VIBROCAST REFRACTORIES-INFLUENCE OF CHAMOTTE GRAINS ON THERMOCHEMICAL PROPERTIES

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ABSTRACT

Refractory materials are designed to have adequate thermochemical and physicochemical properties for the working conditions to which they will be exposed. The vibro-cast method to form refractories is widely employed by refractory producers, mainly for materials to be employed in the glass industry.

In this work three chamottes with different origins and properties were studied in a typical low clay composition. Refractory probes were prepared with an adequate grain size distribution, cast in plaster moulds and calcined at 1420°C for 300 minutes. The textural and mechanical behavior of the materials has been analyzed. The mechanical bending strength, thermal shock resistance, glass attack resistance, density and porosity were determined for these materials.

Results obtained permitted to correlate the mechanical properties and the glass attack resistance with the chamotte used.

1. INTRODUCTION

Refractories based on mullite are extensively employed in the industry of foundry cement, glass, etc. These materials are frequently exposed to severe working conditions, such as mechanochemical and thermal stresses, chemical corrosions and others [1-2].

Refractories based on mullite are manufactured employing different raw materials, but using mainly chamotte grains of variable alumina content. Chamottes are grains shaped with a controlled granulometry. These grains are bounded employing a thin matrix generally composed by clay and an aluminous compound. This matrix generates mullite and glass that form the ceramic bonding of the refractory. In general, it is intended that the clay content will be reduced in order to improve the material quality and have a better dimensional control; however, this content is always conditioned by the manufacture system used since a certain degree of plasticity is always required in the mixtures to be able to shape pieces. Chamotte characteristics determine many of the final properties of the refractory. The chamottes are classified according to the alumina content that determines its refractoriness. Other chamotte properties are also important including porosity, alkali content and mineralogical phases present.

Porosity influences many material characteristics like water adsorption and corrosion resistance. The refractoriness and the service behavior are conditioned by the alkali content, the phases present and the microstructure.

In this study the characteristics of the three chamottes and their influence on the behavior and properties of the materials produced under the same conditions were observed. The materials have been equally formulated regarding the matrix and grain distribution, to observe the influence of the chamotte employed on the final material.

2. MATERIALS AND METHODS

The different chamottes A, R and C were employed to formulate the refractory compositions. The formulations tested had particle size distributions leading to maximum packing with a top particle size below 4-mesh (ASTM). The same grains fractions were used for all chamottes.

The samples contained 70% of coarse and medium chamotte grains. The mullite matrix was generated by reaction between A2G calcined alumina (ALCOA, USA) and a kaolinitic clay (Argentina).

The samples were named A, R and C depending on the chamotte employed.

These mixtures were molded into prismatic test specimens of about 20x20x150 mm. Samples were calcined at 1420°C for 300 minutes with heating and cooling rates of 5°C/min.

The developed crystalline phases were determined by XRD diffraction using a Phillips 3020 Goniometer with PW 3710 controller, Cu-Kα radiation and Ni filter at 40 kV-20mA.

The quantitative determinations were performed by the method of external standards. The glassy phase content was estimated from the background intensity of the XRD patterns.

The bulk density of grains and prismatic specimens were determined for all samples. The apparent porosity and apparent specific gravity were determined for all the prismatic specimens tested.

These tests were performed by water immersion according to the techniques described by the ASTM C-20 standard test method [3] and the bulk density of grains by the ASTM C-357 standard test method (Bulk density of granular refractory materials)[4].

The pore quantity and the pore size distribution of grains were determined by Hg intrusion using Carlo Erba equipment. Dilatometric curves were performed with a Netzsch dilatometer, with a heating rate of 5°C/min, on 50 x 8 x 8 mm^3 calcined samples.

The modulus of rupture was determined by measuring the total load at which the specimen failed in a three-point flexural test. The distance between centerlines of the lower bearing cylinders was 12.0 cm in the entire test (about 80% of the specimen length). The load at failure determinations was carried out with a T22K model J.J. Instrument, using a crosshead speed of 1 mm/min, which corresponds to the load rate required by the ASTM C-133 standard test method (Cold crushing strength and modulus of rupture of refractories) [5].

The thermal shock resistance was determined according to the IRAM 12616 standard test method. This method is based on the determination of the ratio (RMF) between the flexural strengths before and after a double thermal shock as follows: the first step is to introduce the specimen from room temperature to a furnace heated and maintained at 1000°C, the following step is an immersion of the specimen in water at 20°C [6].

