Journal of the European Ceramic Society 37 (2017) 2849–2856

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Porous co-continuous mullite structures obtained from sintered aluminum hydroxide and synthetic amorphous silica

Rafael Salomão*, Leandro Fernandes

Materials Engineering Department, São Carlos School of Engineering, University of São Paulo, Avenida Trabalhador São-carlense 400, São Carlos, Brazil

ARTICLE INFO

Article history:
Received 21 December 2016
Received in revised form 2 March 2017
Accepted 4 March 2017
Available online 18 March 2017

Keywords:
Porous structure
$Al(OH)_3$
Synthetic amorphous silica
Co-continuous porosity
Mullite

ABSTRACT

Porous materials produced from sintered $Al(OH)_3$ show a potentially useful α-Al_2O_3-based coral-like co-continuous microstructure of high porosity (above 70%) and chemical resistance. However, due to the lack of efficient connections among the particles of the solid phase, their poor mechanical properties limit their use in biomechanical and thermo-mechanical applications, as scaffolds for bone tissue and hot air filters, respectively. In this study, authors improved these connections reinforcing the structure with a sintering aid (synthetic amorphous silica, SAS). $Al(OH)_3$ particles (previously sintered at 1500 °C, 5 h) were imbibed with SAS particles, compacted and sintered at 1300 °C, which generated a coral-like mullite-based porous structure. The porosity levels of the material (47%) were similar to those of the initial green state (50%) and achieved high levels of mechanical properties (flexural strength of 50.29 MPa, elastic modulus of 26.00 GPa), with small linear thermal shrinkage (lower than 6% at 1500 °C).

1. Introduction

1.1. $Al(OH)_3$ as a porogenic agent

$Al(OH)_3$ particles are usually produced by a chemical method based on the precipitation of sodium aluminate in an acid aqueous environment [1,2], therefore, they are typically regular in shape and size and of a hexagonal plate-like crystalline habit (Fig. 1a) [3–5]. They have been widely studied for the production of porous structures [4–12]. Their porogenic mechanism is based on a sequence of reactions and phase transformations that take place during the initial thermal treatment and involve water vapor withdrawal during dehydroxylation (208–370 °C) and generation of mesoporosity at the surface of the particles (500–700 °C) [5,12]. During the initial heating, several transition alumina phases were identified and specific surface area levels of 100–300 $m^2 g^{-1}$ could be observed [5,13,14]. At higher temperatures (1100–1300 °C), the only phase present is α-Al_2O_3 and the particles begin to sinter and form necking points. Finally, above 1300 °C, the microstructure stabilizes in a co-continuous coral-like porous morphology [5,11,15,16]. Each filamentous grain is smooth, contains rounded edges, and shows typical dimensions of 0.5 μm diameter by 1–3 μm length (Fig. 1b).

Such porous structures of small average pore size, high melting point, microstructural stability, and chemical inertia can show porosity levels above 70% (after sintering at 1500–1600 °C) and are attractive for applications as thermal insulators, hot gas microfilters, and biological scaffolds. However, their major side effect is the low degree of connection between the filaments, which leads to sintering difficulties and poor mechanical properties (very small strength and elastic modulus) [8,11,12]. Consequently, $Al(OH)_3$ is not used as a single raw material for the production of porous materials. Several studies have described its combination with calcined alumina, which results in stronger, but much less porous structures [5,8–12].

This study investigated a possible solution to such a drawback. It consists in the reinforcement of the contact points among the coral-like α-Al_2O_3 filaments through the addition of a sintering aid (synthetic amorphous silica, SAS, produced by silicon vapor precipitation [17–23]). The authors describe the processing route for the preparation of the sintered $Al(OH)_3$ precursor and the impregnation with SAS nanoparticles. The physical properties and morphology attained for these porous structures after sintering were compared with those of samples comprised of calcined alumina and SAS-free-$Al(OH)_3$ that were also tested as references.

* Corresponding author.
E-mail addresses: rsalomao@sc.usp.br (R. Salomão), leanfernandes@usp.br (L. Fernandes).

http://dx.doi.org/10.1016/j.jeurceramsoc.2017.03.017
0955-2219/

Table 1
Characteristics of the raw materials.

Physic-chemical properties	$Al(OH)_3$ (as-received)[a]	Previously sintered $Al(OH)_3$ (at 1500 °C for 5 h)	Synthetic amorphous silica[b]	Calcined alumina[c]
Denomination	AR-$Al(OH)_3$	PS-$Al(OH)_3$	SAS	CA
Composition (wt%)	$Al(OH)_3$: 99.7; Na_2O: 0.2; Fe_2O_3: 0.07; SiO_2: 0.03	α-Al_2O_3 (single phase)	SiO_2 (amorphous): 97.9; Na_2O: 0.2; K_2O: 0.2; Fe_2O_3: 0.01; CaO: 0.2; MgO: 0.2; Al_2O_3: 0.2; C_{Free}: 0.7; SO_3: 0.3	α-Al_2O_3: 99.8; Na_2O: 0.08; Fe_2O_3: 0.02; SiO_2: 0.03; CaO: 0.02; MgO: 0.07
Solid density (ρ_S, g cm^{-3})	2.42	3.57	2.39	3.98
Surface area (SSA, m^2 g^{-1})	5.8	1.4	24	7.8
Particle size (D_{50}/D_{90}, μm)	0.89/1.19	–	0.086/0.12	0.75/2.9
Loss of ignition (wt%, 900 °C)	36.43	–	0.76	0.12

[a] Hydral 710, Almatis, USA.
[b] Microsilica U971, Elkem, Norway.
[c] A1000SG, Almatis, USA.

