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ScienceDirect
Ceramics International 41 (2015) 6350–6357
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Porous ceramic materials by pore-forming agent method: An intermingled fractal units analysis and procedure to predict thermal conductivity

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Received 28 October 2014; received in revised form 27 December 2014; accepted 15 January 2015
Available online 23 January 2015

Abstract

Porous ceramic materials can be produced by different techniques. One of the most important is pore agent method. The pore fraction, size, shape and distribution are linked to the pore-forming agent. In these materials porosity has a great influence in their physical properties and one of them is thermal conductivity. The role of the pore size distribution has been studied much less than pore fraction, probably because it is very difficult to describe and to characterize it. For this reason, in this paper, an original intermingled fractal model to predict thermal conductivity (taking into account entirely pore size distribution) has been proposed. This model is capable to reproduce fractal or non-fractal microstructure. Calculated data are in good agreement with experimental ones. The model could be considered as a microstructure simulator to improve thermal performance of porous ceramic materials.

Keywords: Fractal geometry; Modeling; Pore size distribution; Porous ceramics; Thermal conductivity

1. Introduction

Porous ceramic materials are used in several applications in many industrial and engineering fields namely filters and membranes, fuel cell electrodes, catalyst supports for biomaterials, piezo-electric materials, acoustically insulating bulk media. These materials often present low, fixed, and well defined thermal conductivity figures. Many different processes, have been reported in the literature in order to obtain porous ceramics [1,2]: gelcasting process [3,4], organic foam technique [5], freeze casting method [6–8] and pore-forming agent method [9,10]. The latter is able to yield high porosity ceramics.

This method is based on the admixture of combustible additives which are burned out leaving a pore fraction into the ceramic matrix. In most cases, this step is followed by sintering which induces mechanical strength to the ceramics. High temperature treatment not only influences the total porosity but it also changes the micro-porosity of the products. The manufacturing process to be used in order to obtain these ceramics can be compaction or extrusion.

Compaction techniques are based on the application of a uniaxial or isostatic pressure to densify the powder bed. The pressure can be applied at room or high temperature. Whatever the compaction process is chosen, the porogen is uniformly mixed to the powder before compaction and, later on, porogen is further eliminated by heating.

Thus, in the compaction process, pore fraction, size, shape and distribution are linked to the pore-forming agent [11].

In extrusion techniques, ceramic powders and pore-forming agent are mixed together. The resulting paste is molded using an extruder. Then, pore-forming agent is burned out and the samples are finally sintered. Often the final microstructure shows highly oriented cylindrical pores parallel to the extrusion direction [12].

One of the most pore-forming agent used is starch [13–15], but its application is limited to the production of large pores (5–50 μm) [9]. A good alternative is represented by polymers. They are very cheap and relatively sustainable. Furthermore, they are easily mixed with ceramic powder and burnt out at a moderately low temperature [9]. Nevertheless, it is difficult to avoid that pore-forming agents determine an irregular and

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http://dx.doi.org/10.1016/j.ceramint.2015.01.069
0272-8842/

Nomenclature

$\overline{c}$	conductance
D_f	fractal dimension
k	conductivity
k_{eff}	effective thermal conductivity
k_f	fluid thermal conductivity
k_s	solid thermal conductivity
IFU	intermingled fractal units
l	length of the piece of material
nth	iteration
n_B	number of units B
$\overline{R}$	resistance
$\overline{R}^1$	resistance for first line of pattern
$\overline{R}^2$	resistance for second line of pattern
$\overline{R}^3$	resistance for third line of pattern
$\overline{R}_s$	resistance of solid phase
$\overline{R}_f$	resistance of fluid phase
R_{eff}	total resistivity
R_f	fluid resistivity
R_s	solid resistivity
ε	pore volume fraction

random microstructure [1,2]. This way to increase porosity is particularly useful to control thermal conductivity value.

