



Processing, microstructure and elastic properties of mullite-based ceramic foams prepared by direct foaming with wheat flour



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ABSTRACT

Mullite-based ceramic foams with bulk densities as low as 0.4 g/cm³, porosities between 49 and 88% and average foam cell sizes in the range 100–320 μm are fabricated by direct foaming from suspensions containing wheat flour and partial sintering at 1600 °C. Stereology-based image analysis is used to determine a complete set of global microstructural descriptors, i.e. the porosity from foam cells (8–88%), interface density, mean curvature integral density and the related pore size measures (mean chord length and Jeffries size). Elastic constants are determined via impulse excitation (Young's moduli 2.3–21.4 GPa, shear moduli 0.9–8.8 GPa, bulk moduli 1.5–12.9 GPa, Poisson ratios 0.193–0.234). Elastic moduli obey the power-law prediction (Gibson–Ashby relation for open-cell foams) for foams with porosities higher than 70%, but for lower porosities they are significantly lower, due to concave pores in the partially sintered matrix.

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1. Introduction

Mullite is a major crystalline phase in many silicate ceramics and refractories and its properties are well investigated [1–3]. Its high melting point of more than 1800 °C makes mullite and mullite-based ceramics highly refractory. On the other hand, the thermal conductivity of mullite is rather low, and thus in combination with a sufficiently high porosity, mullite ceramics and mullite-based refractories are ideal candidates for high-temperature thermal insulation purposes. Introducing porosity into mullite and mullite-based ceramics reduces the heat capacity [2], while the thermal expansion behavior [3] remains essentially unaffected. It is clear, however, that introducing porosity decreases also the mechanical properties of mullite and mullite-based materials, e.g. strength. On the other hand, a decrease of the elastic moduli, e.g. Young's modulus, can be an advantage from the viewpoint of thermal shock resistance, because the porosity dependence of the Young's modulus is always steeper than that of the thermal conductivity [4], so that the influence of porosity on the material properties and behavior is rather complex. While the strength and thermal

conductivity of porous mullite materials have been investigated by other authors [5,6], a systematic work on elastic properties seems to be lacking so far, and the present work is an attempt to fill this gap.

There are many ways to prepare porous mullite ceramics [5–10], and in many of these processes starch plays a key role. For example, starch consolidation casting with modified potato starch has been used for preparing porous mullite ceramics with porosities in the range 35–60% [7], while native cassava, corn and potato starch have been used in combination with a novel “sub-gelatinization route” (i.e. by preheating a starch-containing ceramic suspension at a temperature below the onset temperature for gelatinization) or a “mixing route” (i.e. by mixing ungelatinized native and previously gelatinized starches) to obtain mullite ceramics with porosities in the range 39–64% [8,9]. Also a route using cold-water-soluble starch has been proposed [10]. In all cases the pore size is closely related to the original size of the starch granules.

In this paper we apply a recently developed technique [10] to produce highly porous mullite ceramics with porosities that significantly exceed the aforementioned values. Also this technique is based on a starch product, but in contrast to the aforementioned methods it consists in the direct foaming of a ceramic suspension with wheat flour. Since the foaming step in this technique occurs before the casting step, it can be called an ex-situ direct foaming technique (in contrast to in-situ direct foaming, for example in the case of biological foaming using yeast, where the foaming

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step occurs after casting inside the mold [12,13]). In previous work this method of ex-situ direct foaming using wheat flour has been successfully used for alumina [11], but its application to mullite is new. In this paper we show that the porosity and other microstructural characteristics of mullite-based ceramics can be controlled via the shaking time. In addition to optical and scanning electron micrographs, the microstructure is characterized via the mass-to-volume ratio (bulk density), stereology-based image analysis and mercury porosimetry, and the elastic properties are characterized via impulse excitation.

2. Theoretical

2.1. Stereology-based image analysis

The systematic quantitative description of the microstructure of porous materials by microscopic image analysis requires the determination of global descriptors. In particular, a complete set of descriptors is given by three parameters, viz. the porosity (volume fraction of pores), the interface density (pore surface per unit volume), and the mean curvature integral density. For a systematic account of the procedures to determine these quantities the reader may refer to our previous papers in this field [14,15]. Therefore, for the purpose of the present paper, only a very brief summary is given here:

