests

The slag corrosion resistance of the ULCC refractories was determined according to the DIN 51069-2 standard that is known as the crucible/pot method. For the slag corrosion tests, the slag was obtained from Karabuk Iron & Steel Factories (Karabuk, Turkey) and its chemical composition is given in Table 3. To increase the impact of the slag, it was ground to less than 100 μm. The slag in powder form was poured in to the crucible prepared according to the DIN 51069-2 and then fired at 1450 °C for 5 h using a Protherm™ heat treatment furnace. The heating rate was 10 °C/min. Subsequently, as stated in DIN 51069-2, the refractory castables were cut in half, and the regions that reacted with slag were investigated.

2.5. Microscopic and chemical analyses

The surface morphology and chemical composition of the fired castables at 1450 °C were determined using a digital camera, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). SEM and EDX analyses were performed using a Philips XL30 SFEG scanning transmission microscope.

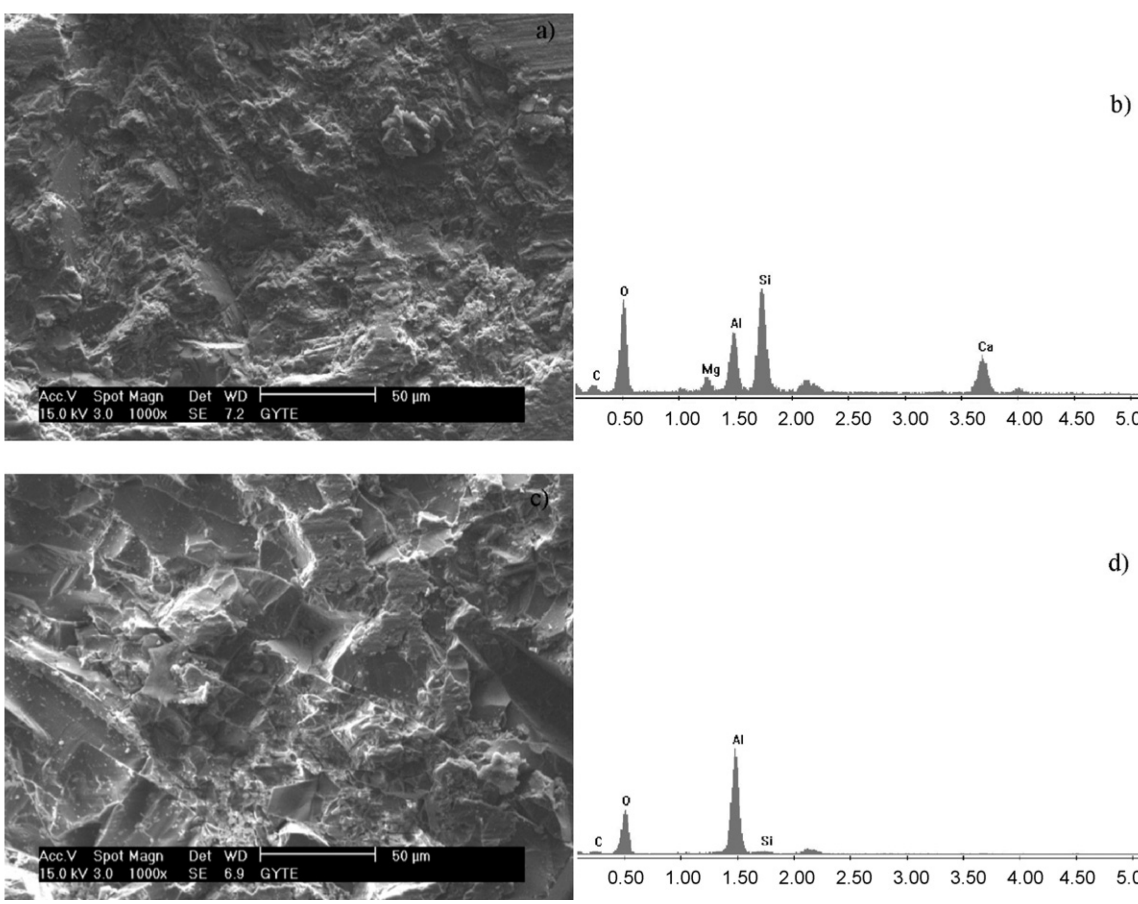

Fig. 3. SEM images and EDX spectrums of cast-1: (a) micrograph of the slag, (b) EDX spectrum of the slag, (c) micrograph of the refractory and (d) EDX spectrum of the refractory.

