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Research Paper

A theoretical model for the effective thermal conductivity of silica aerogel composites

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HIGHLIGHTS

- A theoretical model of the effective thermal conductivity is developed.
- The procedure accuracy is validated with the experimental results within ±10%.
- The influences of porosity, temperature and pressure are investigated.
- Best doping diameter and concentration exists which vary with temperature.

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ABSTRACT

In the present paper, a complete engineering calculation procedure for fast evaluations of the effective thermal conductivity of the silica aerogel composites is developed as follows. First, the spherical hollow model is adopted to calculate the conductive thermal conductivity of pure silica aerogels. Then, a mixing model is used to consider the conduction enhancement effects of doped opacifiers and fibers. Next, the Mie theory is adopted to calculate the temperature-dependent Rosseland mean extinction coefficient of the aerogel composites, and the radiative thermal conductivity is obtained according to the Rosseland equation. Finally, the superposition of the conductive thermal conductivity and radiative thermal conductivity gives the total effective thermal conductivity of aerogel composites. To validate the accuracy of the present model, some corresponding experimental measurements are conducted based on the Hot Disk thermal constant analyzer, and the experiment data agree well with the theoretical calculation values. The maximum deviation is about ±10%. The influences of the temperature, pressure and the structure parameters on the prediction of the effective thermal conductivity are then investigated. To determine the dominant factor of the effective thermal conductivity, the contributions of gas, solid and radiation to the total effective thermal conductivity are investigated individually and some significant results are obtained.

1. Introduction

Silica aerogels are typical nano-porous materials prepared through a sol-gel process and then by the supercritical drying technology. They have been widely used as the insulation materials due to their unique properties including the high porosity, low density, large specific surface area and extremely low thermal conductivity [1–3]. There are three heat transfer modes in aerogels, including solid conduction, gas conduction and radiation. The nano-porous silica aerogel skeleton makes up the extremely long conduction path leading to a small solid thermal conduction. The motion of gas molecules is suppressed in aerogels because the nano pore size (∼20 nm) is less than the mean free path of gas molecules (∼70 nm at atmospheric pressure), therefore limiting the gas thermal conductivity [4,5]. Much attention has been focused on the effective thermal conductivity of the aerogels, and the models can be divided into four categories. The first model is the superposition one which adds the solid, gas and radiation thermal conductivity together, expressed as $\lambda_e = \lambda_s + \lambda_g + \lambda_r$ [6,7]. The second model was developed based on the periodic regular unit cell simplified from the complex nano-porous structure. In this model, simplified unit cell is adopted to analyze the combined solid and gas thermal conductivity (λ_c) to replace the simple superposition of solid and

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gas thermal conductivity. Zeng et al. [8] proposed three cubic array geometry structures, named intersecting square rods, intersecting cylindrical rods and intersecting spheres, to predict the effective thermal conductivity of aerogels. In their model an empirical parameter is needed in the intersecting sphere model which is artificially assumed before the calculations. Wei et al. [9] and Lu et al. [10] then adopted the cubic array of intersecting spheres to theoretically study the heat transfer in aerogels. Recently, Dan et al. [11] proposed a spherical hollow cube model to obtain the effective thermal conductivity of aerogels without any empirical parameters. The third model was developed based on the numerical method using the lattice Boltzmann method [12] or finite volume method [13]. The random generation growth method [12] and diffusion-limited cluster-cluster aggregation method [13] can be used to reconstruct the random structure of aerogels. The fourth model is the experimental method adopting the guarded hot plate [14], hot strip [15,16] or hot wire method [17,18] to directly measure the effective thermal conductivity of aerogels.

Pure aerogels have two main defects: one is its solid skeleton being very brittle and low-strength due to the high porosity; the other is that pure aerogels are almost transparent to the infrared wavelength within the range of 3–8 μm, leading to dramatically increasing radiative thermal conductivity at high temperature [10,19]. Therefore, fibers are added to enhance their mechanical strength and some opacifiers, such as SiC, TiO_2 and C, are doped to improve the extinction coefficient of aerogels. The doped fibers and opacifiers can reduce the thermal radiation meanwhile they will increase the heat conduction in aerogels. Many researchers have investigated the influences of additives on the performance of the composites, and quite a few predict models and experimental methods were developed. Lu et al. [10] used the cuboid unit cell with eight edges made of fibers to replace the random distribution of fibers. Wang et al. [20] adopted the lattice Boltzmann method to investigate the effective thermal conductivity of fibrous materials considering the fibers random distribution. Duan et al. [19] used the finite volume method and Mishra [21] used the lattice Boltzmann method to investigate the combined radiative and conductive heat transfer in fibrous materials. Kuhn et al. [22] adopted the Fourier transform infrared (FTIR) spectrometer to observe the extinction effects of TiO_2 and Al_2O_3, and demonstrated that opacifier-loaded aerogels are more efficient insulation materials at high temperature. Wang et al. [23] used a hot-wire device to measure the effective thermal conductivity of aerogel composites, and adopted the FTIR spectrometer to measure the specific extinction coefficient of aerogels doped with TiO_2. Zeng et al. [24] presented a theoretical method to determine an optimal carbon doping content to minimize the effective thermal conductivity of aerogel composites.

