Effective Thermal Conductivity for Low Density Silicon Nitride Porous Ceramics

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Abstract. Thermal conduction in porous materials generally includes four heat transfer forms, i.e. heat transfer via the gas phase, heat conduction along the solid matrix/skeleton, thermal radiation and gas-solid coupled heat transfer. The size effects on the gas and solid thermal conductivities are introduced to predict the effective thermal conductivity of the silicon nitride porous ceramic at room temperature, and the predictions from the random model present good agreements with the experimental data. The effect of the porosity on the effective thermal conductivity of the low density silicon nitride porous ceramic are studied as well, and the low density porous ceramics can achieve a low thermal conductivity in the range of 0.08-1.2 W/m K for a good performance of thermal insulation.

1. Introduction
Silicon nitride (Si$_3$N$_4$) porous ceramic generally presents low density, high specific surface area and wide range porosity, which is a multiple functional material and can be widely used in many fields, such as industry, aerospace, thermal protection, environmental engineering, chemical engineering, agriculture, energy and buildings [1, 2]. Since the porosity of the Si$_3$N$_4$ porous ceramic can be controlled reasonably during the preparation, the porous ceramic also can be prepared as a porous material with high porosity and low density, which can be easily used as a kind of high performance thermal insulation material [3, 4]. Compared with the super thermal insulation, i.e. nano-porous aerogel (thermal conductivity magnitude: 0.001 - 0.01 W/m K at room temperature [5, 6]), some porous ceramic (such as α-Si$_3$N$_4$) presents a lower performance of thermal insulation (thermal conductivity magnitude: 0.1 - 1.0 [4]) but much higher mechanical properties, such as tensile strength and elastic modulus [7], because the pure aerogel as silica aerogel or carbon aerogel is very fragile which cannot provide good mechanical properties [5, 8, 9]. For this reason, the Si$_3$N$_4$ porous ceramic may be a good candidate for the thermal insulation material when the mechanical properties should be concerned.

Since the effective thermal conductivity can directly reflect the thermal insulation performance of the porous media, many theoretical models, such as Series model & Parallel model [10], Eucken model [11], Russell model [12], Random distribution model [10] etc., were proposed or modified to get accurate predictions. When someone uses these models to calculate the effective thermal conductivity of porous materials, the porosity, the thermal conductivity of the gas filled in the porous media, and the thermal conductivity of porous media solid phase should be known. For most predictions, the porosity can be calculated by the material density directly, but the thermal conductivities of the gas and solid phases are difficult to obtain, and in most cases we have to use the bulk thermal conductivity to complete the calculations. Once we do this, the prediction results will be overestimated inevitably, because the size effect on the thermal conductivity is not concerned. Here, the size effect in porous
material can be understood as follows [6, 13, 14]: (1) for gas thermal conductivity, the porous ceramic includes amount of micro- or nano-scaled pores, so that the mean free path of the gas molecules will be restricted by the pore boundary, and thus the gas thermal conductivity will be lower than the bulk value, and (2) for solid thermal conductivity, once the particle size of the porous ceramic decreases to the magnitude of the solid atom mean free path (or smaller), the thermal conduction along the solid skeleton will be weakened remarkably.

The present study focus on how to make an accurate prediction of the effective thermal conductivity of the Si3N4 porous ceramic by introducing the size effect, and then we shall study the effect of the porosity on the effective thermal conductivity of the low density porous ceramic, of which the objective is to make guidance for the optimization of the Si3N4 porous ceramic to achieve a higher thermal insulation performance.

2. Theory of Thermal Conduction in Porous Material

Thermal conduction in porous materials generally can be classified to four heat transfer forms, i.e. (1) heat transfer via the gas molecules, (2) heat conduction along the solid matrix/backbone, (3) thermal radiation and (4) gas-solid coupled heat transfer. For most porous materials, the pore size generally distributes in the micro-scale or nano-scale magnitudes, so that the heat transfer via the gas molecules generally presents a conduction form instead of a convective form. Therefore, the effective thermal conductivity of the porous material depends on the above four heat transfer forms. The most widely used model is given by [5, 6]:

$$\lambda_{eff} = \lambda_s + \lambda_r + \lambda_g + \lambda_c$$

(1)

where $\lambda_s$, $\lambda_r$, $\lambda_g$ and $\lambda_c$ are the solid thermal conductivity, radiative thermal conductivity, gaseous thermal conductivity and gas-solid coupling conductivity corresponding with the above four heat transfer forms, respectively. Eq.1 denotes the contributions of the solid phase, radiation, gas phase and gas-solid coupling to the effective/total thermal conductivity of the porous material, which also can be called decoupled model. Many previous studies reviewed in Ref. [6] have proved that the decoupled model has a good prediction accuracy for porous material, especially for nano-porous media. The high accuracy of Eq.1 can be attributed to the consideration of several size effects on the heat transfer, and details are described in Refs. [5, 6].