The resistance to the glass attack was performed at 1460ºC for 45 hours. Using cast bars for this study.

The test and evaluation were carried out taking into account the glass penetration, corroded area of the probe and the interphase formed.

The moduli of elasticity (E) were measured using a Grindonic equipment [7].

The micrographs on polished samples were obtained using a Scanning Electronic Microscope Phillips 505.

3. RESULTS AND DISCUSSION

3.1. Characteristics of the Chamotte Grains

Table 1 shows the chemical analysis and the mineralogical phases of the three chamottes. Chamotte C is one of the higher alumina and lower alkali content ($Na_2O + K_2O$). The grains A and R are very similar in alumina content but they differ since chamotte A has a significant TiO_2 content and a higher content of other oxides, except for the Fe_2O_3 content. In spite of the high TiO_2 content in chamotte A, crystalline TiO_2 compounds were not detected. Mineralogical phases evaluated by XRD indicate that chamotte C can be considered of higher quality for its mullite content and for its low vitreous phase content. As it was expected and according to the starting alumina contents A as well as R have both cristobalite as secondary phase and some traces of the phases such as feldspars, TiO_2, etc. The chamotte R has quartz as secondary phase, indicating that a low calcination temperature was used. The presence of quartz can produce stress and cracks in the grains.

Table 2 shows some textural characteristics of the chamottes. C has higher bulk density, due to its smaller porosity and greater alumina content. Chamotte R has an excessive porosity, indicating a low manufacturing temperature.

The apparent specific gravity of these materials are near the theoretical values (based on their composition), which explain that the closed porosity would be lower than 3%. Open pore distribution in the samples show differences in the total porosity as well as in the size distribution.

Figure 1 shows that the chamotte R is the most porous having many big pores of about 1 μm. It also shows a bimodal size distribution. C pores are mainly lower than 0.01μm and the penetrated Hg volume shows the lower open porosity. Chamotte A has an intermediate value showing a more homogeneous pore size distribution and having very little porosity as regarding the macropores (>1μm).

Table 1. Chemical analysis and mineralogical phases of the grains.

CHAMOTTE	A	R	C
SiO_2	50.5	56.0	38.4
Al_2O_3	42.2	39.5	58
Fe_2O_3	0.40	1.60	1.15
TiO_2	4.10	1.20	1.90
MgO	0.15	0.30	0.07
CaO	1.80	0.40	0.06
$Na_2O + K_2O$	0.77	1.00	0.18
Mullite	58	55	77
Cristobalite	12	8	--
Quartz	--	11	--
Glass	29	26	23

Table 2. Physical and textural properties of the grains.

Chamotte	Bulk density (g/cm^3)	Apparent porosity (%)	Apparent specific gravity (g/cm^3)
A	2.54	11.2	2.86
R	2.33	17.7	2.83
C	2.72	7.6	2.94

The microstructure Chamotte C is homogeneous with a good porosity distribution (Figure 2). Figure 3 shows (high resolution) well-developed mullite crystals in a relatively small matrix (glassy phase). The pores of chamotte C are of rounded shape, indicating that high calcination temperature were employed.

Chamotte R (Figure 4) presents a homogeneous microstructure, but with high porosity and absence of mullite grains.

Chamotte A (Figure 5) is not homogeneous but with low porosity, comparing with R. This material showed many cracks in its structure due to the presence of TiO_2 (4%) that forms tialite (Al_2TiO_5) during calcinations. In Figure 6 silica cord is observed between two grains of chamotte A.