In general, there are two geometry scales in aerogel composites, the nanoscale pores and microscale additives, as shown in Fig. 1. The multi-scale system and complex spatial random structure make it hard to fast predict the effective thermal conductivity with enough accuracy. Although the experimental measurements and numerical simulations may have a more precise prediction than other methods, they are time-consuming and resource-intensive. As a result, they cannot meet the requirement of the fast evaluations of the effective thermal conductivity for aerogel composites in engineering applications. To quickly predict the effective thermal conductivity of aerogel composites, a complete calculation algorithm is developed in the present paper based on the simplified regular unit cell structure. The spherical hollow cube model [11] proposed by Dan et al. is adopted in the present paper to determine the effective thermal conductivity of pure aerogels because of its advantage over others such as Zeng et al. [8]. The influences of the doping fibers and opacifiers on the heat conduction and thermal radiation are considered. The spectral extinction coefficients of opacifiers and fibers are obtained theoretically by the Mie theory other than by FTIR spectrometer measurement. To validate the accuracy of the proposed method, a Hot Disk instrument based on the transient plane source method is adopted to measure the effective thermal conductivity of the aerogel composites predicted by the present method. After validations, the influences of environmental parameters and structure parameters on the effective thermal conductivity of aerogel composites are investigated. Here, the environmental parameters include the temperature and the pressure, and the structure parameters include the porosity, the doping sizes, doping concentrations of additives (fibers and opacifiers) and the types of opacifiers. To determine the dominant contribution factor for the total effective thermal conductivity of aerogel composites, the contributions of solid, gas and radiation to the total effective thermal conductivity are decoupled to provide a guideline for decreasing the effective thermal conductivity of the aerogel composites. In the following the above-mentioned contents will be presented in order.

2. Theoretical model

In general, the solid heat conduction, gas heat conduction and thermal radiation coexist in aerogels. The doping fibers and opacifiers increase the solid heat conduction and reduce the thermal radiation. It has been widely recognized that the solid heat conduction and gas heat conduction are coupled. Then, the effective thermal conductivity of aerogel composites is [25]

$$\lambda_e = \lambda_c + \lambda_r \tag{1}$$

where subscript c denotes the combination of thermal conductivity of solid and gas and subscript r denotes the radiative thermal conductivity. In the following the predict methods of λ_c and λ_r will be presented in detail.

2.1. Spherical hollow cube model for thermal conductivity of solid skeleton of pure aerogels

In the present paper, we adopt the spherical hollow cube model [11] to describe the nano-porous structure of the pure aerogels. The spherical hollow cube model is shown in Fig. 2. Fig. 2(a) shows the 8 unit cells model and Fig. 2(b) shows the unit cell model. The characteristic length "a" and "r" are not constants and they can be derived from the equations presented with different porosity ϕ_a and specific area S_s. The whole body of Fig. 2 represents the pure aerogel and no opacifiers and fibers are included in the unit cell.

Suppose that heat is conducted from bottom to top then based on the one-dimensional heat conduction assumption, the heat flux from the bottom to the top can be divided into four parts, as shown in Fig. 3.

The conductive thermal conductivity of the pure aerogels can be derived from the Fourier's law [11]:

$$\begin{aligned}\lambda_{a,c} &= \frac{2(Q_1+Q_2+Q_3+Q_4)}{a\Delta T}\\ &= \frac{2\lambda_s\left[\frac{a^2-\pi r^2}{2}+2\arccos\left(\frac{a}{2r}\right)r^2 - a\sqrt{r^2-\left(\frac{a}{2}\right)^2}\right]}{a^2}\\ &\quad + \lambda_g\pi\left(\frac{r^2}{a^2}-\frac{1}{4}\right)\\ &\quad - \frac{\lambda_s\pi}{k^2 a}\left[kr(\cos\theta_1-\cos\theta_0) - \frac{a}{2}\ln\left(\frac{kr\cos\theta_1+a/2}{kr\cos\theta_0+a/2}\right)\right] + \frac{4}{a}\\ &\quad \times \int_{a/2}^{r} \frac{\arcsin\left(\frac{a/2-\sqrt{x^2-a^2/4}}{\sqrt{2}x}\right)x\,dx}{\sqrt{r^2-x^2}/\lambda_g + (a/2-\sqrt{r^2-x^2})/\lambda_s}\end{aligned} \tag{2}$$

