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Development and characterization of porous moldable refractory structures of the alumina-mullite-quartz system

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ABSTRACT

Efforts to reduce energy consumption have led to the increasing use of microporous refractory ceramics as high-temperature thermal insulation materials. One of the techniques to produce these materials is based on the generation of pores through the phase transformation of hydroxyl or carbonate compounds. This method does not release toxic volatiles but prolonged use at high temperatures limits its use, because the transition compounds that are formed after dehydroxylation/decarbonation tend to accelerate densification, reducing the system's total porosity. The aim of this work was to produce porous moldable ceramics from alumina, aluminum hydroxide and a source of silica (quartz), using the reaction of alumina and quartz in order to form mullite, a compound that is able to decrease densification rates at high temperatures. The samples were sintered between 1100 °C and 1500 °C and characterized by porosity measurements, modulus of elasticity, compressive strength, X-ray diffraction, dilatometry, mercury porosimetry, and scanning electron microscopy. The results indicated that high levels of porosity were preserved up to 1500 °C owing to the formation of mullite.

1. Introduction

The development and optimization of porous ceramics are considered strategic owing to the broad range of technological fields in which they are applied, *e.g.*, catalysts, furnace linings, kiln furniture, environment filters for hot gases and diesel engines, fabrication of glasses and thermal isolators. The properties of porous ceramics render them suitable for a wide variety of applications, especially for high temperatures and aggressive chemical environments where metal and polymer-based materials cannot be used. The development of porous ceramics that combine low thermal conductivity, reasonable mechanical strength, chemical inertness and refractoriness is vital for specific applications in high-temperature thermal insulation [1–9].

Among the existing porous ceramics manufacturing methods, the most popular one involves the addition of porogenic compounds such as organic particulates, *e.g.* starch, or hydroxylated or carbonated inorganic compounds such as $Al(OH)_3$and $CaCO_3$, to dense matrices. In the latter case, pores are generated by the decomposition of porogenic agents and the final microstructure is influenced by the presence of transition phases. The competitive advantages of controlled decomposition of hydroxides include the fact that they release only nontoxic volatiles and that they require the same processing additives, deflocculants and binders used in processing the corresponding matrices [10–14].

Pure porous alumina samples can be produced by sintering Al_2O_3-$Al(OH)_3$ systems. Initially, the green ceramic body is composed of a mixture of α-Al_2O_3 (fused or tabular ceramic) and $Al(OH)_3$ particles, formed by pressing, gel casting or other methods. $Al(OH)_3$ decomposes at temperatures ranging from 200 °C to 500 °C, according to the general equation:

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

Dehydration is followed simultaneously by an increase in density and the formation of a large volume of internal mesopores. After sintering at 1100 °C, the microstructure undergoes a transformation: the relatively dense alumina compact (Fig. 1a) turns into alumina particle agglomerates surrounded by partially decomposed aluminum hydroxide particles (Fig. 1b). The microstructure is porous, which decreases the mechanical properties of this system. Raising the sintering temperature to 1300 °C (Fig. 1c) increases the samples' density and mechanical strength owing to the onset of densification and coarsening of filamentous pores at the surface of transition alumina particles, which occurs simultaneously to a change in the number and diameter of original pores. At 1500 °C (Fig. 1d), there is a visible presence of small rounded α-alumina particles, which have a strong tendency to sinter. In samples sintered at 1500 °C, larger

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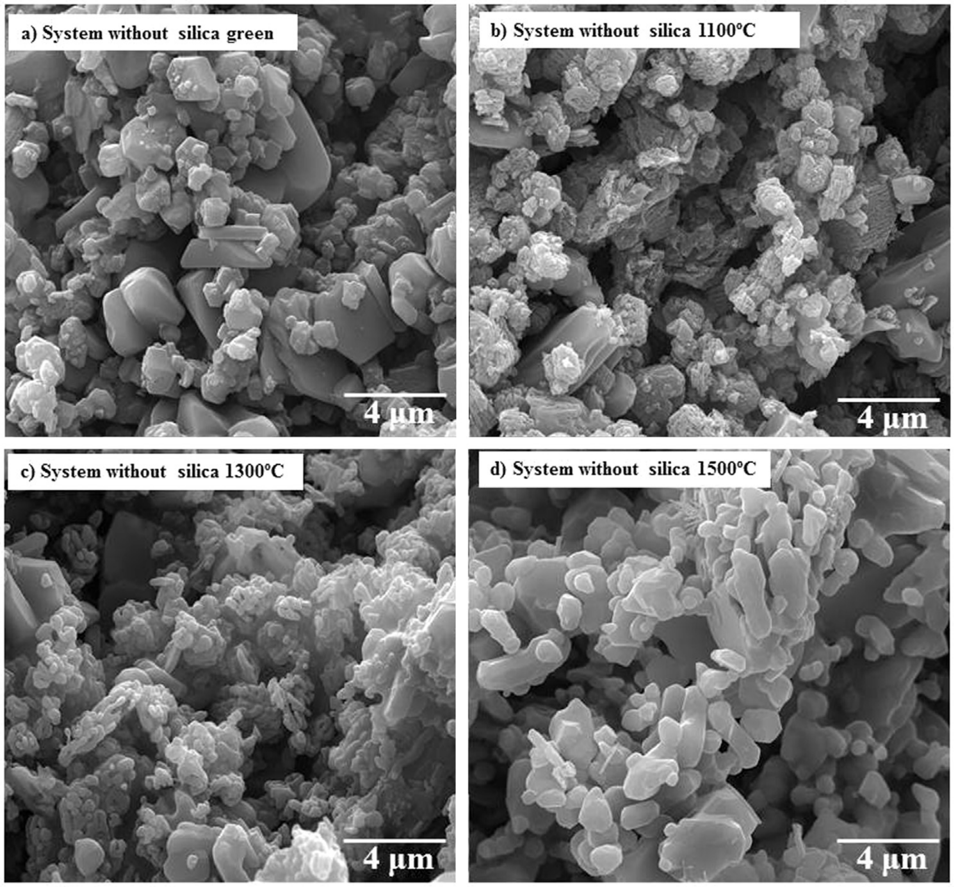

