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High porous yttria-stabilized zirconia with aligned pore channels: Morphology directionality influence on heat transfer

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ABSTRACT

High porous yttria stabilized zirconia with unidirectionally aligned channels is used in engineering applications with extremely low thermal conductivity. This property is strongly influenced by microstructure features such as pore volume fraction, pore size distribution, random porous microstructure and pore morphology directionality. Although several models are reported in the available literature, but their analytical formulas are formalised for homogeneous structures or they are based on proportion between solid and fluid phases. These differences from real microstructures cause significant computational errors especially when thermal conductivity changes as the function of the measurement direction (parallel or perpendicular). In this context, the application of an intermingled fractal unit's procedure capable of reproducing porous microstructure as well as predicting thermal conductivity has been proposed. The results are in agreement with experimental ones measured for parallel and perpendicular directions and suggest improving the formalisation of fractal modelling in order to obtain an instrument of microstructure design.

1. Introduction

Advanced porous ceramics represent a wide range of materials used in different areas of research and applied engineering related to environment, energy and mass transport, health, *etc.* [1]. Generally, the development of pores into the ceramic microstructure, during the production process, has been prevented in order to increase their mechanical properties. However, the unique properties of new advanced porous ceramics, owing to the presence of pore volume fraction, make them appropriate for important applications usually reserved to other materials such as metals or polymers [1,2]. Indeed, especially for aggressive environments, characterised by the presence of corrosive substances and high temperature, only porous ceramics can guarantee an appropriate efficiency and service life. In addition to the peculiarities typical of ceramics, the characteristics acquired due to the presence of pores are low density, low thermal conductivity, high surface area, high specific strength, low dielectric constant and the possibility of controlling the permeability of fluids [1,2].

In this context, porous ceramics are utilised to fabricate filters [3], membranes [4], fuel cell electrodes [5,6], biomaterials [7], piezo-electric materials [8,9], and acoustically as well as thermally insulating bulk media [10,11].

Recently, special attention has been paid to Yttria-stabilized zirconia (YSZ). This large interest is due to its invariable properties in external environmental conditions such as thermal and mechanical stability, high ionic conductivity, elevated compatibility with electrode materials, remarkable hardness, chemical inertness, high corrosion and wear resistance, as well as low density and thermal shock resistance [12–14]. Moreover, fully and partially stabilized zirconia exhibit both low thermal conductivity and high mechanical properties [15]. This fact is more evident for partially stabilized zirconia and make it appropriate for different engineering applications such as in bulk thermal isolators as well as thermal barrier coatings (TBC) [16,17]. The research on ceramic TBC started in 1960s for protection of metal components in the combustion area of the engines [18]. Although remarkable improvements have been made in the fabrication methods and the resulting properties, still the efficiency of TBC remains a debatable issue.

The principal property requested in their applications, as insulator material, is the low capability of heat transfer. Therefore, the thermal conductivity (k_{eff}) depends on (*a*) environment surrounding conditions; (*b*) the characteristics of solid phase (k_s, more than one solid phase can be present in the microstructure of porous materials); (*c*) the thermal properties of the fluid phase (k_f, more than one fluid phase can be present in the microstructure of porous materials) and its state (gas or liquid); (*d*) the quantity of fluid phase trapped in the microstructure, pore volume fraction (ε); (*e*) the pore size range and (*f*) their distribution; (*g*) ordered or disordered structure [16,17,19–22].

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The aspects, with regards to solid and fluid phases as well as the pore volume fraction, have been extensively analysed [23,24], while the influence owing to the morphology of microstructure has been examined much less [20,25]. The reasons of this minor attention to structure characteristics are caused by the difficulty to have complete control on the porous structure development during production process as well as by the complexity of characterising experimentally and describing modelling.

In this context, the number of papers proposing modelling description of porous microstructure in order to predict physical properties is growing fast. Often, these models, which study heat transfer for heterogeneous or composite materials, exhibit several parameters, whose values must be empirically determined or predefined as per microstructure conditions. However, in the literature, not even a single model or prediction procedure with universal applicability has yet been proposed [26].

Concerning the morphology description of porous microstructure, in the last years, interest is represented by the use of concept and methods of Fractal Geometry. The formalisation of Fractal Geometry and its complete development dates back to 1970s by Polish-born, French and American mathematician namely Benoit Mandelbrot. In its famous book titled *the fractal geometry of nature*, various fractal forms in organic and inorganic as well as natural systems have been recognised [27].

The revolutionary idea proposed by the Fractal geometry is based on the fact that the geometric figures can have a non-integer dimension (D_f), but their values are fractional. According to empirical observations, in nature, it is impossible to find shapes which completely respond to Euclidean definition of figures. Mountains are not cones, clouds are not spheres, and surfaces are not smooth [27]. For these reasons, often fractal geometry is also defined as natural geometry.