For engineering calculations, the decoupled model is more complicated and not convenient for engineering design. Therefore, most of engineers prefer simpler formulas to predict the effective thermal conductivity of the porous material. Table 1 shows some commonly used models.

| Model          | Expression                                                                 | Index |
|----------------|---------------------------------------------------------------------------|-------|
| Parallel model | $\lambda_{eff} = \phi \lambda_g + (1 - \phi) \cdot \lambda_s$          | (2)   |
| Series model   | $\lambda_{eff} = \frac{1}{\phi / \lambda_g + (1 - \phi) / \lambda_s}$   | (3)   |
| Random model   | $\lambda_{eff} = \lambda_g \phi \cdot \lambda_s ^{(1 - \phi)}$          | (4)   |
| Eucken model   | $\lambda_{eff} = \lambda_s \frac{1 + 2\phi(1 - \lambda_s / \lambda_g) / (2\lambda_s / \lambda_g + 1)}{1 - \phi(1 - \lambda_s / \lambda_g) / (2\lambda_s / \lambda_g + 1)}$ | (5)   |
| Russell model  | $\lambda_{eff} = \lambda_s \frac{\phi ^{2/3} + \lambda_s / \lambda_g (1 - \phi ^{2/3})}{\phi ^{2/3} - \phi + \lambda_s / \lambda_g (1 - \phi ^{2/3} + \phi)}$ | (6)   |
The parameter of $\phi$ is the porosity of the porous material, which can be calculated from the density of the porous material ($\rho$) and the bulk solid density ($\rho_{\text{bulk}}$), expressed by:

$$\phi = 1 - \frac{\rho}{\rho_{\text{bulk}}}$$  \hspace{1cm} (7)

The size effect on the gaseous thermal conductivity $\lambda_g$ can be used Kaganer model to predict, given by [15]:

$$\hat{\lambda}_g = \frac{\lambda^0_g}{1 + 2 \beta \Lambda_g / D}$$  \hspace{1cm} (8)

where $\lambda^0_g$ is the gaseous thermal conductivity in free space, $\beta$ is a accommodation coefficient (for air and N$_2$, $\beta \approx 1.55$), $D$ is the mean pore diameter of the porous media, and $\Lambda_g$ is the mean free path of the gas molecules, given by:

$$\Lambda_g = \frac{1}{\sqrt{2 \pi d_g^3 n_g}} = \frac{k_B T}{\sqrt{2 \pi d_g^3 p}}$$  \hspace{1cm} (9)

where $d_g$ is the diameter of the gas molecule, $n_g$ is the number density of gas molecule, $k_B$ is the Boltzmann constant, $T$ is the gas temperature, and $p$ is the gas pressure. For air or N$_2$, $\Lambda_g \approx 70$ nm at room temperature.

The size effect on the solid thermal conductivity $\lambda_s$ can be addressed by Chen model [13], expressed by:

$$\lambda_s = \lambda_{\text{bulk}} \frac{3d_p}{3d_p + 8\Lambda_{\text{bulk}}}$$  \hspace{1cm} (10)

where $d_p$ is the average particle size of the porous media, and $\Lambda_{\text{bulk}}$ is the bulk solid mean free path, which can be deduced according to the Kinetic theory, given by:

$$\hat{\lambda} = \frac{1}{3} C_v \nu \Lambda$$  \hspace{1cm} (11)

where, $C_v$ is the solid volume specific heat, $\nu$ is the sound velocity in the solid. Substituting Eqs.8 and 10 into Eqs.2-6, we can believe that the size effects on the gas and solid thermal conductivities are finished.

3. Results and Discussion

3.1. Prediction Validation

The experimental data of the effective thermal conductivity of the ZrP$_2$O$_7$ bonded $\alpha$-Si$_3$N$_4$ porous ceramic published in Ref. [4] are employed to validate the present models. For the experimental samples, the bulk thermal conductivity of the $\alpha$-Si$_3$N$_4$ and ZrP$_2$O$_7$ are 10 and 0.51 W/m K, and the particle size of the porous ceramic is about 500 nm. In the predictions, the mean pore size is assumed 1000 nm, which is two times of the particle size, and then the gas thermal conductivity is about 0.0214 W/m K instead of 0.026 W/m K for air. The solid thermal conductivity of the ZrP$_2$O$_7$ bonded $\alpha$-Si$_3$N$_4$ is calculated by the mass weighted average from the solid components.

