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A multi-level fractal model for the effective thermal conductivity of silica aerogel

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ABSTRACT

In the present paper, the fractal analysis on silica aerogel is performed based on the statistical self-similarity of porous media. A fractal model for the effective thermal conductivity of silica aerogel is proposed in consideration of the tortuosity of heat transfer path and the microstructure of secondary particle. The proposed model assumes that silica aerogel consists of two levels of microstructures: the secondary particles symbolized by improved 2-level Menger sponge and the cluster formed by secondary particles, which can be expressed as a function of density, the contact ratio, and the fractal dimensions. Validation with experimental data and predictions of other theoretical models shows that the present fractal model is reliable and accurate.

1. Introduction

Silica aerogel is a kind of typical nano-porous material with extraordinary properties of low density (0.003–0.500 $g \cdot cm^{-3}$), high porosity (80%–99.8%), large specific surface area (500–1200 $m^2 \cdot g^{-1}$) and ultra-low thermal conductivity (0.017–0.021 $W \cdot m^{-1} \cdot K^{-1}$, in air, 300 K), which together result in its excellent thermal-insulating performance [1,2]. As shown in Fig. 1, silica aerogel shows a nano-scale pearl-necklace structure that consists of loosely tangled strands of roughly SiO_2 spherical particles. These spherical particles are usually considered to consist of smaller primary particles. Helium pycnometry experiment also shows that the measured skeletal density of silica aerogel is smaller than that of amorphous silica [3], which indicates that these particles may themselves exhibit complex internal structure.

The heat transfer in silica aerogel includes heat conduction through solid skeleton and gas phase and thermal radiation. The gaseous heat transfer can be evaluated by Kaganer model [4] or Zeng model [5], and the thermal radiation can be acquired by Rosseland approximation [6, 7]. Therefore, many heat transfer models concentrating on solid conduction have been developed based on the internal structure of silica aerogel, which can be partially controlled in the synthesis process [8]. In the early studies, the solid thermal conductivity was usually evaluated through empirical relation based on the density of silica aerogel [9]. However, the empirical model ignores the relation between the thermal performance and the microstructure of silica aerogel. In recent studies, unit cell model and fractal model have been adopted to symbolize the microstructure in theoretical analysis of the effective thermal conductivity for nano-porous aerogel.

For unit cell model, a representative unit is often chosen on the assumption that the medium has a periodic structure. Based on this idea, different models have been developed to determine the effective thermal conductivity of such nano-porous media. Zeng et al. [8] proposed three kinds of cubic arrays as models for the effective thermal conductivity of silica aerogel. Bisson et al. [10] used the classical Ohm's serial model and parallel model to fit the experimental curves of effective thermal conductivity of divided silica xerogel beds. Yu et al. [11] developed two effective thermal conductivity models, namely the point-contact hollow spherical model and the surface-contact hollow cubic model, for the coupled conduction in high porosity materials such as xonotlite. Zhang et al. [12] considered the pore size distribution for the cubic array of intersecting spheres. Liao et al. [13] presented the proposed element physical model defined as a cubic air parcel containing a hollow silica sphere. Xia et al. [14] and Liu et al. [15] improved the unit cell models of octagonal model, Zeng45 model, and truncated octahedron. However, none of these models can represent the randomness of nanoparticle-aggregate structure of silica aerogel accurately.

For considering the disordered nature of nano-porous media, much attention has been paid to fractal model. Good et al. [16] provided a model for the network structure of secondary particles through the off-lattice DLCA simulation. Huai et al. [17] generated two types of fractal models (Sierpinski carpets (SCs) and Ben Avraham and Havlin carpet (BAH)) to represent the structures of porous media. Spagnol et al. [18] developed a numerical model via two steps: determining the properties of monolith at the nano-scale with a periodic fractal pattern built with fractal Von Koch snowflakes at high order and applying them to macroscopic grain packing. On the basis of the random aggregated structure of

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Nomenclature

A	the total heat transfer area of a representative unit
A_n	an equivalent area of a cross section having the same porosity as the non-included secondary-particles
a, c, l	the structural parameters of the secondary-particle–secondary-particle system
a_0	the pore size inside the solid unit cell model, nm
c_v	the specific heat capacity of porous medium at constant volume, $J \cdot kg^{-1} \cdot K^{-1}$
D_F	the fractal dimension
D_f	the area fractal dimension of the porous medium
D_T	the tortuous fractal dimension of the porous medium
d	particle size, nm
d_g	the diameter of gas molecules, m
d_{po}	the length of the unit cell, nm
k_B	the Boltzmann constant, $k_B = 1.38 \times 10^{-23}\ J \cdot K^{-1}$
k_{co}	the effective thermal conductivity of intersecting square rods, $W \cdot m^{-1} \cdot K^{-1}$
$k_{c,c}$	the effective thermal conductivity of secondary particles, $W \cdot m^{-1} \cdot K^{-1}$
$k_{c,mc}$	the thermal conductivity of the parallel chains, $W \cdot m^{-1} \cdot K^{-1}$
$k_{c,n}$	the thermal conductivity of non-included secondary particles, $W \cdot m^{-1} \cdot K^{-1}$
k_e	the effective thermal conductivity of the representative unit
k_g	the gaseous thermal conductivity in aerogel, $W \cdot m^{-1} \cdot K^{-1}$
k_s	the solid thermal conductivity of the nano-rod, $W \cdot m^{-1} \cdot K^{-1}$
L	the scale of a fractal object
L_o	the representative length of a flow path, nm
L_t	the total length of a solid chain
M	the measure of a fractal object
m_g	the mass of gas molecules, kg
N	the number of particles
N_A	the Avogadro's constant, 6.02×10^{23}, mol^{-1}
p	the ambient pressure, Pa
R_c	the thermal resistance of each chain, $m^2 \cdot K \cdot W^{-1}$
R_{c1}	the thermal resistance of the cubic secondary particle, $m^2 \cdot K \cdot W^{-1}$
R_{mc}	the total resistance of the mixed chains, $m^2 \cdot K \cdot W^{-1}$
S_S	the specific surface area, $m^2 \cdot kg^{-1}$
T	the ambient temperature, K

