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Shaping of porous mullite green bodies by foaming and thermal gelation of bovine serum albumin

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Abstract

The shaping of cellular microstructures of mullite bodies prepared by thermo-gelation of foamed mullite-bovine serum albumin (BSA) suspensions using both a novel forming route and the conventionally reported route were studied. Mullite-BSA and mullite-BSA-methylcellulose (MC) suspensions specific for each route were prepared and then characterized by measuring viscosity. They were subsequently foamed by stirring, and their foaming capacity and foam stability over time were evaluated. Bubble size distributions vs. stand time were obtained by analyzing images captured by confocal laser-scanning microscopy (CLSM). Green bodies were formed by pouring each system into heated molds, by heating and by drying, and were characterized by porosity measurements and microstructural analysis by SEM. The obtained results showed that the use of certain experimental conditions for each route allowed the shaping of homogeneous mullite porous bodies with different microstructural features, namely, ceramic foams with open cells or cellular ceramics with closed cells and thick walls.

Keywords: Protein-forming; Foaming; Mullite; Pre-firing porous microstructure

Introduction

In recent years, the increased demand of porous ceramic materials with properties adequate for new applications in highly diverse technological fields has been notable. The development of a porous ceramic material with a specific and controlled microstructure supposes not only the previous microstructural design but also the control of the characteristic parameters for porosity (type of pores, pore morphology, amount of pores and pore size distribution) during the different processing steps since they are determinant aspects of the final properties. However, control of these parameters is not always adequately resolved and for this reason, it constitutes one of the more critical aspects of processing of this type of material.

Among the different types of porous ceramics can be found the classically denominated cellular materials, such as foams, among others. The cellular materials are defined as those formed by a continuous three-dimensional solid network of struts, which enclose individual cells of a different nature and morphology. These can be either open cells, which have holes in them (cell windows) or closed cells, which do not have windows. These types of materials bring together a unique combination of different properties such as low density, low thermal conductivity, high surface area, and high permeability, all of which determine their specific use in thermal or acoustic insulating, catalyst supports, biomedical implants, scaffolds for cell growth and high efficiency combustion burners, among others.[1,2] In particular, closed-cell materials are needed for thermal applications, while open-cell materials are required for uses such as filters and catalysts. Microstructural features such as density and type of cells, size and morphology of cell, interconnection degree of the network and strut dimension are relevant factors that determine potential applications for these materials,[3] as is the ceramic matrix composition, which must be properly selected.[1–4] Mullite ceramics ($2SiO_2{\cdot}3Al_2O_3$) are important materials due not only to their good mechanical properties at high temperature, but also their low thermal conductivity, low thermal expansion coefficient and good chemical stability.[5–7]The main processing

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routes employed to make cellular materials can be divided into three categories, each one including some variations: the replication technique, the direct-foaming technique and the sacrificial template method.[4] Each of these methods presents a series of advantages and disadvantages with respect to the versatility and ease of fabrication, as well as their influence on the microstructure and properties of the developed porous ceramics.

In the direct-foaming method in particular, cellular ceramics are prepared by incorporating a gas (e.g. air) into a ceramic suspension, generally by mechanical stirring. Then, the foamed suspension is consolidated and sintered at high temperature. The forming and sintering processes finally convert the bubbles into pores (cells) among the solid particles of the ceramic matrix. When the film surrounding the bubbles remains intact during the complete consolidation of the suspension, foams with closed bubbles are formed. If the films are partially broken, however, foams with open cells are produced.[3,8] This method is versatile, very simple, inexpensive, and presents some advantages compared to the replica method: a) some shapes, compositions and densities can be easily obtained, b) it allows convenient control over the porous structure of the ceramic material,[9] and c) leads to the development of materials with small cells (smaller than 200 μm), which can be either open and closed depending on the foaming and processing conditions. Furthermore, unlike the replica method, the struts do not have holes, and they possess a small quantity of defects; in consequence, the mechanical resistance is higher compared to structures obtained by the replica method.[4] However, since the starting system (wet foam) is unstable, the direct-foaming method, in general, requires the addition of a consolidator/binder agent (e.g. some additive that promotes the formation of a gel) in order to allow the consolidation of suspended ceramic particles to occur before the foam destabilization processes begin, which ends up rupturing the bubbles. In most cases, the addition of a surfactant that reduces the surface tension of the gas-liquid interface and stabilizes the gas bubbles inside the ceramic suspension is usually required.[3,4]

In this context, "protein casting", an innovative non-contaminant colloidal processing of cellular ceramics, is based on thermal consolidation (at temperatures lower than 90 °C) by gelling an aqueous ceramic suspension foamed with globular proteins and the formation of a macro-cellular ceramic structure after removing organics and applying sintering treatments at high temperature. The amount and size of cells in the developed cellular structure depend on the foamed suspension properties and the ability of protein molecules to stabilize the foam before the gelling process occurs (the gas bubbles have to remain occluded in the ceramic suspension for a certain amount of time).[1,3,4,10–13] In this case, a globular protein acts as both a foaming and binder/consolidator agent for the ceramic suspension. These properties are associated with the ability of globular proteins to reduce the surface tension of gas–liquid interfaces and thus stabilize the gas bubbles developed within the suspension (the protein molecules adsorb at the air–water interface and their structure unfolds, which increases the hydrophobicity of the film favoring the foaming), and form a gel in water after heating at 70–80 °C.

Few papers relating to the processing of ceramic materials by protein forming have been published, and most relevant within the last decade. In many of them, albumins as egg-albumin and whey protein concentrate were used; bovine serum albumin, however, was used very little. Many factors related to protein and the other components of the starting suspension, such as protein solubility, protein concentration, ionic strength, pH, type and form of addition of the processing additives and the presence of ceramic particles, influence the foam properties. Due to the highly complex foamed ceramic-protein system, which makes controlling the cellular microstructure difficult, the design and evaluation of various forming routes different from those conventionally reported on are presented as a viable way to obtain cellular materials with controlled microstructures and high homogeneity. These issues and other factors, such as the low heat transfer throughout the porous material and the influence of ceramic particles and organic processing additives on the protein gelation process, which affect the kinetic of ceramic body formation and therefore its final characteristics, reveal the need to investigate in this area. Moreover, it is worth noting that in general, dilute ceramic suspensions (less than 20–25 vol%) were used to prepare cellular materials with very high porosity; however, control over porosity and the problems associated with poor mechanical properties caused by the development of cells with fine walls cannot to be taken lightly.

Based on the above-mentioned concepts, this paper studies the shaping and pre-firing cellular microstructures of mullite bodies developed by direct thermal consolidation of concentrated ceramic suspensions foamed with bovine serum albumin. The inclusion of modifications to the conventionally used processing route is presented as an alternative way to develop materials with controlled and homogeneous pre-firing cellular microstructures.

Experimental procedure

Characterization of the raw materials

The used ceramic raw material was a high-purity (alkaline impurity level <0.2 wt%) commercial mullite powder (MULS, Baikowski, Annecy, France). The complete characterization of the mullite powder was reported in previous works of the authors.[14,15] 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, the Netherlands; radiation of CuKa at 40 mA and 40 kV). In addition, a low intensity band located in the zone of the more intense diffraction peaks corresponding to the silica polymorphs (20–30° 2θ), which are associated with non-crystalline silicate phases, was also observed. The powder density measured by He-pycnometry (Multipycnometer, Quantachrome Co., USA) was 3.07 g/cm^3. Considering these results, it was 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.[16] Moreover, the mullite powder which consists of