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High Purity Mullite by Slip Casting Method from Calcined Alumina and Kaolinitic Clay

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Abstract

The mullite – $3Al_2O_3.2SiO_2$-, has different applications, specially in refractory materials, as it is the silicoaluminous refractory material for excellence. The most frequent methods used to prepare mullite are based on the thermal decomposition of clay or kaolin, supplemented with alumina to achieve the desired stoichiometry, or also by mixing silica with alumina with the suitable thermal treatment.

In this work mullites were obtained from two different mixtures of two clays as raw materials (Tincar Súper clay and La Rioja clay) and one source of alumina (calcined alumina) using in both cases a $3Al_2O_3.2SiO_2$ stoichiometry. With the aim of proceeding to formulate synthetic mullite with 3-2 stoichiometry (100 gr of Tincar Super clay with 147.2 gr of calcined alumina (AtinAcal) and 100 gr of La Rioja clay with 80 gr of calcined alumina (AriojAcal)), a suspension of 78 wt% of solids in distilled water was prepared using ammonium polyacrylate as dispersant.

To shape specimens casting method in plaster moulds was used, obtaining probes of 0.80 by 0.80 by 6.0 cm^3, dried at 110° C and later calcined at 1550° C for 4 hours. Probes calcined were characterized by X-Ray diffraction (XRD), modulus of rupture, thermal shock resistance, density and porosity by Archimedes method (open pores), and permanent lineal change with respect to the forming mold.

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Keywords: Mullite, Kaolinitc Clay, Alumina

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1. Introduction

The mullite – $3Al_2O_3.2SiO_2$ –is the silicoaluminous refractory material for excellence. Its high melting point (≈1800°C), good thermal expansion coefficient (≈3-5 10^{-6} $°C^{-1}$), and excellent characteristics to support moderate thermal shocks make it irreplaceable in most of silicoaluminous refractory formulations. G. Aliprandi et al. (1979).
Mullite material has reached a great importance as traditional ceramic material as well as within the advanced ceramics, because of its advantageous thermomechanical properties. This material is a silocoaluminous ceramic oxide which can be presented with many Al/Si relations, since the oxide of those elements can produce solid solutions in certain region of their phase diagram: $Al_{4+2x}Si_{2-2x}O_{10-x}$ where x is between 0.2 and 0.9, although the most usual is $3Al_2O_3.2SiO_2$ or $2Al_2O_3.SiO_2$ corresponding to alumina mass compositions of 71.8% and 77.3% respectively. Bulens et al. (1978) and M. Schmücker et al. (2002).
It is expected in this work that the mullite material will reach a stoichiometry of $3Al_2O_3.2SiO_2$ since this is the silicoaluminous refractory material that is present in most of the refractory materials of technological purpose. H Schneider et al. (2008). The most frequent methods to prepare mullite are based on thermal decomposition of clay or kaolin, supplemented with alumina to reach the stoichiometry expected, or also mixing silica with alumina with the suitable thermal treatment.

There are different processes of shaping specimens to reach varied shapes and structures, some of them are pressing, casting or extrusion. In the present work the shaping of specimens by casting in plaster molds of aqueous suspensions of clays and alumina was studied. Mullites obtained by this method were performed from two different mixtures, using two clays as raw materials (Tincar Super and La Rioja Clays) and one alumina source (calcined alumina). In order to proceed to formulate synthetic mullite with 3-2 stoichiometry stoichiometry (100 gr of Tincar Super clay with 147.2 gr of calcined alumina and 100 gr of La Rioja clay with 80 gr of calcined alumina), a suspension of 78 wt% of solids in distilled water was prepared using ammonium polyacrylate as dispersant.

The aim of this work is to characterize 2 mullites obtained with two different clays and using casting in plaster molds as a shaping process.

2. Experimental procedure

Two types of clays were used in this work (Tincar Super and La Rioja) and one source of alumina (calcined alumina); these raw materials were analyzed and characterized in a previous work. Angela X. Moreno E et al. (2013). Both clays had a grain size distribution lower than 74 μm (mesh # 200 ASTM). Chemical analysis of clays are shown in detail in table 1.

Table 1. Chemical analysis of clays as raw materials.

	Tincar Súper Clay	La Rioja Clay
SiO_2	64.40	44.57
Al_2O_3	24.20	39.60
Na_2O	0.06	0.07
K_2O	0.53	0.39
CaO	0.42	0.05
Fe_2O_3	0.60	0.46
MgO	0.18	0.11
TiO_2	0.49	0.60
PxC	9.12	14.15

In table 1 it can be observed that both clays have silica and alumina in high proportions, characteristics of silicoaluminous clays of kaolinitc base.

In the diffractograms, figure 1, it can be seen that the only crystalline phases present in these clays are quartz and kaolinite, Tincar Súper clay showed greater intensity of quartz, and La Rioja clay greater intensity of kaolinite.

