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Highly refractory mullite obtained through the route of hydroxyhydrogels

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ABSTRACT

Depending on the features required from refractory materials, such as the handling of extreme conditions of temperature and pressure, there is a high demand in industry and home for these resources; their reliability must be assured and the resulting high cost can only be eased by mass production. The search for new refractory materials, which are more reliable and less expensive, has focused research on a material like mullite, which offers a very high refractoriness.

In the present work, the synthesis of mullite was achieved by the route of the hydroxyhydrogels; dried colloidal silica and aluminium hydroxide gel were used as raw materials; the mullite was obtained with reduced processing time and cost than contrasting with conventional methods. The resulting products were analyzed by X-ray diffractometry (XRD), scanning electron micrography (SEM) and pyrometric equivalent cone (PCE) to conclude that an extremely competitive refractory material can be obtained through this method.

1. Introduction

Mullite is a silicoaluminate mineral rarely found in nature it is formed under very special conditions of temperature and pressure, it is considered part of the silimanite group Al_2SiO_5 (Aksay et al., 1991; Schneider et al., 2008) and, at high temperatures and 1 atm pressure, it is the only crystalline stable phase of the silica–alumina system (Jovani et al., 1979; Sales and Alarcón, 1994; Somiya and Hirata, 1991). In the industry, silicoaluminate compositions such mullite, constitute 70% of the used refractory materials (Schneider et al., 2008; Jovani et al., 1979). There is a tendency towards the consumption of refractory materials with high and very high alumina content due to the highest temperatures and more extreme conditions to which they are subjected and to their incidence in the production costs to the users.

The importance of mullite formation in refractory products, fundamentally responds to the fact that mullite is the only stable compound of alumina and silica at high temperatures under ordinary pressures (Juettner et al., 2007), and the other aluminium silicates, such as silimanite, andalucite and cyanite, become mullite at temperatures of 1545 °C, 1390 °C and 1370 °C, respectively (Tcheichvili and Butschkowskyi, 1975). Besides, mullite confers interesting properties to the materials that contain it, such as chemical stability, mechanical resistance, low thermal expansion at high temperatures, and thermal impact strength (Schneider et al., 1994; Villar Castro et al., 2004; Jain, 1996; Ananthakumar et al., 2006).

In general, microstructure formation of mullite and refractory materials depends on many factors such as raw materials characteristics, nature and concentration of sludges, calcination temperature, processing time, kiln atmosphere, pressure

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Table 1 – General properties of mullite

Property	Value	Authors	
Formula weight	0.425 kg/mol		
Crystal system		Burnham	
Orthorhombic	$a = 0.7584 – 0.003$ nm $B = 0.7693 – 0.003$ nm $c = 0.2890 – 0.001$ nm		
Unit cell volume	16.861–20 nm^3		
Theoretical density	3160–3220 kg/m^3	Burnham	
Melting point	1850 °C	Aramaki and Roy	
Hardness (Mohs)	7.5	Grofcsik and Tamas	
Refractive index (n_D)	1.65	Grofcsik and Tamas	
Birefringence	0.012	Grofcsik and Tamas	
Optical character	Positive	Grofcsik and Tamas	
Crystal habit	Acicular or prismatic	Lohre and Urban	
		d	I/I^0
Position and intensities of three strongest X-ray reflections		3.428	95
		3.390	100
		2.206	60

during calcination and phases distribution on the initial system. More importantly, it depends on the treatment of the system, the previous mechanical treatment, the blending of the components and the heat treatment during firing (Jovani et al., 1979; Skoog and Moore, 1988). Some mullite properties are presented in Table 1.

The orthorhombic symmetry and the atomic structure are responsible for the frequently acicular shape of mullite crystals. These structural characteristics do not seem to be related to the composition (ranging from 3:2 to 2:1) but to the used method in its production (Skoog and Moore, 1988; Douy, 2006; De Sola Ruiz et al., 2005).

The regular methods for producing mullite are by thermal decomposition of kaolinite (or other similar materials) (Juettner et al., 2007; Mazdiyasni and Brown, 1972; Kolli et al., 2007) at 1850 °C firing temperature, or by processes involving mixtures of pure Al_2O_3 and SiO_2 (usually with excess of Al_2O_3) (Tcheichvili and Butschkowskyi, 1975). New technologies such as sol–gel, hydrothermal synthesis, pyrolysis, CVD, ceramic powders combustion and synthesis of hydroxyhydrogels have been developed (Somiya and Hirata, 1991; Samanta et al., 2001; Ismail et al., 1987; Pask et al., 1987; Segal, 1989; Tucker et al., 1990; Basu et al., 2006; Bhattacharyya and Ghatak, 2007; Kurajica et al., 2007).