Greek symbols

γ	the specific heat ratio
$\gamma_a, \gamma'_a, \gamma_{a1}', \gamma_c$	the geometric length scale ratio
ρ_a	the density of silica aerogel, $kg \cdot m^{-3}$
ρ_s	the density of bulk silica, $kg \cdot m^{-3}$
τ	the tortuosity of a flow path
ϕ	the porosity of the porous medium
φ	the porosity of the secondary-particle aggregation structure
φ_a	the measured porosity of silica aerogel
φ_c	the porosity of the secondary particle
φ_{c0}	the porosity of the model of intersecting square rods

Subscript

av	average
p	particle
max	maximum
min	minimum

secondary porous nano-particles, Zhao et al. [19] developed a 3-D finite-volume numerical model to predict the total thermal conductivity of silica aerogel. Xie et al. [20] developed a fractal-intersecting sphere model for nano-porous silica aerogel. With respect to the above fractal models, the analysis of solid thermal conductivity is still obtained based on the unit cell analysis although the characteristic structure developed or proposed are fractal.

In this paper, we mainly focus on the tortuosity of the solid heat transfer path and aim to develop a fractal model suitable for describing the micro-structural characteristics of silica aerogel. The atmosphere temperature keeps 300 K in the calculation. Since the extinction coefficient of pure silica aerogel is larger ($>10^4\ m^{-1}$) when the temperature is low [21], the radiative thermal conductivity is about $0.0035\ W \cdot m^{-1} \cdot K^{-1}$ for silica aerogel with the density of $110\ kg \cdot m^{-3}$, which is much smaller than the value of the thermal conductivity of silica aerogel. Thus, the radiative heat transfer is ignored. Firstly, fractal analysis for the effective thermal conductivity of silica aerogel is presented. Then the predicted results of the fractal model are compared with those of other theoretical models and experimental data. Finally, the effects of structural parameters and fractal dimensions on the effective thermal conductivity of silica aerogel are discussed.

2. Fractal nature of silica aerogel

It is found that numerous objects are irregular and disordered in nature, such as rough surfaces, mountains, coastlines, lakes, rivers, and islands, all of which cannot be described with Euclidean geometry. Such objects are called fractals, and their dimensions are non-integral and defined as fractal dimensions [22]. In the fractal theory, the measure of a fractal object, $M(L)$, is governed by the scale L through a scaling law [22] in the form of $M(L) \sim L^{DF}$, where D_F represents the fractal dimension with its value depending on the dimension of the object. Such geometrical structures as Sierpinski gasket, Sierpinski carpet, and Koch curve are examples of the exactly self-similar fractals. However, the exactly self-similar fractals are rarely found in nature in a global sense. Many objects found in nature (such as the coastlines of islands) are statistically self-similar. These objects take on self-similarity in some average sense and over a certain local range of length scales L [23].

Silica aerogel typically has such a microstructure (Fig. 2): the smallest feature is a 'primary' particle of amorphous silica, typically 1–5 nm in diameter; the primary particles aggregate to form 'secondary' particles, typically with a higher order of magnitude; and these, in turn, form pearl-necklace structures whose details depend on the density [16,24]. There are two types of particles: primary particles inside one secondary particle and secondary particles inside a cluster. Both of them form irregular and tortuous particle chains which construct the solid backbone of silica aerogel (Fig. 1). Small-angle X-ray scattering

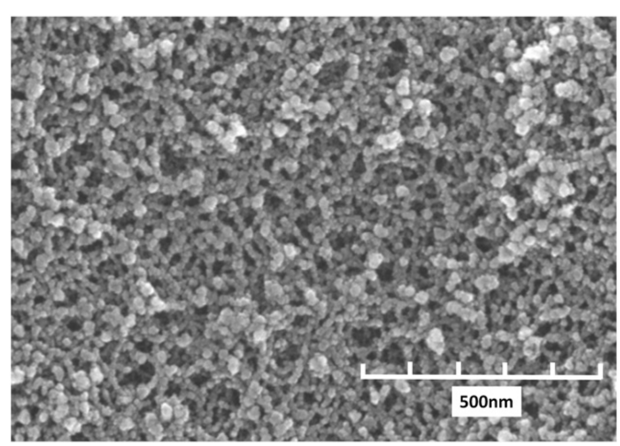

Fig. 1. SEM image of silica aerogel.