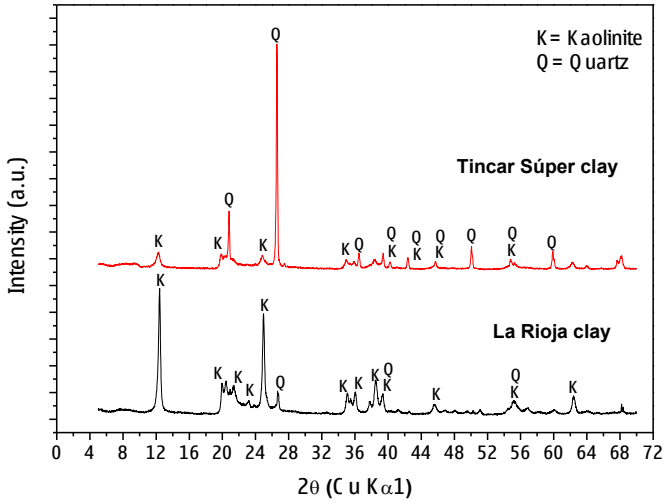

Fig 1 Diffractograms of Tincar Súper and La Rioja clays

From the thermogravimetric analysis it was concluded that Tincar Super clay presented a 43.8 % of kaolinite and La Rioja clay a 96.7% of it, calculated in relation with the loss observed at the ~558 °C peak corresponding to dehydration. Calcined alumina (Almatis A2G) presented an average particle size of 5 μm and a 99.5% purity of Al_2O_3. Angela X. Moreno E et al. (2013).

According with the chemical analysis of the raw materials the mixtures were prepared (each clay with calcined alumina) to produce 3-2 stoichiometric mullite. In table 2 are shown the amounts of calcined alumina mixed for every 100 gr of each type of clay in order to obtain 3-2 mullite when calcined to total conversion. Stoichiometric calculations were made based on the percentage values of Al_2O_3 and SiO_2 of each kind of clay and alumina used.

Table 2. Percentages of mixtures formulation (clay-alumina) with their respectively nomenclature

Nomenclature	Tincar Súper Clay (gr)	La Rioja Clay (gr)	Calcined Alumina at 99.5% (gr)
AtinAcal	100	---	147.15
AriojAcal	---	100	80.04

Mixtures as shown in table 2 were performed in a Hobart mixer. Shaping method of specimens was made by casting, consisting of pouring the mixture suspension in a porous plaster mold whose porosity allows to eliminate water (specimen size was 0.80 x 0.80 x 6.0 cm^3), then the paste consolidates and shrinks making easier to remove the specimen from the mould. Aqueous suspensions had 78 wt% of solids in distilled water, using as dispersant ammonium polyacrylate at 0.5% for both mixtures.

Once casted, specimens stayed in the mould during one day, then were dried at 110°C for one day, then calcined at 1550°C for 4 hours with a heating rate of 5°C/min. Later they were characterized by X-Ray Diffraction (XRD), density and porosity by the Archimedes method, linear variation as regard the mould, rupture modulus to flexion (MOR 1) , elasticity modulus (E1), rupture modulus to flexion and elasticity modulus after thermal shock (MOR 2 and E2). Thermal shock consist of placing specimens into the furnace at 1000°C instantaneously, maintaining them at that temperature for 20 minutes and then to cool them suddenly in water, examining the rupture and elasticity modulus drop after that treatment (MOR2 and E2). N. Rendtorff (2009).

3. Results and discussion

Superposed X-Ray diffractograms of the mixtures (AtinAcal and AriojAcal) produced by the casting method and calcined at 1550°C for 4 hours are shown in figure 2.

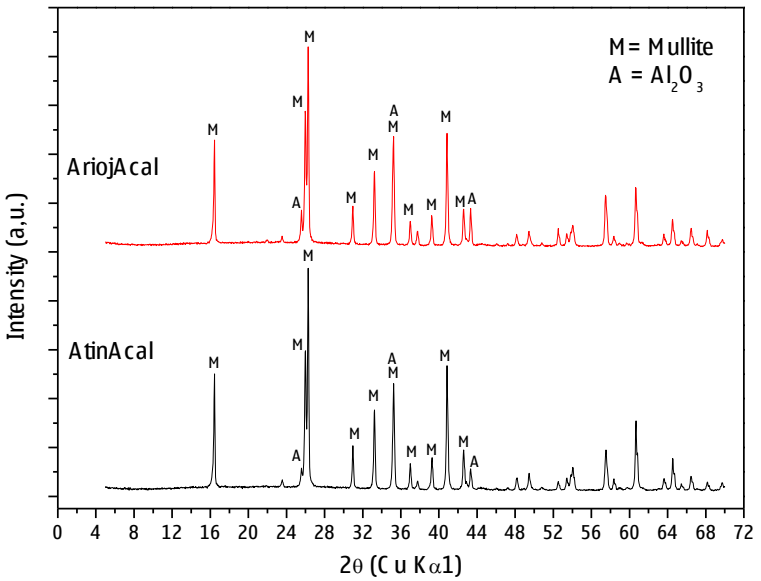

Fig 2. Diffractograms of specimens shaped by the slip casting method, calcined at 1550°C for 4 hours.