2.6. Structural analysis

The X-ray diffraction method was used to determine the present phases in the fired castables. XRD measurements were performed at a 0.02°/0.3 s scan rate using a Bruker Advance D8 X-ray diffractometer operated at 40 keV and 40 mA.

3. Results and discussion

The bulk density of the ULCC refractories is given in Table 4. As observed from the table, the densities of the refractory castables after drying at 110 °C and firing at 1450 °C are similar. When the densities of the castables are compared, it can be observed that the brown fused alumina and rotary bauxite-based castables had the largest and the smallest densities, respectively.

The porosity (%) of the ULCC refractories is given in Table 5. As observed from the table, the porosities of the dried castables are similar and firing the castables at 1450 °C resulted in lower porosity. The reduction in the porosity of the refractory castables is between 2.83% and 13.37%. The largest and the smallest reductions in the porosity were observed in brown fused alumina and bauxite-based castables, respectively.

The cold crushing strength of the ULCC refractories is given in Table 6. Firing the castables at 1450 °C for 5 h increased the CCS of the refractory castables significantly such that the CCS of cast-1, cast-2, and cast-3 increased 494.25%, 650.70% and 294.44%, respectively.

The relative values of the specific cold crushing strength and the porosity of the castables were plotted against the castable number (1 for cast-1, 2 for cast-2 and 3 for cast-3) in Fig. 1. This figure indicates that cast-2, tabular alumina-based ULCC, had a better specific cold crushing strength with an acceptable percent of porosity than the others.

The cross sections of the refractory castables after the slag corrosion tests are shown in Fig. 2. As observed from the figures, the slag particles were melted during the corrosion tests and filled the bottom of the mold cavities. The fact that mold cavities were not broken during slag-refractory corrosion and that there are straight fine lines between the slag and the refractory imply that the refractory castables have a strong resistance to slag penetration.

SEM micrographs and EDX spectrums of cast-1 are given in Fig. 3. The images and spectrums were taken above and below the interfaces that correspond to the slag and refractory, respectively. When the EDX spectrum of the slag (Fig. 3b) is analyzed, it is observed that the spectrum contains the elements of the slag components. Similarly, the EDX spectrum of the refractory (Fig. 3d) confirms the elements of the raw refractory materials. Because similar results were obtained from cast-2 and cast-3, they are not reported here.

The results of the X-ray diffraction analyses are given in Fig. 4. From the XRD patterns of the refractory castables, it was determined that alumina, silicon carbide, graphite and mullite were present in all of the ULCC. Mullite forms as a result of the reaction that takes place between alumina and microsilica during firing. The reaction can be represented as follow:

