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Development of densification-resistant castable porous structures from *in situ* mullite

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Abstract

Ceramic porous structures are technologically important materials for several high-temperature applications. Many recent studies have aimed at increasing their temperature of use and refractoriness, preserving their pores characteristics (content, shape, and permeability) and creating different forming and placing techniques. The present manuscript reports on the development of highly porous castable structures based on mullite ($3Al_2O_3 \cdot 2SiO_2$) formed *in situ* from calcined and hydratable alumina, aluminum hydroxide and amorphous silica. The evolution of their physical properties and microstructure during thermal treatment was evaluated by mechanical (compression strength and elastic modulus) and dilatometric tests, porosity measurements, X-ray diffraction and scanning electron microscopy. The results indicate the mullite's intrinsic difficulty for densification (which is a detrimental effect in the production of dense parts) can be a powerful mechanism to prevent porosity loss at high temperatures.

Keywords: Porous ceramics; *In situ* mullite; Castable; Aluminum hydroxide; Amorphous silica

1. Introduction

1.1. Al_2O_3–$Al(OH)_3$ porous ceramics

Catalysts, filters for hot gas (above 1000 °C) and molten metals, and thermal insulators are manufactured from porous ceramics due to their unique combination of high refractoriness, resistance to corrosion, creep and thermal shock, and versatility to be produced in several tunable microstructures [1–3]. The most common methods for the production of such materials involve the addition of porogenic agents to a ceramic matrix. The literature describes many combinations of ceramic phases (Al_2O_3, SiO_2, ZrO_2, $MgAl_2O_4$, SiC, amongst others) with organic particles (starch, casein, chitosan, alginate, polymer latexes, saw-dust) and foams (stabilized with surfactants and nanoparticles) [2,4–6]. Particles of inorganic hydroxylated or carbonated compounds can also be used as pore generators [7–9] and offer important technological advantages: i) they can be easily added to many matrixes through standard equipment and additives; ii) during the forming step, the structure attained is less sensitive to variations in the environmental and application conditions; iii) they do not release toxic volatiles during the first heatup.

The Al_2O_3–$Al(OH)_3$ system is the most explored example of this technique [2,4,5,8,9] and its mechanism of pore formation involves a two-step process, described as follows [2,5,8,9]. 1) $Al(OH)_3$ particles are consolidated with the Al_2O_3 (α-Al_2O_3, from calcined alumina, for instance) ones by means of pressing or use of a binding agent. 2) During dehydroxilation, $Al(OH)_3$ shrinks and decomposes into transition phases (χ-Al_2O_3 and κ-Al_2O_3, for example), which generates intense cracking on the particles' surfaces [10–14]. The combination of these effects can generate porosity levels higher than 70% [5,9]; however, when the temperature reaches 1100–1200 °C, the transition Al_2O_3 particles promote intense sintering with the α-Al_2O_3 matrix, which reduces the total porosity levels at the same time the average pore size increases significantly [9,14]. Consequences of this behavior

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Table 1
Characteristics of the different routes for the production of mullite.

Characteristics	**Preparation methods**		
	Fused-mullite	**Chemical-mullite**	**Sinter-mullite**
Useful references	[19–21,26,34,35,45]	[16,17,20,27,28,44]	[19,20,22,24,29–32,41,42,44]
Principle	Raw materials are melt in electric furnaces, cooled at room temperature and milled	Al^{3+} and Si^{4+} mixed at atomic level are produced by chemical processes (sol–gel, coprecipitation, hydrolysis, and chemical vapor deposition) and calcined	Solid state diffusion-controlled reactions or *via* transient liquid-phase reaction, with Al^{3+}, Si^{4+} and O^{2-} interdiffusion
Temperature range	> 2000 °C	500–1300 °C	1200–1700 °C
Raw materials	Oxides (Bayer alumina, quartz sand, fused silica), hydroxides ($Al(OH)_3$) and clay minerals (bauxite and kaolinite)	High purity sols, salts, and Al–Si–alkoxides	Micrometric sized oxides, hydroxides ($Al(OH)_3$, $AlO(OH)$), and clay minerals ($2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$)
Parameters that affect reaction, final composition and microstructure	Cooling rate and presence of glassy phase	Degree of Al^{3+} and Si^{4+} proximity; calcination conditions	Particles size, surface area and degree of proximity; heating schedule; reaction temperature; amorphous/crystalline reactants
Contaminants	No contaminants (if high-purity reactants are used)	No contaminants (if high-purity reactants are used)	Presence of glassy phases on boundaries. Non-reacted material at particles' cores
Microstructure of the product formed	Long-prismatic to acicular crystals; monocrystalline cornered and angular particles (after milling)	Nano-micrometric particles of several possible shapes (equiaxial, spherical, continuous thin film)	Equiaxial (high-purity reactants) or acicular (in presence of glassy phases) grains