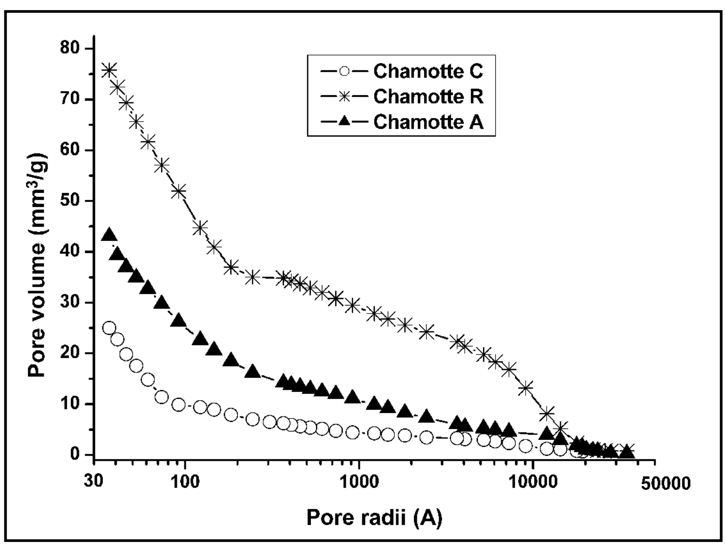

Figure 1. Pore size distribution of the materials formulated with A, R and C grains.

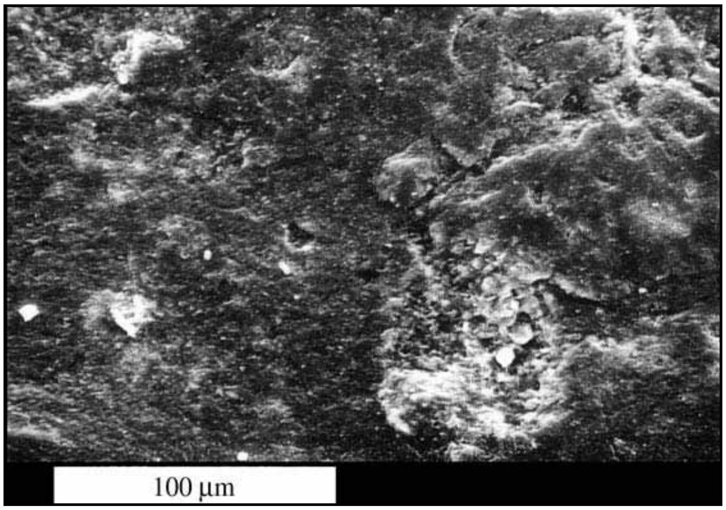

Figure 2. Micrographics (SEM) of the chamotte C grains (white scale bar 100 µm).

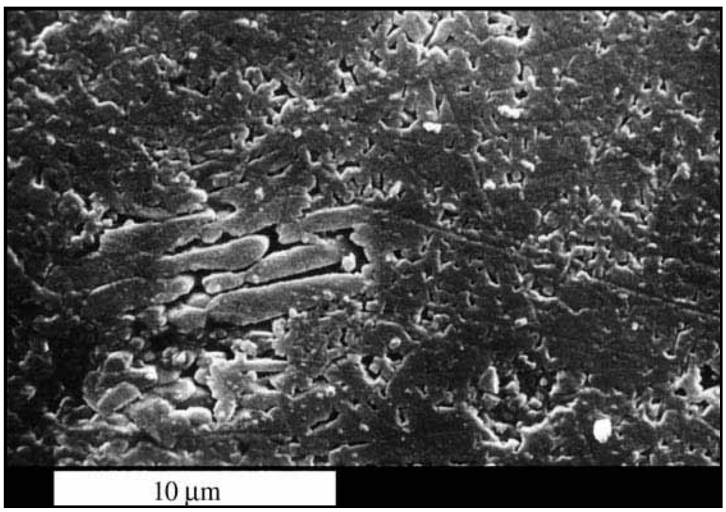

Figure 3. Micrographics (SEM) of the chamotte C grains (white scale bar 10 µm).

3.2. Materials, Preparations and Properties

The chamotte grains are bonded with a matrix of which compositions lead to mullite-Al_2O_3 phases after firing. So, the bonded phases (matrix) are very similar in the three compositions formulated in this study.

Table 3 shows the characteristics of the materials prepared after being calcined at 1420ºC for 5 hours.

Having the materials the same matrix it can be observed the chamotte influence on the final density and on the porosity of the probes. The little difference between the green density and the calcined probe density indicates a low contraction caused by firing. The C material has a lower open porosity, while A and R are very similar. The probes have the same apparent density as those of the grains