Although both samples shown a very good quality of mullite, it was observed that there was a greater conversion in the AtinAcal mixture, by observing the intensity of peaks corresponding to mullite as well as for the lower waste amount of alumina (see figure 2). This is due to the fact that even if both clays were of < 74 μm size, La Rioja clay was harder to mill as its grain size would have been distributed in sizes nearer the 74 μm, being lower its reactivity and then lower its conversion. On the other hand, when clays are mixed with water in order to make a suspensión, the harder one (La Rioja) needs more time to dissolve than the soft one (Tincar Súper), then at equal time of mix proccess the real size of Tincar Super clay in suspensión will be lower than La Rioja.

After submitting specimens to calcinations their physical and thermomechanical properties were evaluated by different methods. The technique used to determine porosity and density was that the standard IRAM 12510 (Archimedes), while the percentage of closed porosity was calculated on the basis of the theoretical value of mullite (3.17 gr), the linear variations was also determined in relation with the length of the mould. Results are shown in table 3.

In table 3 it can be observed that both samples have similar porosity values (open porosity), and shows little differences between densities. The last can be explained by the values obtained of the density in water (density of the solid), observing that AriojAcal has a very near value to the theoretical density (3.17 gr/cm^3), what indicates a low amount of closed pores. However, AtinAcal moved away from that value because of the greater amount of closed porosity. This is a consequence of that AtinAcal has a greater amount of vitreous phase that can contribute to lower density in water, this contribution is not significant enough compared with that generated by closed porosity. AtinAcal showed greater contraction because of its greater amount of impurities that contributed to sintering phenomena, what confirms in turn the great amount of closed porosity mentioned before, because of the greater amount of vitreous phase as just mentioned.

Table 3. Results of physical properties of the mixtures shaped by casting and calcined at 1550°C for 4 hours.

	TINCAR CLAY + CALCINED ALUMINA (AtinAcal)	LA RIOJA CLAY + CALCINED ALUMINA (AriojAcal)
DENSITY(gr/cm^3) (of the specimen)	1.8 ± 0.01	1.9 ± 0.01
DENSITY IN WATER (gr/cm^3) (from solid)	2.9 ± 0.06	3.1 ± 0.03
POROSITY % (Open)	37.3 ± 1.26	37.6 ± 0.76
POROSITY % (Closed)	7.6 ± 0.06	2.5 ± 0.03
LINEAR VARIATION IN RELATION WITH THE MOULD (%)	-3.6 ± 2.85	-2.1 ± 2.12

Results of the thermomechanical properties of both mixtures (AtincAcal and AriojAcal) shaped by the casting method and calcined at 1550°C for 4 hours can be observed in table 4.

Table 4. Results of the thermomechanical properties of the mixtures shaped by casting and calcined at 1550°C for 4 hours.

	TINCAR CLAY + CALCINED ALUMINA (AtinAcal)	LA RIOJA CLAY + CALCINED ALUMINA (AriojAcal)
Modulus of Rupture (MOR 1) (MPa)	45.8 ± 2.16	26.0 ± 2.81
Modulus Rupture (MOR 2) (MPa)	9.6 ± 1.59	10.5 ± 1.88
% Retention	21.0 ± 1.20	40.5 ± 2.07
Elasticity modulus (E1) (GPa)	44.3 ± 4.16	33.8 ± 2.27
Elasticity modulus (E2) (GPa)	27.5 ± 5.72	25.1 ±2.16
Relation between E1 and E2	62.0 ± 2.36	74.3 ± 1.04

In table 4 it can be observed that the results of MOR1 and E1 of the mixture with Tincar clay are greater as regards those of La Rioja, this is because the first one presented a greater amount of closed pores generated by its higher content of vitreous phase produced by impurities, as it was previously mentioned.

The methodology used to induce damages has two steeps. The first one is the tension occurred during the rapid heating from ambient temperature until 1000 ºC, in which some kind of cracks were produced (iniciation), and in a second steep a violent cooling in water produce the propagation of the just mentioned cracks and probably the initiation of new ones. Then the observed values of MOR2 and E2 for the two samples are the consequence of the overall process, without discrimination between initiation or propagation.

As regards the MOR2 and E2 values corresponding to the mixtures calcined at 1550°C and after performing the thermal shock described before, they reflected that the greater the elasticity modulus (E1), the lower its thermal shock resistance (MOR2). This is due to the porosity and the vitreous phase generated within the system as it is the case of AtinAcal. As regards the retention percentage and the relation between elasticity modulus, the AriojAcal shows higher values, due to that mentioned before.

4. Conclusions

Taking into account the results obtained for the materials studied it can concluded as follows:

- Both materials shown high mullite presence, but the AtinAcal presented higher conversion and lower amount of waste alumina, as it was observed by XRD.
- In relation with values obtained for the density in water (solid density), AriojAcal has a value near the theoretical density (3.17 gr/cm3) indicating a low amount of closed pores.
- AtinAcal mixture showed a greater shrink due to its higher content of fluxing impurities and thus greater sinterization.
- MOR1 and E1 values were greater for the AtinAcal mixture.

- Thermal shock demonstrates that the greater the elasticity modulus (E1), the lower it's the thermal shock resistance.

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