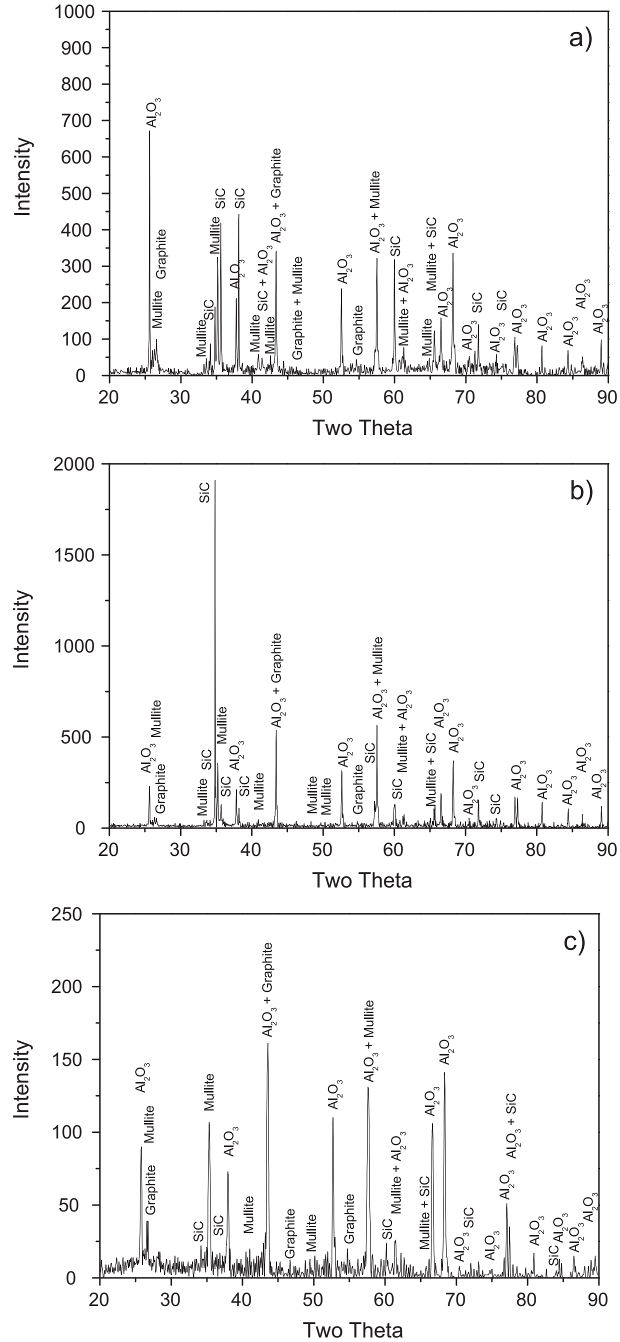

Fig. 4. XRD patterns of the refractory castables: (a) phases in cast-1, (b) phases in cast-2 and (c) phases in cast-3.

$$3Al_2O_3 + 2SiO_2 \rightarrow Al_6Si_2O_{13}$$

Because the enthalpy of the reaction upto 1500 °C is positive, the entropy of the reaction makes the free energy of the reaction zero at 981 °C and then negative with further increases in temperature [21,22]. Therefore, the mullite formation becomes energetically favorable above 981 °C. Because mullite has a high melting temperature, a low thermal expansion coefficient, a low thermal conductivity, a high chemical stability and a high mechanical strength, the presence of mullite can contribute to the physical, chemical and mechanical properties of the refractory castables. The amount of the contribution will depend on its volume fraction, size and shape.

Earlier studies showed that mullite grains are elongated needle-like crystals that lock the structure, creating strong, tough and refractory bonds [7,19,21]. Although it is very difficult to determine the volume fraction of the mullite crystals, information about the amount of mullite in the castables can be extracted from the X-ray intensities of the mullite peaks because the intensities of the peaks are closely related to the volume fractions of the crystals. When the intensities of the mullite peaks are compared, it can be observed that the peaks in the tabular alumina-based castable are slightly higher than those in the brown fused alumina-based castable, but much higher than those in bauxite based-castable. Because the particle sizes of the raw materials and the processing conditions were the same for all of the castables studied here, it is not expected that the packing efficiency and processing conditions will alter the mechanical strength of the castables. Therefore, the higher CCS of the tabular alumina-based castable can be attributed to its higher mullite content.

4. Conclusion

The physical, chemical and mechanical properties as well as slag corrosion resistance of brown fused alumina, tabular alumina and bauxite-based ultralow cement castable refractories were investigated. Three different refractory castables were prepared by mixing each type of alumina with silicon carbide, carbon, cement, metallic silicon and microsilica.

It was found that all of the ULCC refractories had a strong slag penetration resistance. From theta-two theta measurements, it was observed that mullite formed in all of the castables during the firing of the refractory castables at 1450 °C. Compared with brown fused alumina and bauxite-based castables, the tabular alumina-based refractory castable had the largest specific cold crushing strength with an acceptable porosity among the refractory castables.

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