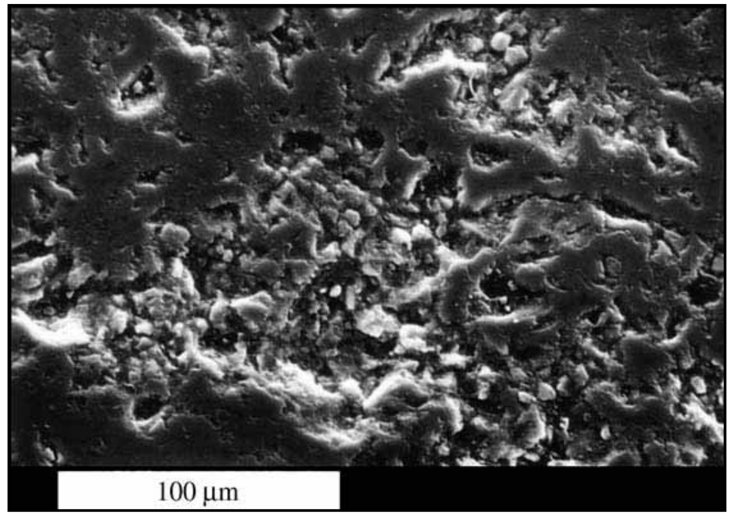

Figure 4. Micrographics (SEM) of the chamotte R grains (white scale bar 100 µm).

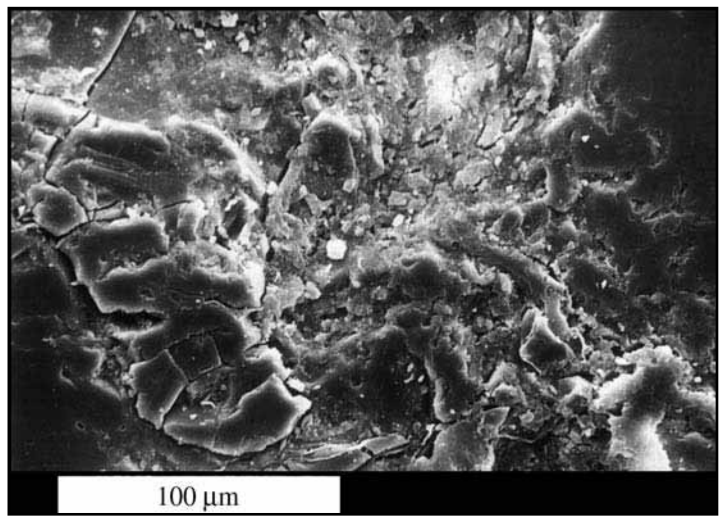

Figure 5. Micrographics (SEM) of the chamotte A grains (white scale bar 100 µm).

which they are composed. The lower bulk density is due to the high porosity of the matrix. This matrix has an open porosity near 30%.

The C material has a greater mechanical flexural resistance and it is almost twice in size compared with A and R due to its more compact structure and its greater mullite content.

The expansion coefficient values (α) indicate that the C material has values similar to those of the mullite (5-6x10^{-6}/°C) whereas A and R have slightly lower values, probably due to the presence of a greater content of a vitreous phase rich in silica. Those differences in expansion coefficient are evidenced by the thermal shock resistance since the moduli relation (RMF) is the greatest for the material made with C grains. This lower resistance to sudden changes in temperature can be explained by the greater α value and the lower

Table 3. Physicochemical properties of the materials prepared with the chamottes A, R and C.

Chamotte	Green density (g/cm^3)	Bulk density (g/cm^3)	Apparent porosity (%)	Apparent specific gravity	MOR (kg/cm^2)	α(200-1200)x10^6/°C	RMF
A	2.30	2.30	20.1	2.80	123.5	4.56	2.01
R	2.15	2.12	21.0	2.70	116.3	4.56	2.06
C	2.40	2.40	18.5	3.00	265.8	5.51	3.71

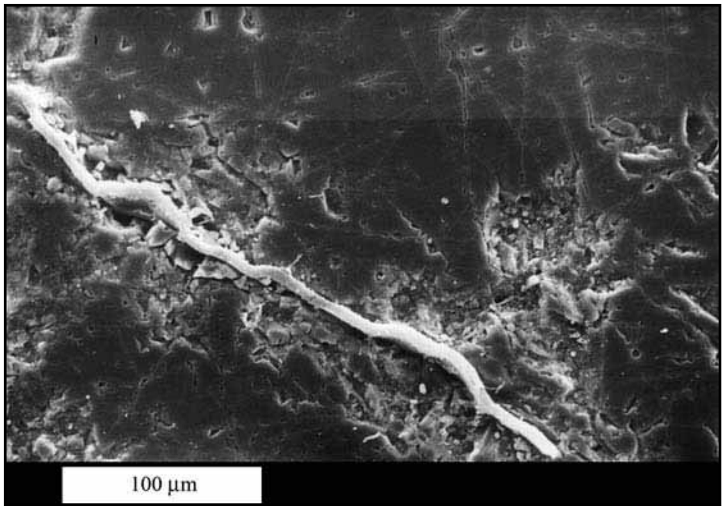

Figure 6. Micrographics (SEM) of the chamotte A grains (white scale bar 100 μm).

