INFLUENCE OF THE SILICA GEL TECHNOLOGY ON THE HIGH TEMPERATURE MECHANICAL BEHAVIOUR OF ALUMINA CASTABLES

Olga Burgos-Montes[1], Margarita Álvarez[1], Edward Restrepo[2,3], Antonio H. de Aza[3], Pilar Pena[3], Carmen Baudín [3]*
[1]REFRACTARIOS ALFRAN S.A., 41500 Sevilla. Spain, [2] University of Antioquia, 050010 Medellín. Colombia.
[3]Instituto de Cerámica y Vidrio, CSIC, 28049 Madrid. Spain.

*cbaudin@icv.csic.es

ABSTRACT

One of the most successful innovations in the past decade has been the development of cement-free binders for monolithic refractories, no-cement castables (NCCs). The use of colloidal silica suspensions as bonding component has been widely extended at industrial scale. The major advantages of these castables are a low and fast dry-out, a maximum thermal shock resistance and high mechanical properties. Their success is close linked to development of the microstructure that defines the behavior of the material at high temperatures. However, their installation and transport are more difficult than those of cement castables due to the use of a colloidal silica suspension instead of water. In this context, the use of microsilica powder as a valuable alternative to colloidal silica has been proposed. Recent reports disclose that the flowability behavior and mechanical properties of colloidal silica gel castables and microsilica gel castables are similar. This work deals with the study of the properties of alumina castables fabricated using both silica gel technologies in terms of flowability, setting time, dry-out behavior and mechanical properties. The paper pays special attention to the high temperature strength and Young´s modulus, which determine their performance in the industrial processes.

INTRODUCTION

Along the last years, many investigations have been addressed to the development of calcium free binders for monolithic refractories. The use of colloidal silica gel in no-cement castables (NCCs) has been widely investigated and is extended at the industrial scale. Despite the benefits of castables containing this binder, low and fast dry-out, a maximum thermal shock resistance and high mechanical properties, some well known disadvantages (storage and transportation, frost sensitivity of the suspension, etc.) are also highlighted in many researches [1-3]. In this framework, the use of microsilica powder as a valuable alternative to colloidal silica has been proposed. The incorporation of small contents of calcium aluminate cement (0.5 wt.%) to the dry-mix during its preparation is also recommended, as the binding effect of microsilica gel is carry out by the presence of cations [4].

The success of NCCs is close linked to development of the microstructure that defines the behavior of the material at high temperatures. In this sense, the formation of the equilibrium mullite phase at the use temperature is fundamental for the performance of the materials, and this aspect is usually addressed in the research works. However, the materials need to present sufficient strength at lower temperatures to assure structural integrity of the installation during heating.

Based on these aspects, this work deals with the study of the properties of alumina castables fabricated using both silica gel technologies with the aim of identifying whether microsilica could be an alternative to replace colloidal silica suspension in the castable.

The paper pays special attention to the mechanical behavior at high temperature which determines their performance in the industrial processes.

MATERIALS AND METHODS

Colloidal silica and microsilica alumina castables containing 82.2 wt.% tabular alumina were formulated as summarized in Tab.1 using the Andreasen packing model with q = 0.30. The consistency and fluidity of the mixtures were determined according to ASTM 860. Specimens for testing were cast under vibration.

Specimens cured at 20ºC were used for dilatometry (DIL 402 PC/4, Netzsch, Germany) up to 1500°C and using 5°C/min as heating and cooling rates.

Specimens for mechanical testing (230x65x55 mm) at room temperature were treated at 110°C for 24h and subsequent thermal treatments were performed at 1300, 1400 and 1500°C for 5h using 5ºC/min as heating rate up to 1250, 1350 and 1450ºC, respectively, and then 2ºC/min to the maximum temperature. 5ºC/min was used as cooling rate.

Cold crushing strength (CCS) and cold modulus of rupture (CMOR) were determined using UNE-EN 1402-5. Density and permanent linear changes (PLC) during the thermal treatments were determined according to the ISO 1927:2012 standard.

Cubic specimens (≈ 20x20x20 mm^3) were diamond machined from the tested ones to determine bulk density and apparent porosity according to ASTM CXX; reported results are the average of six determinations and errors are the standard deviation.

