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Processing of porous mullite ceramics using novel routes by starch consolidation casting

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Abstract

In this article, the development and characterization of porous mullite bodies prepared using two novel forming routes with native starches were studied with the aim of developing bodies without deformation and with homogeneous porous microstructures. Mullite–starch suspensions specific for each route were prepared by mixing and characterized by measuring viscosity. Mullite green bodies were fabricated by heating the suspensions in metallic molds and by burning out the starch, while final porous materials were obtained by sintering at different temperatures. Bodies obtained before and after the burning-out process, and sintered disks, were characterized with porosity measurements and microstructural analysis by SEM. The phases generated after the sintering process were determined by XRD, and pore size distributions were studied by Hg-porosimetry. The obtained results showed that the use of both routes allowed the shaping of homogeneous mullite bodies without causing cracks or deformations and the consequent development of controlled porous mullite microstructures.

Keywords: Starch consolidation casting method; Mullite; Microstructure; Porous ceramics

1. Introduction

In recent years, much attention has been focused on porous ceramic materials due to their wide range of technological applications as thermal insulators, catalyst supports, bioceramics, filters and combustion burners, among others. These materials exhibit several specific properties, such as low density, low specific heat, low thermal conductivity, high surface area and high permeability, which are required for such uses. When they are used for thermal insulation, the materials have to contain a large pore volume fraction, namely high porosity. In particular, porous mullite ($3Al_2O_3{\cdot}2SiO_2$) materials are suitable as thermal insulators because of their low thermal conductivity, moderate thermal expansion coefficient, good chemical durability, and excellent mechanical properties at high temperature.[1–4]

Several processing methods, in particular those based on the direct consolidation of ceramic suspensions into non-porous molds, have been developed with the purpose of preparing porous ceramics. Among them, a non-contaminating low-cost consolidation technique called 'starch consolidation casting' (SCC) has become one of the most popular processing routes for porous ceramics.[5,6] In this method, the starch is used as a body-forming agent of the ceramic suspension when the system is heated between 50 and 85 °C, and as a pore former at high temperature after burning. When the aqueous ceramic–starch suspension is heated, the starch granules swell by water absorption, decreasing the available free water. Thus, the ceramic particles, usually of smaller size than the starch granules, are pressed together in the interstitial space to consolidate into a solid body. After calcination and sintering treatments, a porous material is obtained whose porosity, which is associated with highly interconnected open pores, depends on the amount, shape and size of the swollen starch granules.

In the first reported investigations concerning this forming method,[5,6] the use of native starches as a body-forming agent was not recommended because highly deformed green bodies were obtained. Furthermore, the most satisfactory results were achieved when chemically or physically modified starches

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were used.[5–8] Recently, we have reported[8] that the use of a small amount of cold-water-soluble starches (physically modified starch whose granules have the ability to instantly swell in water at room temperature) made the shaping of homogeneous mullite bodies without cracks or deformations possible along with the development of controlled porous microstructures. In addition, we have studied the feasibility of preparing high-quality ceramic green bodies by introducing some other modifications into the conventional route of processing.[9]

Due to the problems associated with using native starches to form ceramics by direct consolidation, two alternative forming routes for aqueous mullite–native starch suspensions are studied in this paper with the aim of developing green bodies without deformation and with homogeneous porous microstructures.

2. Experimental description

2.1. Raw materials

A high-purity commercial mullite powder (MULSM, Baikowski, Charlotte, NC) was used as the ceramic raw material (the alkaline impurity level was less than 0.2 wt%). Excess alumina with respect to the stoichiometric composition (Al_2O_3 = 71.8 wt%, SiO_2 = 28.2 wt%) was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Mullite 3/2 (JCPDS File 74-2419) as the primary phase, and α-alumina (JCPDS File 82-1399), θ-alumina (JCPDS File 11-0517), and cristobalite (JCPDS File 77-1317) as secondary phases, were identified by X-ray diffraction (XRD; X'Pert PRO, PANalytical, Almelo, the Netherlands; radiation of CuKα at 40 mA and 40 kV) (pattern diffraction is included in Fig. 3). In addition, a low-intensity band was also observed in the zone of the more intense diffraction peaks of silica polymorphs (20–30°2θ), which is associated with noncrystalline silicate phases. The mullite powder presented a medium crystallinity that was associated in part with the presence of narrow- and medium-height diffraction peaks when compared to the characteristic peaks of diffractograms of highly crystalline commercial mullite powders.[10] The powder density (3.07 g/cm^3) measured by He-pycnometry (Multipycnometer, Quantachrome Instruments, Boynton Beach, FL, USA) was lower than the theoretical densities of mullite (3.16 g/cm^3), α-Al_2O_3 (3.98 g/cm^3), and θ-alumina (3.28 g/cm^3) due to the contribution of cristobalite (2.3 g/cm^3) and noncrystalline silicate phases (~2.2 g/cm^3).