The most efficient method to determine the porosity (volume fraction of pores) is via the point fraction of grid points falling on a pore section. According to the Delesse–Rosival law, the volume fraction of pores (porosity) $\phi = V_V$ is then given by

$$\phi = V_V = A_A = L_L = P_P \quad (1)$$

(in standard stereological notation [14,15]). The interface density S_V is determined from the number of intersection points between grid lines and the pore section outlines, related to the length of the grid lines, via the relation

$$S_V = 2P_L. \quad (2)$$

In a similar way, in the case of convex pores, the mean curvature integral density M_V is determined from the number of pore sections per unit area N_A

$$M_V = 2\pi \times N_A. \quad (3)$$

Note that all these methods are counting techniques, that means it is not necessary to measure lengths or areas. Therefore they can be applied to unbinarized and even low-contrast images. Another advantage of counting techniques is that the standard error for the volume fraction of pores (porosity) can be predicted before the measurement without any empirical parameter, and even in the case of interface density and mean curvature integral density good estimates of the standard error are available [14]. That means, it is possible to estimate in advance the number of counts necessary to achieve a desired precision, while the observed standard errors can be calculated according to usual statistics from standard deviations after the measurement. For more details and explicit equations the reader may refer to our previous papers [14,15].

From both the interface density S_V (or the quantity P_L) and the mean curvature integral density M_V (or the quantity N_A) size measures can be derived, viz. the mean chord length (mean intercept length)

$$L = \frac{4\phi}{S_V} = \frac{4V_V}{S_V} = \frac{2\phi}{P_L} = \frac{2P_P}{P_L} \quad (4)$$

and the Jeffries size

$$J = \sqrt{\frac{2\pi\phi}{M_V}} = \sqrt{\frac{2\pi V_V}{M_V}} = \sqrt{\frac{\phi}{N_A}} = \sqrt{\frac{P_P}{N_A}}. \quad (5)$$

The corresponding standard errors of the two size measures have to be calculated via the law of error propagation, because both the volume fraction (porosity) ϕ and the parameters S_V and N_A have their own errors [14,15].

2.2. Determination of elastic constants via impulse excitation

The determination of elastic constants via impulse excitation is based on the measurement of resonant frequencies. In the case of rod- or bar-shaped specimens it is possible to record damped oscillations of flexural vibrations and thus to measure flexural resonant frequencies, from which one elastic constant, the Young's modulus, can be determined [16]. However, even in the simplest case (isotropic materials) two independent elastic constants are needed for a full description of the elastic behavior [17].

With disk- or plate-shaped specimens it is possible to determine two elastic constants, because when the specimen fixation is appropriate, two types of vibrations can be excited, viz. flexural and anti-flexural vibrations. Of course each of these vibrations has its own resonant frequency. From the ratio between the flexural and the anti-flexural frequency it is possible to calculate the Poisson ratio, using a numerical solution by Glandus [18]. Then, using the thus determined Poisson ratio, two values of the Young's modulus can be calculated, one from the resonant frequency of the flexural vibration f_1 and one from that of the anti-flexural vibration f_2 . As long as the ratio of the flexural and anti-flexural resonant frequencies is in the range $1.35 \leq f_1/f_2 \leq 1.90$, the Poisson ratio of sufficiently thin circular discs (with diameter D , thickness t and aspect ratio $D/t \geq 4$) can be determined directly from the measured resonant frequencies, using tabulated values [16]. As soon as the Poisson ratio is known, two values of the Young modulus can be calculated from the resonant frequencies of the flexural and anti-flexural vibration, respectively, via the relation

$$\begin{aligned} E_i &= 3 \times \rho \times D^4 \times (1 - \nu^2) \times \left(\frac{\pi f_i}{t C_i} \right)^2 \\ &= 12\pi (m f_i^2) \left(\frac{D^2}{t^3} \right) (1 - \nu^2) \frac{1}{C_i^2}, \end{aligned} \quad (6)$$

where f_i is the frequency (with $i=1$ for flexural and $i=2$ for anti-flexural vibrations), m the specimen mass, ρ the bulk density, and C_i a geometric factor (specimen shape coefficient) for the respective frequency that is tabulated for aspect ratios larger than 4 (up to infinitely thin discs) [16]. The two Young's modulus values thus calculated should be very close, and the arithmetic mean of them is taken to be the final value of the effective Young's modulus. Of course, as soon as both the Poisson ratio and the Young's modulus are known, all other elastic constants of isotropic materials, including shear and bulk moduli, can be calculated via elasticity standard relations [17].

2.3. Theoretical predictions for the porosity dependence of elastic constants

The porosity dependence of elastic constants has been treated in many previous papers [19–28], and therefore only a shortcut directly related to the present work is given here: In contrast to the Poisson ratio, for which no micromechanical bounds are available (only the thermodynamic bound $-1 < \nu < 0.5$) [19], the elastic moduli M (in the sequel standing for E , G or K) of porous materials are all subject to micromechanical upper bounds. For all these moduli the upper bound in the case of porous materials is [20]

$$M_r = \frac{M}{M_0} \leq 1 - \phi, \quad (7)$$

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