Efficient energy control is a critical issue of this time. A fundamental role is fulfilled by the availability of materials that could guarantee better performances when it comes to insulation (or transmission) of energy systems.

The research, in materials science and technology fields, is constantly investigating for advanced answers that could substitute and improve former performances.

It appears reasonable that thermal conductivity of materials is a basic characteristic for classifying them into different areas of applications. This physical magnitude is appreciably influenced by porosity.

It is very important to explain that the effective thermal conductivity (k_{eff}) of porous materials is a function of the: (a) intrinsic characteristics of the solid phase (k_s, one or more); (b) intrinsic characteristics of the fluid (k_f, one or more); (c) pores fraction of the voids (ε); (d) pore size distribution; (e) random level of microstructure [16,17].

The role of the volume fraction of voids has been widely investigated so far [18,19]. On the other hand the role of distribution has been studied much less [20,21].

This fact is probably due to the complexity of managing it during the production process, but also to the difficulty of describing and characterizing it from a geometrical point of view. Indeed, Euclidean geometry is not often suitable to reproduce complex shapes existing in nature. For this reason, the study and application of the basis related to Fractal Geometry are of great interest.

Fractal Geometry has been formalized and developed all over the 1970s by Mandelbrot.

He recognized a large number of fractal forms in organic and inorganic systems of nature [22]. 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) [23].

For example, the well known Sierpinski carpet is obtained by repeatedly 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 [22,23]. Fig. 1 shows Sierpinski carpet with three pores and its geometrical construction procedure (iteration $i=0, 1, 2, 3, 4$).

Fractal characteristics have been recognized in several aspects of the microstructure of the materials and they are relevant in order to describe and/or predict different aspects of their macroscopic behaviour.

Buiting et al. [24] studied porosity–permeability relationships for a tortuous and fractal tubular bundle. Xu et al. indicated that the geometrical parameters like porosity, fractal dimension for pore size distribution and tortuosity fractal dimension, have significant effect on the multiphase flow through unsaturated porous media [25]. Cai et al. [26] proposed a generalized fractal model to study spontaneous imbibitions process in different rock types, fibrous materials, and silica glass. Liang et al. [27] introduced an analytical model for streaming current in porous media obtaining a good agreement with available experimental data. Li and Horne [28] demonstrated that the heterogeneity of the Geysers rocks can be determined quantitatively using fractal dimension.

Eric et al. [29] studied heat flux performance for a prototype wick structure fabricated from compressed carbon foam when used with a Loop Heat Pipe (LHP) containing a fractal-based evaporator design. Atzeni et al. [30] measured fractal dimension, derived from pore size distribution, to correlate it with mechanical properties of vesicular basalt used in prehistoric buildings. Jin et al. equated the fractal dimension of air voids size-distribution

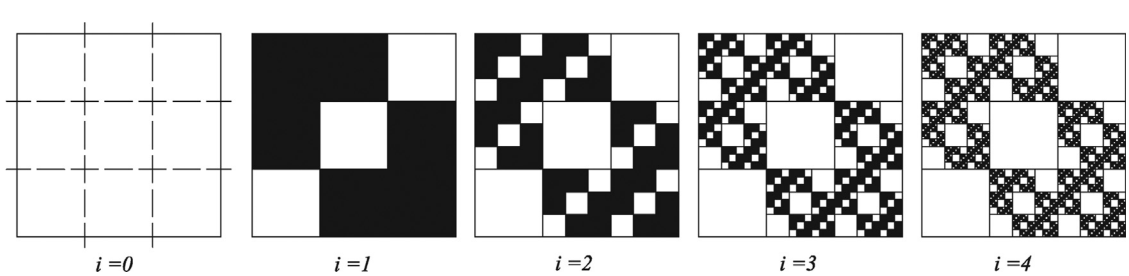

Fig. 1. Fractal scaling ($i=0, 1, 2, 3, 4$) for Sierpinski carpet with three pores at first iteration.