Considering these results, it could be inferred that the commercial mullite powder comes from a synthesis process in which the total conversion of the starting mixture (ammonium alum and silica) was not achieved.[11]

The mullite powder presented a bimodal particle size distribution (Mastersizer S, Malvern Instruments, Malvern, UK) with a low mean volume diameter (D_{50} = 1.5 μm), a high volume percentage (~30%) of fine particles <1 μm, and contained agglomerates up to 50 μm in size due to the presence of the very fine particles. These results are consistent with the high value of the specific surface area (13.5 m^2/g) determined by the BET method (Monosorb, Quantachrome Instruments, Boynton Beach, FL, USA). Moreover, it was previously determined[9] that the mullite powder consists of very small three-dimensional particles, some of them faceted, with equiaxial morphology, as well as agglomerates of the smallest particles, which is in agreement with the granulometric distribution.

Commercial native starches (AVEBE Argentina, Buenos Aires, Argentina) derived from cassava, corn, and potato (Table 1), were also used as raw materials. Real densities and total lipid content were determined by He-pycnometry (Multipycnometer, Quantachrome Instruments) and the Soxhlet extraction method, respectively. The values obtained for these parameters were in the range of the values reported for these types of starch.[12] Based on the X-ray diffraction peak positions (X'Pert PRO, PANalytical), the cassava and corn starches were identified as A-type (15.2, 17.1, 18.0, and 22.9°2θ), whereas the potato starch was identified as B-type (5.4, 15.0, 17.2, 21.8, and 24.0°2θ).

The particle size distributions were analyzed (Mastersizer S, Malvern Instruments) using stabilized aqueous starch suspensions. The three starches presented bimodal granulometric distributions with a low volume percentage (<5%) of small granules, which can be linked to impurities or broken granules. The moisture weight percentage was determined by thermogravimetric analysis (TGA; TGA-50, Shimadzu, Kyoto, Japan) at 10 °C/min up to 700 °C, in air. Starch transition temperatures were determined by differential scanning calorimetry (DSC; DSC-50, Shimadzu, Kyoto, Japan) at 5 °C/min up to 120 °C. The granule morphology analysis of the dry starches was performed by scanning electron microscopy (SEM; JSM-6460, JEOL, Tokyo, Japan). Potato starch exhibited the largest granules, with smooth surfaces and oval or spherical forms. Corn and cassava starches presented granules with polyhedral form, but the corn starch granules were the most representative of this type.

2.2. Forming and characterization of green bodies

Based on previously selected experimental conditions, aqueous mullite–starch suspensions (40 vol% total solid loading) were prepared by: (a) mixing mullite powder in water to a solid content of 40 vol% and dispersing with 0.45 wt% Dolapix CE-64 (Zschimmer & Schwarz, Lahnstein, Germany) with respect to the powder amount; (b) homogenizing in a ball mill for 6 h; and (c) adding a volume of aqueous starch suspension (40 vol%) and mixing for 5 min to obtain a final starch and mullite content of 10 vol% and 30 vol%, respectively.

Two novel routes for forming aqueous mullite suspensions with native starches, which were proposed as alternative routes to the conventional route, were designed with the aim of developing green bodies without deformation and with homogeneous porous microstructures.

With the "Sub-gelatinization Route" (SGR) (this route was also called "Pre-gelling Route"),[9] aqueous mullite–starch suspensions were heated at temperatures lower than the onset temperature of gelatinization for each system (59 °C for mullite–cassava starch and mullite–potato starch suspensions, and 64 °C for mullite–corn starch suspension). The temperatures used are the maximum possible temperatures at which each mullite–starch system can be heated without the formation