Fig.1 shows the predictions of different models and experimental data. Only the results of Eq.4, i.e. Random model, are in good agreements with the experimental data, in which the errors is in the range of 4% to 14.6%, while the Parallel model (Eq.2), Series model (Eq.3), Eucken model (Eq.5) and Russell model (Eq.6) fail to make accurate predictions, and this phenomenon can be attributed to random pore structures in the porous ceramics.
### 3.2. Structure Effects on Effective Thermal Conductivity of Porous Ceramic

The porosity, mean pore size and average particle size are the most important structure parameters of the porous ceramic. Since the three structure parameter are not independent, and the micro- or nano-scaled structure of the porous ceramic often present an amorphous structure instead of an ordered matrix structure, in the present study we shall learn from the structure characterization method of the nanoporous aerogels to define the porous ceramic structures, expressed as [16]:

$$d_p = \frac{3}{2} D \frac{1 - \phi}{\phi}$$  \hspace{1cm} (12)

Fig. 2 shows the ratio of the particle size and pore size as the function of the porous ceramic porosity, in which we shall define $\phi > 0.6$ as high porosity porous ceramic because on this condition the particle size will be less than the pore size gradually, and with the pore size increases the density of the material will decrease.

In the previous work [7], we prepared several samples of $\beta$-Si$_3$N$_4$ porous ceramic by carbothermal reduction–pressureless reaction sintering in nitrogen using SiO$_2$ and $\alpha$-Si$_3$N$_4$ as raw materials. The samples with a porosity range of 0.55-0.85 and the raw material of $\alpha$-Si$_3$N$_4$ particles clusters are selected to study the effective thermal conductivity of the porous ceramic. The SEM image of the sample of porosity 0.7 are shown in Fig.3.

The samples has a mean pore size about 2000 nm, and the average solid particle size (microwire diameter) is about 1000 nm, which is almostly equal to the raw $\alpha$-Si$_3$N$_4$ particle size. The values of 10 W/m K and 150 W/m K are choosed as the bulk thermal conductivity of $\alpha$-Si$_3$N$_4$ and $\beta$-Si$_3$N$_4$, respectively.
respectively. The sound velocity in the bulk Si$_3$N$_4$ can be deduced from the Young's modulus ($E$) and Poisson coefficient ($\sigma$) of the pure Si$_3$N$_4$. For $\beta$-Si$_3$N$_4$, we choose $E = 30000$ MPa and $\sigma \approx 0.3$ for the predictions, and then one can obtain the sound velocity as $v = 3569$ m/s, and the mean free path of the solid atoms/phonons is about 56 nm. Substituting these parameters into Eqs. 8 and 11, one can obtain the thermal conductivities including the size effects, i.e., $\lambda_e = 131$ W/m K and $\lambda_g = 0.0235$ W/m K. The effective thermal conductivity of the porous ceramic is shown in Fig.4.

![Fig.3 SEM image of sample S50 $\beta$-Si$_3$N$_4$ porous ceramic [7]](image)

![Fig.4 Effective thermal conductivity of $\beta$-Si$_3$N$_4$ porous ceramic. (a) low density. (b) high density](image)

Fig.4(a) shows the effective thermal conductivity of low density ($\phi > 0.6$, $\rho \in [300, 1200]$ kg/m$^3$, the density of raw Si$_3$N$_4$ is about 3100 kg/m$^3$) as the function of the porosity. Compared with the bulk value 150 W/m K, the thermal conductivity of the low density porous ceramic. The thermal conductivity of ceramics is almost two orders (even three orders, such as the sample of $\phi = 0.85$) of magnitude lower than that of the bulk one. The thermal conductivity of the present samples mostly in the range of 0.08-1.2 W/m K, and can be regarded as one of the good performance thermal insulation materials. In addition, Fig.4(b) is the predictions for the high density porous ceramics, the thermal conductivity can achieve 20 W/m K when the porosity is higher than 0.2, which can be comparable to that of the carbon steel and also prove that Si$_3$N$_4$ porous ceramics can be regarded as a good pertential thermal conduction material at a certain porosity.

4. Conclusion

The effective thermal conductivity of Si$_3$N$_4$ porous ceramic was theoretically studied by introducing the size effects of pore size and particle size of the porous ceramic. The experimental data of the ZrP$_2$O$_7$ bonded Si$_3$N$_4$ porous ceramic were used to validate the present prediction method, and the
results proved that the random model has a good prediction accuracy for the effective thermal conductivity of the $\text{Si}_3\text{N}_4$ porous ceramic. Low density $\beta$-$\text{Si}_3\text{N}_4$ porous ceramics with a porosity range of 0.55-0.85 were prepared for the study. The effect of the porosity on the effective thermal conductivity was studied, and the thermal conductivity of the low density porous ceramics can achieve a low thermal conductivity in the range of 0.08-1.2 W/m K, which can be regarded as one of the good performance thermal insulation materials.

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