Fig. 1. SEM micrographs of Al_2O_3-$Al(OH)_3$ sintered at different temperatures: (a) Green samples, (b) 1100 °C, (c) 1300 °C, and (d) 1500 °C.

Table 1
Tested compositions.

Raw materials		Compositions (vol%/mass%)			
		00QZ	02QZ	04QZ[a]	06 QZ
CA (Calcined Alumina)	50 vol%	45.00/ 56.66	30.50/ 41.72	16.35/ 24.42	2.35/3.68
AH (Aluminum Hydroxide)		45.00/ 34.75	45.00/ 37.75	45.00/ 41.22	45.00/ 45.35
QZ (Quartz)		0.00/0.00	14.50/ 11.20	28.65/ 24.17	42.65/ 39.58
HA (Hydratable Alumina)		10.00/ 11.20	10.00/ 9.33	10.00/ 10.19	10.00/ 11.21
Water	50 vol%	50.00/ 24.03	50.00/ 24.03	50.00/ 24.03	50.00/ 24.03
Dispersant (mass%)		0.07	0.09	0.11	0.13
Silica Molar Fraction		0.00	0.20	0.40	0.60

[a] Composition for the formation of 100% stoichiometric mullite.

aluminum hydroxide and calcined alumina grains are not clearly distinguishable, which confirms that the structure is less porous than those sintered at lower temperatures.

Due to the simultaneous phenomena of dehydration, volumetric shrinkage and densification, a variety of transition phases, porosity levels and specific surfaces can be produced, depending on the $Al(OH)_3$ content and the heating parameters. Compositions with up to 70 vol% of $Al(OH)_3$ form highly porous structures (above 50%, sintered at 1100–1200 °C) with fairly good mechanical properties.

Despite the significant scientific and technological advances in recent decades, porous ceramics still present a challenging aspect: in general, prolonged operation at temperatures above 1100 °C reduces the porosity of these ceramics because of densification and grain growth. This phenomenon precludes their use in applications involving continuous exposure to high temperatures, such as thermal insulators. Therefore, to ensure the performance and stability of porous ceramics at high temperatures, mechanisms to preserve their porosity are required. An alternative is the use of compounds that are intrinsically difficult to densify, such as spinel ($MgAl_2O_3$), calcium hexa-aluminate

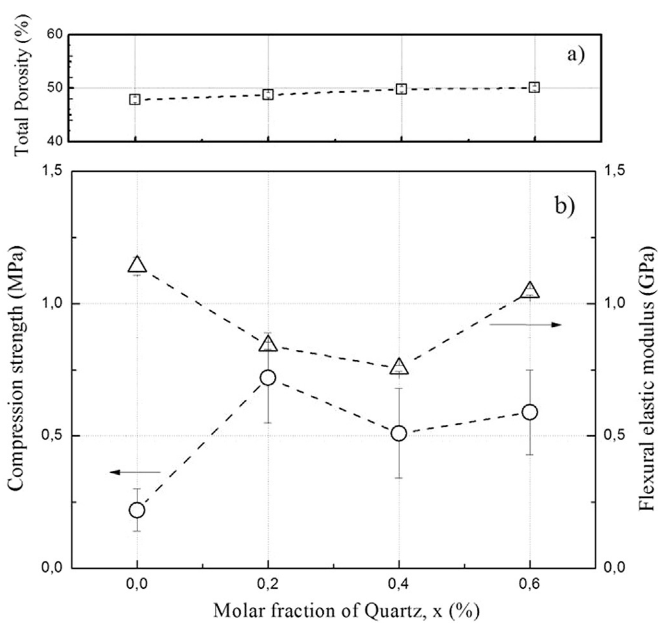

Fig. 2. (a) Geometric Total Porosity; (b) Modulus of elasticity (E) and Compressive Strength (σ) of green samples with different quartz contents.