The chemical route of hydroxyhydrogels produces material with higher purity than the regular processes, with a similar quality to the ones obtained by sol–gel and other new methods. In this research, the hydroxyhydrogels route was used aiming a decrease in processing time and the temperature with an optimization of dispersion, gelation and thermal treatment.

2. Experimental

The chemical route of hydroxyhydrogels was applied using silica and alumina precursors to obtain a three-dimensional inorganic network. Under high shear, the precursors form colloidal or molecular aqueous solutions that polymerize into an inorganic network. Then, with the addition of a gelling agent at room temperature the network is stabilized and immobilized (Samanta et al., 2001; Basu et al., 2006; Meher et al., 2005). The material was dried and thermal treated according to the DTA data of each case.

Some factors that affect the process are the type of precursor, the pH, the temperature and the thermal treatment length. To generate very fine sizes particles in an aqueous medium, the principles of chemistry of colloids were used in this route (Basu et al., 2006; Meher et al., 2005; Burgos-Montes et al., 2007; Wasan et al., 2005; da Costa et al., 2003). The hydroxyhydrogels were prepared from colloidal silica (Glassven, SiO_2, 99.8%; superficial area of 200 m^2/g), aluminum hydroxide gel (DisproAlquímicos; 9.5% of Al_2O_3) and some additives like antifoams, dispersants and flocculants. The experiments were carried out under normal laboratory conditions.

Dispersion took place in a “rotor-stator” mixer (Heidolph DIAX 900). The dried colloidal silica, the aluminium hydroxide gel, the water, the antifoaming agent and the dispersant were mixed at a high shear stress in order to achieve an “intimate contact mix” between the alumina and the silica particles, to induce the aluminium hydroxide and colloidal silica molecules hydrolysis. It is believed that a polymerization process takes place at this stage (Li et al., 1997) and silica and alumina macro-molecules are formed (Basu et al., 2006), as it is shown in Fig. 1.

Immediately after dispersion, a flocculant agent was added to produce a gel. Afterwards, the gel was subjected again at high shear to obtain a well-homogenized mixture. At this stage, the particle aggregation state is reflected in the high viscosity, and it is already possible to find linked particles. The gel formation leads to a three-dimensional solid structural network able to fix the remaining solvent and to exhibit visco-elastic properties. The gel sedimentation volume is similar to the original solution one; therefore it is guaranteed that segregation of the components does not take place.

The thermal treatment was designed according to the endothermic and exothermic reactions registered in a differential–thermal-analysis (DTA), carried out in an equipment of TA Instruments, Model 160. Table 2 shows the thermal treatment conditions. Some samples were dried at 100 °C in a stove and then macerated and fired in a Sentro Tech Corp INC-1700X oven. The other ones were fired without drying and macerated.

The crystalline phases were characterized using X-ray diffraction analysis (XRD) in a RIGKU miniflex diffractometer

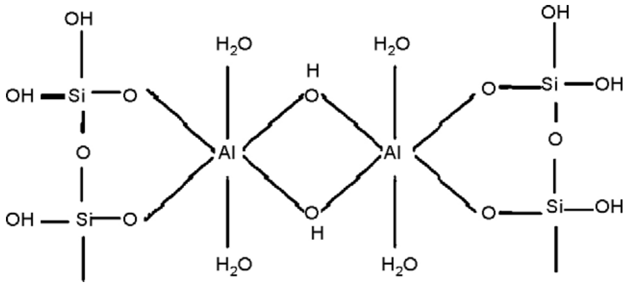

Fig. 1 – Macro-molecules formed in silica and alumina hydroxyhydrogels.

Table 2 – Thermal treatment conditions

Sample	Dried	Firing temperature (°C)	Firing time (h)
MURG 1300	X	1300	10
MURG 1500A	X	1500	4
MURG 1500B		1500	4

Table 3 – Chemical analysis of the obtained material

	1300 °C × 10 h sample	1500 °C × 4 h sample
Na_2O	1.53%	0.95%
MgO	0.34%	0.35%
Al_2O_3	73.68%	75.08%
SiO_2	23.90%	22.84%
P_2O_5	0.00%	0.00%
K_2O	0.16%	0.19%
CaO	0.41%	0.40%
TiO_2	0.11%	0.10%
Fe_2O_3	0.05%	0.09%

(Cu Kα radiation). X-ray fluorescence was chosen to check out the system stoichiometry. The scanning electron microscopy analyses (SEM) were carried out in a JEOL JSM-5910LV to describe the morphology of the particles. Finally, the material refractoriness was determined using the "pyrometric cone equivalent test" (PCE) (Chesters, 1957).

