International Journal of Heat and Mass Transfer 129 (2019) 28–36

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

A generalized thermal conductivity model for nanoparticle packed bed considering particle deformation

Lin Zizhen [a,b], Huang Congliang [a,*], Li Yinshi [b,*]

[a] School of Electrical and Power Engineering, China University of Mining and Technology, Xuzhou 221116, China
[b] Key Laboratory of Thermo-Fluid Science and Engineering of MOE, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, China

ARTICLE INFO

Article history:
Received 10 July 2018
Received in revised form 3 September 2018
Accepted 14 September 2018

Keywords:
Nanoparticle packed bed
Thermal conductivity model
Thermal resistance
Thermal insulation material

ABSTRACT

Theoretically understanding the thermal conductivity of the nanoparticle packed beds (NPBs) is critical for designing high-performance thermal insulation materials. Currently, the classical effective medium assumption (EMA) model, Nan model, just show their good prediction at a high porosity of NPBs ($\geq$0.75). Herein, we propose a generalized model of the thermal conductivity that almost covers the whole porosity range by considering the effect of the nanoparticle deformations on the thermal contact resistance (R). It has been demonstrated that our model matches the experimental results great well. It is also found that at high porosity R is dominated by the phonon diffusive scatterings (R_{cd}), while it is determined by the phonon ballistic scatterings (R_{cb}) at a low porosity. More interestingly, R can determine the porosity at which the lowest thermal conductivity of NPBs appears. This work opens a new way to design the desired thermal insulation materials.

1. Introduction

The silica nanoporous materials, such as silica aerogel [1,2], MCM-41 [3] and SBA-15 [4], have drawn a wide interest because of their quite low thermal conductivities (k) for potential applications as thermal insulation materials. For such kinds of materials, even without considering the air and the thermal radiation in pores, the thermal conductivity could still be higher than the Einstein limit (k_E) [5] corresponding to the amorphous bulk. These thermal insulation materials are still somewhat not competent for their applications in several areas, such as high temperature energy storage tanks [6–9] and space applications [10]. To probe a nanoporous material with a quite low thermal conductivity is still desirable.

The nanoparticle packed bed (NPB) as one typical powder-moulding material is focused on in this work. Compared to the traditional nanoporous material, the NPB has an advantage of high density of inter-nanoparticle contact interface, which could provide an effective scattering mechanism for mid-and long-wavelength phonons that contribute heavily to the thermal conductivity [11–13]. Because of large amounts of interfaces, the NPB could possess a quite low thermal conductivity [14–17]. To understand the effect of the interface on the thermal conductivity of NPBs, an effective medium approach (EMA) phonon thermal conductivity model is proposed in this work including the interface effect. Before introducing our model, the feasibility of using the phonon concept in describing the thermal transport properties of NPBs is firstly discussed.

Phonon is usually introduced to describe the heat transfer in crystalline materials by the lattice vibration approach. In general, the definition of phonons is applicable when the character size of materials is larger than the lattice constant which is less than 1 nm for most materials. Therefore, if the pore is not less or not much less than 1 nm in a nano-porous material, the phonons can be applied to describe the heat transfer. On the contrary, the phonon framework fails to describe the heat transfer when the materials is amorphous or the character size of materials is less than the lattice constant, such as single atom or chemical bond, where an ab-initio calculations should be used to calculate the heat transport properties. Considering the sizes and the crystalline structure of the silica nanoparticles in this work, the phonon framework should be applicable.

Several phonon models have already been proposed to theoretically understand the effect of interfaces on the thermal conductivity of composites. The classical acoustic mismatch model (AMM) [18–20] and the diffuse mismatch model (DMM) [21] are originally proposed to predict the effective thermal conductivity (k_e) of composites by taking phonons as mechanical waves in the processes of

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* Corresponding authors.
E-mail addresses: huangcl@cumt.edu.cn (H. Congliang), ysli@mail.xjtu.edu.cn (L. Yinshi).

https://doi.org/10.1016/j.ijheatmasstransfer.2018.09.067
0017-9310/

Nomenclature

k_e	effective thermal conductivity
k_s	thermal conductivity of solid phase
k_a	thermal conductivity of air
k_r	radiative thermal conductivity
R	thermal contact resistance
E_λ	spectral extinction coefficient
τ_λ	spectral transmittance
θ_D	Debye temperature
P	pressure
T	temperature
r	radius of nanoparticles
l_m	phonon mean free path
a	radius of contact surface
S	cross-sectional area of nanoparticles
ω_m	maximum phonon frequency
ω	phonon frequency
k_E	thermal conductivity of amorphous bulk
φ	porosity
ρ_1	density of NPB
ρ_2	density of bulk
σ	Stefan–Boltzmann constant
E_R	Rosseland extinction coefficient
λ	wavelength of the radiation
I_λ	black body spectral radiative intensity
P^*	reduced pressure
d_{pore}	diameter of nanopores
γ	Gruneisen constant
δ	pore characteristic length
K	elastic constants
A_c	NPB cross-sectional area
v	phonon group velocity
m^*	effective electron mass