After drying the specimens, they were ball milled (< 100 µm, ball mill Retsch, Germany) and mixed to be used for powder characterizations. X-ray diffraction analyses were performed (Bruker D8 Focus, CuKα radiation [λ=1.5418 Å] Ni, scanning step = 0.02).

On the basis of the obtained results, the temperature of 1300^0C was selected for high temperature mechanical characterization in a specially developed testing machine that allows characterizing 6 specimens in a single thermal treatment [6]. Tests were performed in displacement control using a rate of 0.5 mm/min. The load-displacement curves were recorded for each experiment and the engineering stress and strain were calculated assuming linear

elastic relationships. The lateral surfaces of the specimens were observed by macro-photography to identify damage.

RESULTS AND DISCUSSION

Tab. 1: Composition (wt.%) and working properties

Raw materials	Castable	
	DT 95	SioxX 95
Tabular alumina 10 - 0 mm (ALMATIS)	82.2	82.2
Reactive alumina (ALMATIS)	15.1	12.5
Microsilica (ELKEM 971)	2.5	4
MgO	0.2	
CAC 70% A (Secar 712 Kerneos)		0.5
SioxX-Flow / SioxX-Set		3
Coloidal silica suspension (40wt.% solids)	8.5 wt.% respect to solids	
Water (wt. %)		4.1
Setting time (h:min)	2:30	1:00
Flowability (mm)	125	130

As reported in Tab.1, both castables present similar flowability while the setting time of SioxX is the shortest. Densities are also similar and according to those expected in high alumina concretes (Tab. 2). Note that SiOxX 95 presents the lowest apparent porosity for all treatment temperatures and the highest PLC at 1300ºC (Tab. 2). This material also presents the highest CMOR and CCS after treatments at high temperature (Tab. 3).

Tab. 2: Physical properties as a function of temperature

T (ºC)	Property	Castable	
		DT 95	SiOxX 95
1300	PLC (%)	-0.3	-0.7
	Bulk Density (g/cm^3)	3.02 ± 0.04	3.08 ± 0.02
	Apparent Porosity (%)	11.84 ± 0.77	8.45 ± 0.46
1400	PLC (%)	-0.4	-0.4
	Bulk Density (g/cm^3)	3.05 ± 0.02	3.01 ± 0.05
	Apparent Porosity (%)	8.99 ± 0.51	4.53 ± 0.32
1500	PLC (%)	-0.3	-0.1
	Bulk Density (g/cm^3)	3.05 ± 0.02	3.03 ± 0.03
	Apparent Porosity (%)	7.94 ± 0.51	4.00 ± 0.34

It would be necessary to make a detailed microstructural analysis to explain the low CCS value of SiOxX 95 specimens treated at 110ºC as compared to those of DT 95, in spite of their similar values of CMOR.

Tab. 3: Room temperature mechanical properties as a function of the temperature

T (ºC)	Property	Castable	
		DT 95	SiOxX 95
110	CCS (MPa)	82.7	34.0
	CMOR (MPa)	7.8	7.0
1300	CCS (MPa)	121.0	158.2
	CMOR (MPa)	19.0	26.6
1400	CCS (MPa)	130.8	144.3
	CMOR (MPa)	20.6	27.1
1500	CCS (MPa)	110.1	150.5
	CMOR (MPa)	13.5	14.7

Results from the dilatometric tests are shown in Fig. 1. Both compositions experienced significant shrinkages at temperatures ≈1300ºC and the castable prepared using SioxX combination showed additional shrinkage at temperatures in the range 900-1000ºC. For this material PLC was relatively high in specimens treated at 1300ºC (Tab. 2).

XRD revealed that mullite was formed in both materials after firing at 1400 (traces) and 1500ºC while only silica crystalline phases were detected in the materials treated at 1300ºC. Reaction was complete in the material treated at 1500ºC, in which only mullite and corundum were detected.

The above mentioned results revealed that 1300ºC is a critical temperature for both castables, therefore, it was chosen for the mechanical characterization.

