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# Preparation of cellular alumina ceramics via biological foaming with yeast and its microstructural characterization via stereological relations

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**Abstract**

The preparation of highly porous (cellular) alumina ceramics via biological foaming with yeast is described and its microstructure is characterized via image analysis using stereological relations. The ceramics prepared usually have total porosities in the range 78–84% and the porosities related to large pores (volume fraction of foam bubbles) are usually in the range 58–75%. The mean chord length and Jeffries size, i.e. pore size measures related to the interface density and the mean curvature integral density, respectively, are rather close to each other (usually 0.8–1.4 and 0.8–1.2 mm) with a ratio close to unity (0.9–1.4), and the mean surface-to-surface distance gives a realistic picture of the average wall thickness (usually 0.46–0.69 mm). Using a special processing variant (excess ethanol addition) it is possible to obtain microstructures with lower porosity (total porosity 68–70%, foam bubble volume fractions 50–56%) and smaller pore size (approx. 0.5 mm).


*Keywords:* Biological foaming with yeast; Shaping; Microstructure-final; Porosity; Alumina

## 1. Introduction

Porous and cellular ceramics (ceramic foams) are known to have a wide range of applications, ranging from light-weight materials and thermal insulation, where the volume fraction of pores (porosity) is the key characteristic, to filters and catalyst support media in which pore size, shape and surface are the most important microstructural parameters.[1,2] The properties of these materials are determined by the solid phase, which ensures e.g. their high-temperature behavior and corrosion resistance, as well as the microstructure, which is responsible for most structural and functional properties and features of behavior.[3–6] On the other hand, the microstructure of porous ceramics is a result of processing and can be controlled by choosing appropriate processing methods,[7–9] e.g. using pore formers,[10–12] possibly in connection with swelling of the latter,[13–16] or direct foaming methods,[17–20] and optimized processing conditions.[21] In particular, the shaping step is crucial for the resulting microstructure, because it determines the overall microstructural features of the ceramic, so that the high-temperature processing (drying and firing) results in strengthening and densification of the microstructure, during which possible defects (principal or accidental) cannot be eliminated any more. A famous example of such principal microstructural defects are the pore channels in the struts of ceramic foams prepared by the polymer sponge template method (replica technique), which seriously limit their mechanical properties.[22,23] Therefore considerable research efforts are directed toward developing processing techniques that avoid this type of defects, while at the same time maintaining a high overall porosity. For this purpose direct foaming techniques have become popular, because they allow porosities of more than 70% to be readily attained (in contrast to the use of pore formers, even swelling ones, where porosities of more than 60–70% usually cannot be attained). A very recent development among direct foaming techniques is biological foaming with yeast. This method has been tested for preparing porous ceramic bodies in our laboratory many years ago (around 2007), but probably the first published papers in the open literature were those by Schunk et al.[24] who proposed the use of yeast to prepare zeolite catalyst supports and, three years later

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(2010), by Menchavez et al.[25] who used yeast to prepare porous silicate ceramic materials from red clay. At about the same time (2009/2010) Manap and Jais used yeast for preparing porous silica granules, usable e.g. as fillers, from rice husk ash.[26,27] Some hints on yeast-based foaming techniques are also hidden in the patent literature, where we found two US patents,[28,29] one of which concerns porous phosphate ceramic bone graft materials[29] and the other mentions yeast – among many other substances – as an example of a foaming agent in a very general way,[28] two older German patents[30,31] and three very recent Chinese patents.[32–34] However, only three of the latter concern the use of yeast as a foaming agent,[30–32] mentioning building and insulating materials as well as "granular aggregates" of alumina, zirconia, mullite and metal particles as examples, while the other two[33,34] use dry yeast powder as a mere pore former, obviously without exploiting its foaming capability. The same holds for several published journal papers, where dry yeast granules are used as pyrolizable pore formers.[35–42] Thus it can be concluded that up to now there seems to be only one journal paper and about three or four (not very clear) patents in which the use of yeast as a foaming agent is proposed for preparing highly porous cellular ceramics (ceramic foams). In none of the works mentioned the roles of sugar and starch during processing and the microstructure of the resulting ceramic foams have been systematically analyzed.