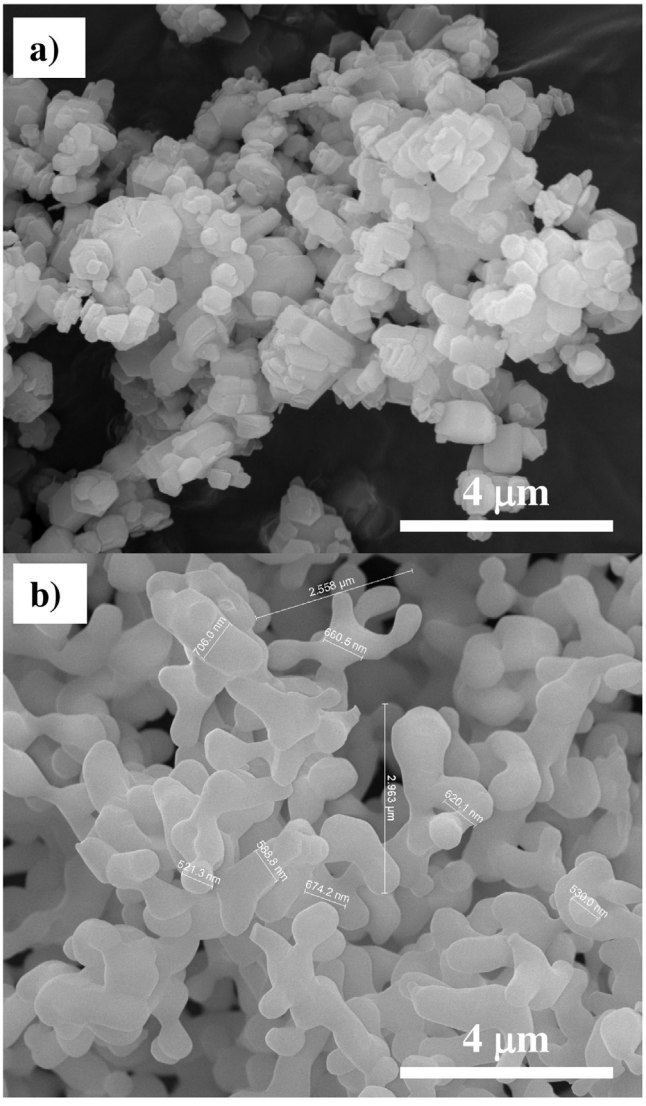

Fig. 1. Aluminum hydroxide ($Al(OH)_3$) particles: (a) as-received and (b) after sintering (2 °C min^{-1} up to 1500 °C, 5 h hold, 10 °C min^{-1} cooling rate).

2. Experimental

2.1. Raw materials

All raw materials were previously characterized regarding composition (X-ray dispersive spectroscopy, Shimadzu, EDX 720, Japan), crystalline phases (X-ray diffraction, Rotaflex RV 200B, Rigaku-Denki Corp., Japan; with Kα = Cu radiation, λ = 0.15406 nm, in the 3° to 100° 2θ range at a 2° min^{-1} scan rate), solid density (ρ_S, 99.999% purity helium picnometry (Ultrapyc 1200e, Quantachrome Instruments, USA), and specific surface area (SSA, BET method, Nova 1200e, Quantachrome Instruments, USA, ASTM C 1069-09 standard "Standard Test Method for Specific Surface Area of Alumina or Quartz by Nitrogen Adsorption"; the samples were previously degassed at 150 °C for 3 h, prior to each measurement; 99.999% purity N_2 was employed as the adsorption gas; P/P_0 ranged from 0.05 to 0.3), particle size distribution (D_{50}/D_{90}, DT-1202, Dispersion Technology Inc., USA) and loss of ignition (900 °C for 5 h, heating and cooling rates of 5 °C min^{-1}) (Table 1).

2.2. Preparation of the coral-like microstructure

The coral-like filaments of sintered $Al(OH)_3$, which are the main elements of the structure, show remarkable microstructural stability even if exposed to high temperatures for long periods [5,15,16]. Plain $Al(OH)_3$ must be previously prepared at high temperatures (1500 °C) to be stabilized. If the sintering aids are added in the initial thermal treatment of $Al(OH)_3$, they will possibly interfere with the formation of the coral-like filaments and reduce porosity. Therefore, they must be added to the system after $Al(OH)_3$ sintering and prior to compaction, in a rational content, so as to prevent an excessive formation of low melting point compounds. SAS is one of the most studied and effective sintering aid for alumina-based systems [18,20–22]. Its small average particle size improves packing [18,20,21] and its viscous flow deformation promotes a localized liquid sintering that strongly binds the surrounding particles [24–31]. Moreover, at a proper dosage, it can induce the formation of mullite, $3Al_2O_3{\cdot}2SiO_2$, a high refractoriness aluminum silicate [31–34]. The external shape of the coral-like structure and its porosity can be preserved if the SAS's particles generate a uniform layer at the surface of the filaments during sintering. After the reaction, the formation of mullite at the connections among the filaments possibly increases strength and refractoriness.

A suspension containing SAS (10 vol%, Microsilica U971, Elkem, Norway, Table 1) and poly(vinyl butiral) (1 vol%, PVB, Sigma,