total porosity of the materials made with C. The C material has grains with high mechanical resistance and low thermal shock properties, while A and R with grains with high porosity and low hardness which is of low mechanical resistance but good thermal shock resistance. These two factors are more important than the greater content of vitreous phase and cristobalite of the A and R materials.

The refractories under the load of three materials are similar up to the temperature of the test, indicating that the matrix is the responsible for this behavior and that the microstructure of the grains are of low influence in this test.

The moduli of elasticity (E) of these materials must also be taken into account. While C material has an E= 67 GPa the values for A and R are 26 GPa and 32 GPa indicating that they are much more elastic materials and it is well known that more rigid materials as C would have lower thermal shock resistance. The lower E of the A and R materials is probably due to the characteristics of the grains and the total porosity of the materials, which are greater than those of C.

Figure 7 includes images of the cup tests showing glass attack of the three materials. No remarkable difference was observed that could allow predicting the behavior of corrosion by glass. The attack areas measured are similar, but the C sample shows the formation of a colored interphase between material and glass that would diminish the attack at longer times.

CONCLUSIONS

The chamotte grains have influence on mechanical (flexural) resistance and thermal shock resistance of the materials.

The refractories under load and the corrosion by molten glass are mainly controlled by the matrix composition. It should be noted. that the glass attack was made using a cup test (static test) as opposed to a more simulative dynamic test.

The chamotte is important to design a refractory material and many properties and behaviors can be controlled with the chamotte grain quality.

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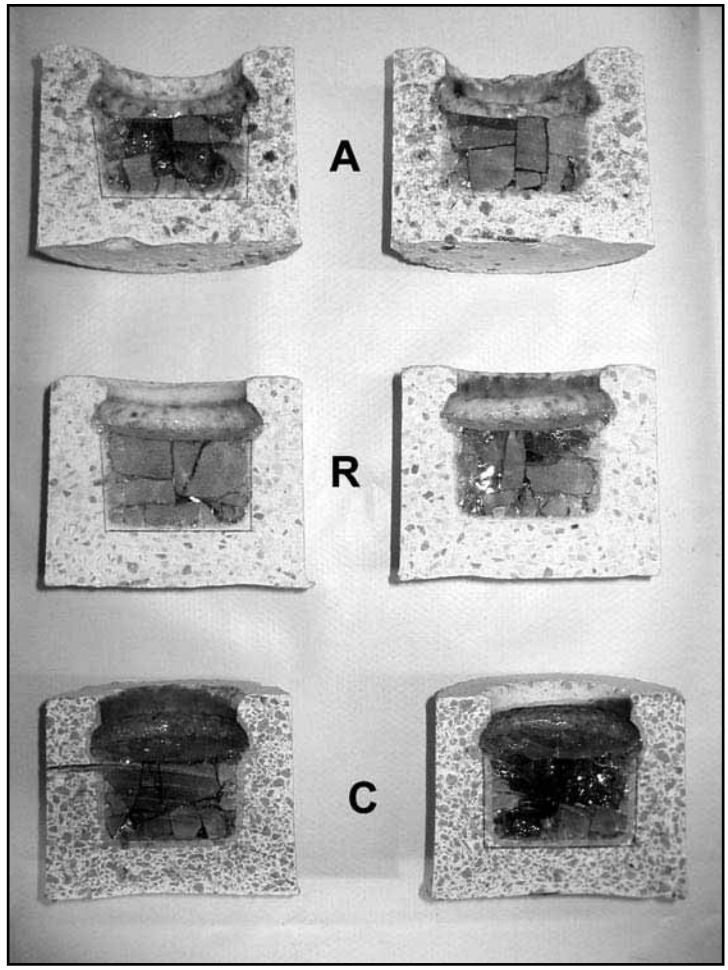

Figure 7. Glass corrosion test of the materials.

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