Therefore the preparation of cellular alumina ceramics by biological foaming with yeast has been the subject of a recent thesis at the ICT Prague,[43] and in previous work the influence of the type and amount of sugar and starch on the processing and the resulting ceramic have been investigated.[44] Sugar is used as a fuel for the yeast cells, i.e. the fermentation process consists in reaction of sugar (in aqueous media) to ethanol and carbon dioxide, the latter being responsible for the foaming. Three types of sugar – glucose, fructose and sucrose – have been tested with the outcome that the influence of the type of sugar on the resulting ceramic is negligibly small. Therefore it was concluded that sucrose, which is the cheapest and most easily available one, is the sugar of choice for this process. On the other hand, swelling starch serves as a foam stabilizer,[44] and when its swelling ability in hot water is exploited (like in starch consolidation casting[12–16]) it is ideally suited as a foam stiffener. From the starch types tested in previous work, i.e. rice, corn and potato starch,[43,44] potato starch performed best, probably because of its high swelling ability. Therefore, rice and corn starch have been discarded at an early stage and have not been considered in subsequent research. The concentrations of sugar and starch have been optimized for alumina suspension, resulting in 1.5 wt.% of sucrose and 20 vol.% of potato starch (both related to alumina).[43,44] Moreover, it has been found that the pH value has a decisive influence on the foaming process. While yeast cells are able to survive at pH values in the range 2–8, pH values in the range 4–6 are optimal for the fermentation process.[43,44] In the present paper we give a detailed account of the microstructure of alumina foams or cellular alumina ceramics prepared under these optimized conditions. We also report on first results concerning the possibility of controlling the microstructure by adding ethanol and give an example of how a mold with a porous interface may affect the resulting microstructure.

In spite of the current interest in yeast as a foaming agent for the preparation of porous ceramics, including highly porous cellular ceramics, and despite the fact that yeast has been used for food preparation since prehistorical times e.g. for the baking of bread, and has been used in polymer technology as a foaming agent as well,[45] there seems to be no work dealing with the quantitative microstructural characterization of the resulting (ceramic) materials. The present paper is meant to fill also this gap. For this purpose we apply stereology-based image analysis.[46–50] After briefly summarizing the basic stereological relations, including those which are less commonly used (e.g. mean curvature integral density and Jeffries size), we give a detailed account on processing items concerning the preparation of cellular alumina ceramics and finally present the results of the microstructural characterization in the form of correlation charts and tabulated values, including statistical errors.

## 2. Theoretical

Porous materials can be considered as a special case of heterogeneous materials, i.e. materials with internal phase boundaries. The microstructure of heterogeneous materials can generally be characterized by microstructural parameters (global descriptors), which are representative of the whole sample if the material is uniform (i.e. gradient-free). Two-dimensional (2D) sections through three-dimensional (3D) microstructures of heterogeneous materials allow the determination of metric parameters, but not topological ones.[47] The number of independent metric parameters that can be determined from 2D sections is limited to three. Using the standard index notation common in stereology,[47,48] these are the volume fraction $\phi = V_V$. (dimensionless, e.g. porosity), the interface density $S_V$ (units [mm$^{-1}$], e.g. pore surface density) and the mean curvature integral density $M_V$. ([mm$^{-2}$], characterizing e.g. pore surfaces).[47] When the microstructure is isotropic, uniform and random, estimators for these parameters can be determined from arbitrary single sections by superimposing straight lines in arbitrary directions and periodically arranged points, e.g. realized by superimposing square grids onto micrographs. Based on these basic parameters, or the quantities directly measured for estimating them, other common parameters, such as size measures (mean chord length, Jeffries size) and other measures (e.g. distance measures) can be derived.[47,48] With respect to the focus of this contribution (porous materials) we confine ourselves here to two-phase microstructures.The volume fraction of the phase of interest, e.g. porosity, is determined via the Delesse-Rosiwal law[46–49]

$$\Phi \equiv V_V = A_A = L_L = P_P, \qquad (1)$$

where $A_A$, $L_L$ and $P_P$ are the area, line and point fractions, respectively. Usually, i.e. when the porosity is not too low, point fractions are used for this purpose, because point counting (e.g. using the grid points of a square grid) is the most efficient method from a statistical point of view.[47,48]