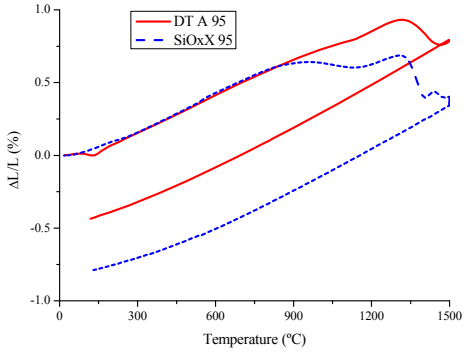

Fig. 1: Results from the dilatometric tests

Results from the mechanical tests at 1300ºC are shown in Fig. 2. For both materials, the specimen tested after the minimum soaking time presented the highest strength and the curves for specimens tested after a minimum of 45 min were similar. Material SioxX showed the highest strength. Both materials presented similar levels of deformation after testing ($\varepsilon \approx 0.1\%$). In the case of material DT 95, such deformation was associated to significant damage, as observed in Fig. 3 a-b in which cracks are observed in the lateral surfaces of tested specimens.

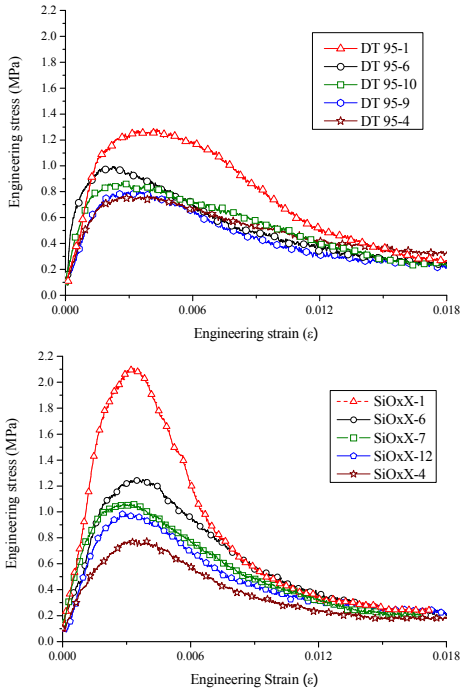

Fig. 2: Results from mechanical tests at 1300ºC.
Specimens nr1 were tested after 30 min soaking time.

The non-lineality of the curves shown in Fig. 2 together with the deformation observed in the specimens demonstrates that significant plastic deformation occurred before the complete failure. In this kind of materials containing free silica, this deformation is associated to viscous flow of liquid phases formed at the testing temperature. Formation of these phases takes time so specimens soaked during the shortest time present higher strength.

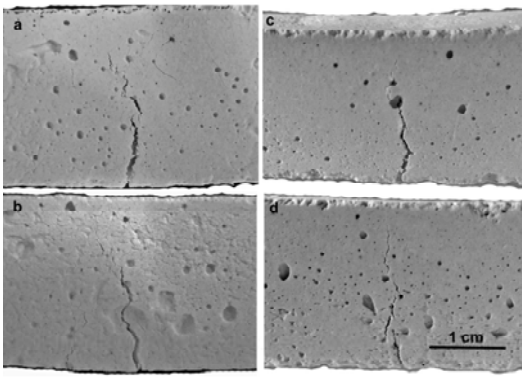

Fig. 3:Lateral surfaces of specimens tested at 1300ºC
a) Castable DT tested after 30 min soaking time
b) Castable DT tested after 45 min soaking time
c) Castable SiOxX tested after 30 min soaking time
d) Castable SiOxX tested after 45 min soaking time

The large differences between the behaviors of the two studied castables that present similar density values and coincident crystalline phases at 1300 ° C, should be due to microstructural differences. Detailed analysis of the microstructures will further clarify this aspect. Potential factors influencing the thermo-mechanical behavior of the materials are the specific additive packages used as activators and the homogeneity of the matrix at the micrometric level. Both factors will be responsible for the behavioral differences between the intermediate silica-rich liquid phases formed in the studied materials. The higher damage and lower strength will be due to increased viscous flow of the liquids.

The "all-in-the-bag" solution, promoted by SioxX that avoids the use of colloidal silica suspension, exhibits improved setting behaviour and slightly improved thermo-mechanical properties at the intermediate temperature 1300ºC. However, further studies should be made in order to understand the potential drawbacks associated to the low values of CCS at 110ºC.

CONCLUSIONS

The properties of alumina castables fabricated using two different silica gel technologies - microsilica powder and colloidal silica suspension additions – has been investigated. The characteristics of the added silica has no influence on the crystalline phases formed at high temperatures (1300-1500ºC).

Both technologies lead to the formation of a liquid phase at intermediate temperatures which composition has to be carefully monitored to limit the extension of viscous flow creep damage at these temperatures at which mullite is not yet formed.

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