their colliding with interfaces, where the interface is treated to be specular or diffusive respectively. While normally the interface is not fully specular or diffusive, these two models (AMM and DMM) only give the upper and lower limits of thermal contact resistances (R). Importantly, the size effect of interface on R is not included in these two models, when different sizes of interface at nanoscale could give different R. Taking the size effect of interface into account but assuming interface to be diffusive, the k_e model has been widely established based on the effective medium approximation (EMA) approach, including the size effects of interface by shortening the mean free path of phonons for the restriction of the small interface, such as the Bahadur model [22] and the widely-used Nan model [23]. By carefully taking the ballistic and diffusive transport of phonons into account, Prasher [24,25] have successfully taken the size effect of interface into account in modelling R between two nanoparticles. Although the size effect of interface has already been carefully considered, the nanoparticle deformation which could importantly affect the interface and will show up at a low porosity, has not been considered before. In this work, by modeling the nanoparticle-deformation influenced R, we extend the theoretical understanding of the thermal conductivity of NPBs from a high porosity to a low porosity.

This paper is organized as follows: In Section 2, the preparation of silica NPB and the measurement of thermal conductivity are represented. In Section 3, the k_e-prediction model with nanoparticle deformation considered is established. For Section 4, we further separate this part into four parts. In Section 4.1, the k_e-prediction model is testified with the experimental approach. The k_e predicted by the classical EMA model also added for comparison. In Section 4.2, the thermal conductivity of radiation (k_r), confined air (k_a) and solid phase (k_s) are experimentally studied in this part, and the experimental k_s is also compared with that predicted by the classical EMA model to reveal the effect of nanoparticle deformation on NPB-thermal conductivity. Finally, the influence of nanoparticle deformation on R is discussed to reveal the influence of nanoparticle deformation on k_e.

2. Sample preparation and characterizations

2.1. NPB preparation and structure characterization

Commercial silica nanoparticles (Beijing DK Nano Technology Co., Ltd) with diameters of 10 nm and 50 nm are adopted in this work. The macrostructure of 50-nm silica nanoparticle powders are shown in Fig. 1(a), and the microstructure is shown in Fig. 1(b), observed with the field-emission scanning electron microscopy (SEM) on a QuantaTM-250 instrument (FEI Co., USA) with an accelerating voltage of 30 kV. The diameter of nanoparticles keeps almost same, and some clusters are formed by nanoparticle aggregations in Fig. 1(b). To eliminate the aggregation, the nanoparticles are firstly treated with a physical ultrasonic dispersion for 60 min, and then the ball-milling method is utilized to uniformly blend nanoparticles (200 rpm for 60 min, then 100 rpm for 60 min). The microstructures of the physical-dispersion silica nanoparticles are shown in Fig. 1(c), observed by the transmission electron microscope (TEM) method with an accelerating voltage of 80 kV performing on Tecnai G2 F20 instrument (FEI Co., USA). It shows that the nanoparticles distribute uniformly and the aggregations of nanoparticles are eliminated. Finally, the widely-used cold-pressing method [13,26,27] is applied to prepare the NPBs, the pressing process is illustrated in Fig. 1(d). Sixteen different stamping pressures (1, 2, 3, 4, 8, 14, 20, 24, 28, 32, 34, 36, 38, 40, 42 and 44 MPa) are applied to press the nanoparticles into different-porosity NPBs. The microstructure of 50-nm NPB with a tableting pressure of 42 MPa is shown in Fig. 1(e), and the details of interface in Fig. 1(e) is further depicted in Fig. 1(f), where the deformation of nanoparticles can be obviously seen. The length scale of the inter-nanoparticle contact area is 10–30 nm, as illustrated by the red line in the inset of Fig. 1(f). The high resolution transmission electron microscope (HRTEM) is further utilized to character the microstructure of silica nanoparticles in our work as shown in Fig. 1(g). An ordered crystal structure is observed indicating that the silica nanoparticles used in this work is crystalline. Additionally, the inset diffraction patterns also confirm the crystalline nature of the silica nanoparticles.

2.2. Thermal conductivity measurement

The k_e measurement is performed on a commercial device (Model TC3000, Xian XIATECH Technology Co.), according to the hot-wire method [28,29]. More details about the measurement can be found in our previous works [15,17]. With every sample independently measured for five times, a mean k_e is obtained with a deviation less than 4.5%. The air thermal conductivity (k_a) in a NPB is estimated by subtracting k_e measured at indoor atmospheric pressure with that measured in a vacuum environment (k_v) (detail refer to Appendix A). The radiative thermal conductivity (k_r) is calculated by the diffusion approximation model based on the measurement of spectral transmittance (τ_λ), which is observed with a Fourier transform infrared spectrometer