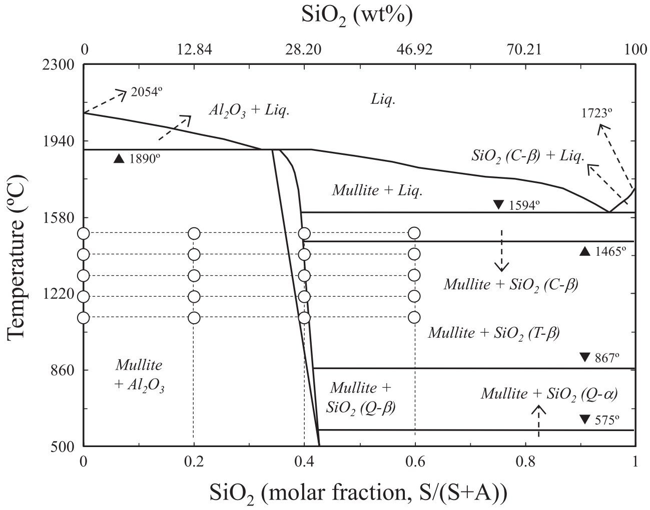

Fig. 1. Alumina (Al_2O_3 or A)–Silica (SiO_2 or S) phase diagram [33–39]. Open circles represent the composition-temperature conditions tested (see Table 3 for a detailed description). Q-α: Quartz-α; Q-β: Quartz-β; T-β: Tridymit-β; C-β: Cristobalite-β.

involve reduction in permeability, mechanical strength, thermal shock resistance, and structure's ability for thermal insulation [2,5,9,14]. To overcome such drawbacks, several authors have proposed the use of *in situ* solid state reactions that generate large contents of pores and low density products concomitantly (to promote volumetric expansion and avoid the Al_2O_3 matrix densification) [2].

The combination of Al_2O_3 and hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$) produces a highly porous structure comprised of spinel ($MgAl_2O_4$) particles formed *in situ* [2]. The dehydroxilation and decarbonation reactions of hydrotalcite generate large contents of pores at temperatures between 230 °C and 450 °C. The solid-state reaction between the MgO and Al_2O_3 formed and the Al_2O_3 present in the matrix produces spinel, which hinders the densification of the structure by means of three effects: 1) spinel formation, which is expansive and tends to keep particles apart (because of the mismatch amongst $\rho_{MgO} = 3.5\ g\ cm^{-3}$, $\rho_{Al2O3} = 4.0\ g\ cm^{-3}$ and $\rho_{MgAl2O4} = 3.2\ g\ cm^{-3}$); 2) its low sintering rate due to the occurrence of the inter-diffusion of Mg^{2+} and Al^{3+} ions at different rates in Al_2O_3 and MgO, respectively; 3) grain growth, which occurs more easily than densification because spinel is a solid solution with a large interval of composition and temperature and no precipitated phases at its grain boundaries [2,15]. Inspired by these results, we propose here the use of *in situ* generated mullite ($3Al_2O_3 \cdot 2SiO_2$) as a porosity preservation mechanism in a system comprised by calcined alumina (α-Al_2O_3), hydratable alumina (hydraulic binder), $Al(OH)_3$ (gibbsite, as porogenic agent) and amorphous silica (SiO_2) [16,17].

Mullite ($3Al_2O_3 \cdot 2SiO_2$ or $Al_6Si_2O_{13}$) is a raw material widely used in refractory ceramics due to its microstructure stability [18–20] and resistance to chemical attack [21–24] and thermal shock (a combination of high fracture energy and low thermal conductivity and expansion coefficient) [18,19,22,25]. Rare in natural occurrences, synthetic mullite can be prepared by three main routes [20,23]: fusion in electric furnaces [19–21,26], calcination of chemically prepared precursors [20,27,28] and *in situ* reaction that generates sinter-mullite [24,29–32]. Each process has several variations and produces mullite structures and particles of different characteristics (Table 1). The next section provides a more detailed explanation of the *in situ* process.