3. Results and discussion

The XRD of the fired samples and the corresponding indexation patterns are shown in Fig. 2 (Mincryst pdf 2994 y 1029) (CCDMSA, 2006). Two phases were identified: α-Al_2O_3 and mullite; this last one was well crystallized and with a 3:2 alumina–silica ratio in samples fired at 1300 °C and at 1500 °C.

XRD analyses show that samples with and without a previous drying process have a very high quality of crystallinity, with the last one have a higher sintering degree, probably because they have differences in the initial porosity of the materials. The gel that was directly fired, had probably a lower porosity than the macerated and pressed one, obtaining a more sintered material using it.

The obtained mullite crystals present an acicular form, whereas the α-alumina are recognized by their hexagonal plates (Fig. 3). In the samples obtained at 1500 °C, an excellent mullitization and neck formation between particles are observed, probably due to sintering.

Table 3 shows the results of the chemical analyses. The sample treated at 1300 °C was found to have an alumina–silica molar ratio of 1.8, while the sample treated at 1500 °C had a 1.9 ratio. This confirms that there is an excess of alumina in the samples, since the mullite 3:2 stoichiometric relationship is 1.5. It can also be observed in Table 3 that there are appreciable quantities of Na_2O, MgO and CaO in the product. These impurities are associated with contamination of raw materials.

The refractoriness analysis of the samples showed a PCE higher than the Orton 37 cone; therefore, the material maintains its chemical and dimensional stability up to 1820 °C. The PCE tests also showed that the cones did not suffer any appreciable deformation, indicating that their refractoriness could be even higher. These results reveal that the sodium content in the samples does not affect the final product, and the excess of alumina can even help the refractoriness of the final material.

The X-ray and the electron microscopy showed two crystalline phases, mullite needles and α-aluminium oxide (corundum) plates, confirming the used experimental stoichiometric relationship (75% in alumina by weight). The products obtained by this synthesis route, based on hydroxyhydrogels, are located in the solid solution region of the phases diagram of mullite–corundum (Fig. 4). From this diagram, it is also deduced that this material will probably maintain its refractory properties up to 1832 °C.

Using the hydroxyhydrogels route of synthesis, it is possible to obtain pure mullite at 1500 °C in 4 h and at 1300 °C in 10 h, which is a considerably less demanding energy method than with traditional methods like melting or thermal decomposi-

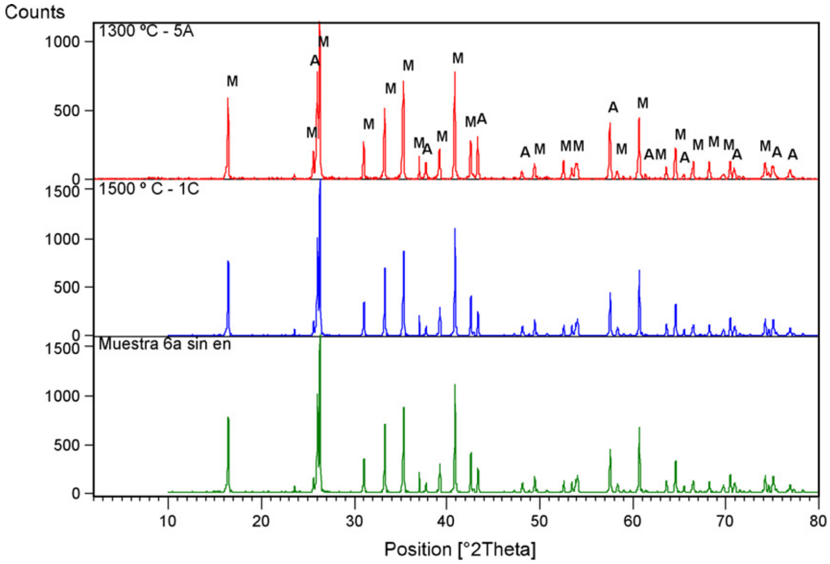

Fig. 2 – XRD patterns of the samples obtained. M: mullite, A: α-Alumina.