Deterministic fractals are constructed following an iteration process which is based on the repetition of the same scheme at different scales. Consequently, the self similarity generates intricate as well as complex structures comparable with those of several material microstructures.

The possibility of describing porous microstructure of materials by using models is important in order to understand their macroscopic behaviour. In this context, several attempts to apply Fractal Geometry as modelling procedure have been proposed.

Yu et al. developed a fractal procedure to study fluid flow into porous media taking into account tortuosity and pore-area fractal dimension, phase fractal dimension, saturation, and microstructural parameters without taking into account empirical constants. This approach has been compared with the existing measurements founding an excellent agreement with experimental values [28]. Li et al. found a good correspondence between experimental capillary pressure curves of the Geyser rocks and their model data [29]. Cai et al. elaborated a generalised fractal modelling of spontaneous imbibition based on Hagen–Poiseuille flow. The proposed model calculations, taking into account different sizes, shapes and tortuosity of the pores, and the initial wetting-phase saturation, show that this model can describe the imbibition process in several porous media, natural or artificial [30–33].

At the same time, Fractal Geometry has been applied also to study heat transfer in porous media. Fan et al. calculated the fractal dimensions of wood porous microstructure by box counting on SEM images approximately equal to 1.4. The geometrical model, based on resistance method, predicts data in agreement with experimental thermal conductivity measured perpendicular to the fibres of wood [34]. Huai et al. carried out research on the effective thermal conductivity of fractal porous media [35]. They found that the heat transfer is principally influenced by the pore volume fraction, but the pore size and their distribution have significant effect. Zhou et al. established a fractal model to study the irregularities of the aquifer porous medium and their influence on thermal conductivity. By using this model, they reduced the computational difficulty typical of utilising analytical or numerical methods [36]. Huang et al. conducted a study on the thermal conductivity of salt/expanded graphite composite material [37]. They proposed a theoretical model in order to predict thermal conductivity values of this three-phase medium. The results show that these model predictions better fit experimental data than traditional model used for these materials [37].

Recently, a generalised modelling procedure based on the fractal base units intermingling has been proposed in order to describe fractal or non-fractal porous microstructure of several materials [20,38]. In particular, the Intermingled Fractal Units model (IFU) is used to reproduce every type of pore size distribution. In this way, it is possible to understand the relationship between structure and properties. Once the porous microstructure has been replicated, IFU is converted into electrical patterns in order to predict thermal conductivity [20,39,40].

However, unexplored case is represented by materials, as YSZ, characterised by unidirectionally aligned pores. These structures present different values of thermal conductivity as the function of the direction in which the measurement is made. For this reason, different models based on random structure are not able to be in agreement with experimental data for every direction considered.

In order to show the capability and the potentially of the IFU modelling, in this paper, for the first time, this fractal approach has been applied at the same time for both principal directions of the YSZ ceramics with unidirectionally aligned channels obtained by different freezing temperatures [41]. Moreover, the results will be compared with data from Maxwell-Eucken equations, Effective Medium Theory (EMT) and Bart model [26,42].

The possibility to develop a modelling procedure capable of controlling thermal properties, fluid flow kinetic as well as elastic behaviour of advanced porous ceramics could be very important to plan entirely their production process.

2. Materials and methods

IFU model procedure aimed at predicting thermal conductivity values is applied to porous ceramic materials by Hu et al. [41] named C1-9. These ceramics are obtained from commercially available yttria stabilized zirconia powder (ZrO_2–8 mol% Y_2O_3, AR grade, Fanmeiya Powders Co. Ltd., Jiangxi, China) with average dimension and specific surface respectively equal to 1.26 μm and to 6.49 m^2/g. Freeze casting process is used, wherein the shaping vehicle and the binder are Tert-butyl alcohol (TBA) and polyvinyl butyral (PVB). The fabrication method is carried out imposing three different temperatures −30 °C, −78 °C and −196 °C.

The premixed solution is obtained mixing 0.5 wt% of PVB into TBA, which is blended with YSZ powder, in the proportion respectively equal to 85 vol% and to 15 vol%. The homogeneous suspension is ensured by the ball-milling process, conducted for 4 h [41].

After these steps, the mixture was moulded and subjected to unidirectional freezing using freezing agents. After freezing process, cylindrical samples, which have the height of 18 mm and a diameter of 25 mm, were fabricated and sintered at 1450 °C for 2 h in the air.

Thermal transport option (TTO) of Physical Properties Measurement System has been used in order to measure thermal conductivity values [41]. Mercury intrusion porosimetry, MIP, by Auto Pore IV 9510, has been used to obtain pore volume fraction, pore cumulative curve, pore size distribution, pore range [41].