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## On the elastic deformation properties of porous ceramic materials obtained by pore-forming agent method

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## Abstract

The influence of the pore size distribution on the elastic modulus has been studied using an intermingled fractal model (IFU) capable to reproduce entirely pore size distribution of materials. The results obtained from IFU modelling are in good agreement with experimental ones. The model could be considered as a microstructure simulator to improve mechanical properties of porous ceramic materials. © 2015 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Elastic modulus; Fractal modelling; Material design; Pore size distribution; Porous ceramics

## 1. Introduction

Porous ceramics are a class of materials used in several applications of industrial and engineering branch. It is due to several unique properties such as relatively low mass [1,2], low fractional density [3], low thermal conductivity [4], resistance to chemical attack [5], high specific surface area [6–8], high permeability and resistance to high temperature and thermal cycling [9–12]. For these reasons several materials are usually utilized for filters and membranes, as well as fuel cell electrodes, catalyst supports for biomaterials, piezo-electric materials, acoustically and thermally insulating bulk media [13–15].

Over the past few years, researchers have made several attempts in order to find innovative processing technologies for porous ceramics. These efforts aimed at obtaining a better control of the porous structures and substantial improvements of the ceramic properties.

There are a number of effective methods to obtain porous ceramics, namely: the gelcasting process [16,17], the organic foam technique [18], the freeze casting method [19–21] and pore-forming agent method [4,22]. The latter method is based

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on mixing ceramic raw materials with combustible additives, which are burned out leaving a pore fraction into the ceramic matrix. In most cases, this step is followed by a sintering process which induces mechanical strength on ceramics.

Porosity features (pore size, pore size distribution, pore volume fraction, tortuosity, etc.) are influenced by high temperature treatment. It also changes the micro-porosity of the products.

The main manufacturing procedures to obtain porous ceramics are compaction and extrusion. Compaction is a method which consists of the action of a uniaxial or isostatic pressure which densifies a powder bed. This application can be carried out at room or high temperature. In both cases, the pore-forming agent is uniformly mixed to the powder before compaction and, later on, it is further eliminated by heating. Thus, in the compaction process, pore fraction, size, shape and distribution depending on the pore-forming agent [23].

When it comes to the extrusion method, after having mixed ceramic powders and pore-forming agent, the resulting paste is molded using an extruder. Again, pore-forming agent is burned out and, eventually, the samples are sintered. Often, the final microstructure shows highly oriented cylindrical pores obtained from the uniform convergent flow of the matrix [24].

Pore-forming agents influence the final microstructure of pores. They determine the formation of an irregular and

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random microstructure [25,26]. Starch is one of the most used pore-forming agents, but it only produces large pores within the range of  $5-50 \ \mu m \ [4,27-29]$ .

An effective choice is represented by the use of polymers. The strong points are represented by the possibility to be easily mixed with ceramic powder and to be burnt out at a low temperature. Moreover they are low polluting and very cheap [4].

This way to influence porosity is particularly useful to control physical properties: thermal conductivity, permeability and mechanical behaviour. Indeed, it is very important to keep suitable mechanical strength. As a matter of fact, as porosity level increases, mechanical properties decrease.

It is not simple to obtain a good balance between thermal and mechanical properties. As far as thermal properties go, porosity is favourable because it represents a discontinuity of the solid phase. When it comes to mechanical properties, porosity is not favourable as it makes the resistant surface decrease.

Mechanical strength and elastic properties depend on several aspects, but they usually hinge on intrinsic characteristics of the solid phase, on pores fraction of the voids [30–32], on random level of microstructure and on pore size distribution [33–35].

Roberts et al. utilized the finite-element method (FEM) to study the influence of porosity and pore shape on the elastic properties of the porous ceramics model. They proposed a number of easy formulas to predict ceramics elastic properties. Those formulas allow an accurate interpretation of the empirical relations between property and porosity when it comes to pore shape and structure. Young's modulus of the models is in good agreement with experimental data [36]. Bernard et al. developed a model to investigate the effect of leaching of some solid phases of cement paste on the mechanical performance of cement pastes and mortars. Their simulation predicts the influence of different phases on elastic modulus and compressive strength [37]. Atzeni et al. presented an example of application of fuzzy modelling procedures to predict mechanical properties, using the porosimetric, mineralogical and weathering data determined for a series of vesicular basalt stones [38].

The role of the volume fraction of voids on the elastic properties, has been widely investigated so far [39,40]. On the other hand the role of pore size distribution has been studied much less [41,42]. That is probably due to a number of difficulties of representing pore size distribution as a parameter in many different formulas. It is necessary to have a good representation of porous microstructure from a geometrical point of view. This is very difficult using Euclidean geometry. Complex shapes found in nature are not easily reproducible by standard geometrical tools. Reference to this problem, the applications of the basic concept related to Fractal Geometry are of great and important interest.

Although many concepts and tools derived from Fractal Geometry were developed a long time ago, they were framed by Mandelbrot in 1975. He observed that many shapes presented in nature cannot be described using Euclidean

geometry. Clouds are not simple spheres, mountains are not simple cones, and surface (bark) are not smooth. It is possible to recognize a large number of fractals and hierarchical forms in organic and inorganic systems present in nature [43]. As a matter of fact these characteristics can be found in several vegetables and trees, in human or animal organs, in the outline of costs, in the island distribution on the archipelago, in the path of a river, etc.

The most revolutionary idea steaming from Fractal Geometry is the concept of fractional dimension. Indeed, in the Euclidean geometry, dimensions are considered integer. Dimension 0 for points, 1 for lines, 2 for surfaces and 3 for volumes. Moreover, in fractal geometry, dimension is the main (although not the only) parameter which represents the geometrical structure.

In general, fractals are geometric figures characterized by: fractional dimension  $(D_f)$ ; intricate and complex structure; geometric construction based on iteration procedure; geometric schemes that are repeated on different scales (self-similarity) [44].

For example, Sierpinski carpet is constructed by an iteration scaling procedure consisting in removing squares from an initial square of unit side-length. While the number of iterations increases, its geometrical structure shows a higher number of voids. As a result, it is highly intricate and detailed at all scales [43,44]. Fig. 1 shows the geometrical construction of Sierpinski carpet with  $D_f$ =1.77 (iteration *i*=0, 1, 2, 3).

Studying relationships between structures and properties of materials, fractal geometry represents a satisfactory tool to investigate and predict macroscopic behaviour of complex systems.

Indeed, in several aspects of microstructure of the materials, fractal characteristics have been recognized.



Fig. 1. Fractal scaling (i=0, 1, 2, 3) for Sierpinski carpet with two pores at first iteration.

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