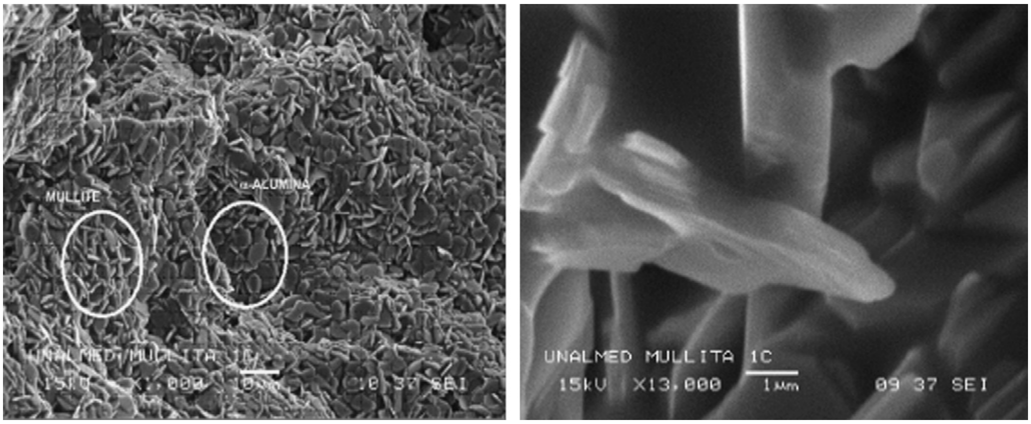

Fig. 3 – Photomicrographies SEM of the obtained samples of mullite.

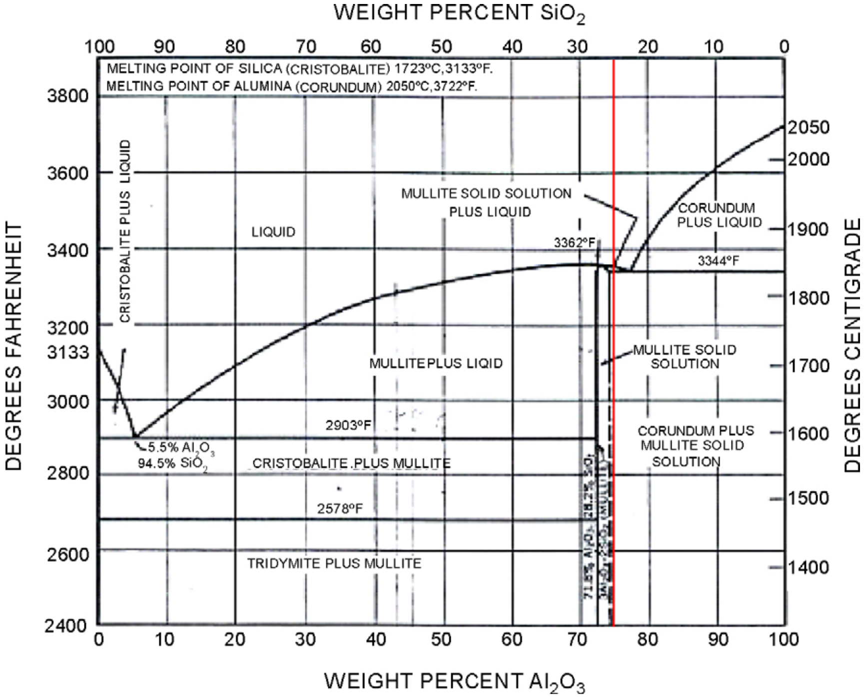

Fig. 4 – The binary system Al_2O_3–SiO_2.

tion. In colloidal systems, mullite has been produced by other authors at 1700 °C in 96 h (Sanchez Conde, 1996). In chemical processes, as the sol–gel method, it is possible to obtain it below 1500 °C. However the cost of sol–gel route is higher than the one proposed here by the use of alcoxides as precursor.

The hydroxyhydrogels route seems to be a good alternative for the ceramic processing, since it gives special characteristics to products such as high purity, homogeneity, crystallinity and it is more efficient in terms of energy consumption.

4. Conclusions

High quality crystallized mullite has been obtained at 1500 °C in 4 h through the route of the hydroxyhydrogels.

Monophasic gels of very high homogeneity were produced using raw materials with high superficial area, mechanical dispersion processes and some additives. Besides, the dispersant addition seems to contribute to the speed reaction, since it probably helps the colloidal silica polymerization, and prevents the mixture components segregation.

The time and the processing temperatures needed to obtain mullite were considerably reduced in contrast with the standards, and the product showed high refractoriness, according the PCE test results.

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