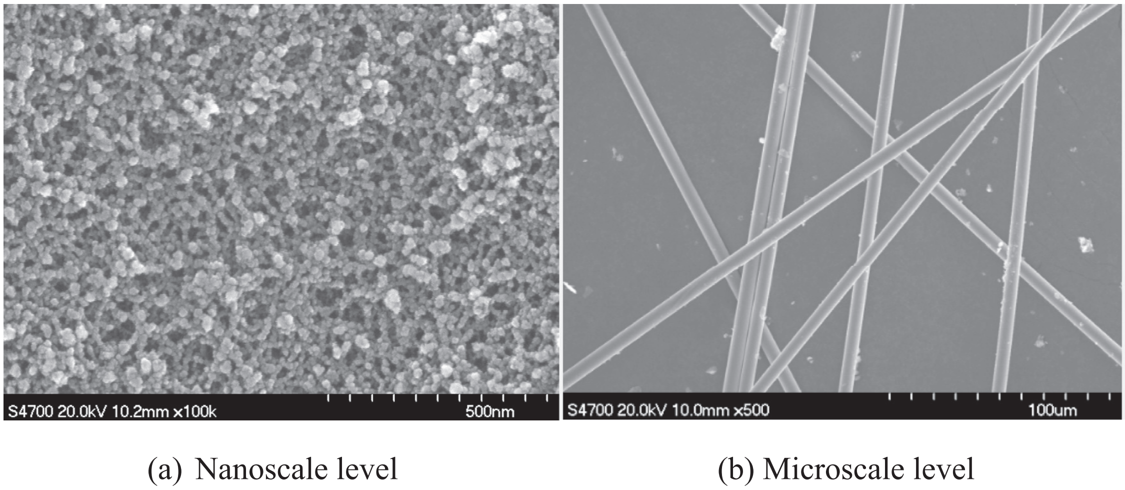


Fig. 1. Scanning electron microscope pictures of the aerogel and its composites [3]

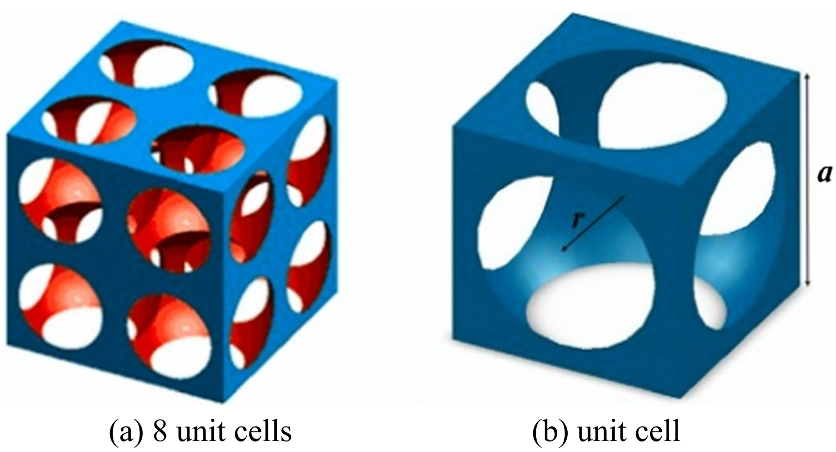


Fig. 2. Unit cell of spherical hollow cube model.

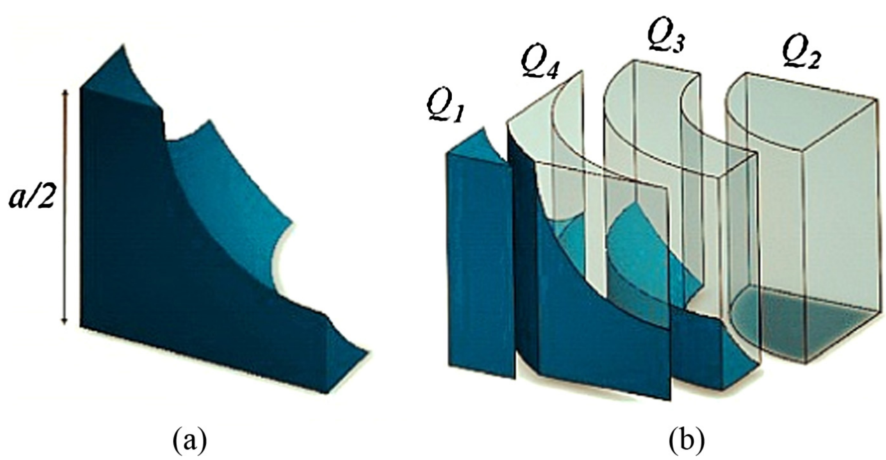


Fig. 3. One-dimensional heat conduction.

where a is the side length of the cube, r is the radius of spherical hollow. The geometry parameters, namely a and r, can be obtained from the specific surface area and porosity.

The relationship between the geometric parameters and specific surface area is [11]:

$$S_a = \frac{6\pi r}{\rho_a a^2} - \frac{8\pi r^2}{\rho_a a^3} \tag{3}$$

The relationship between the geometric parameters and porosity is [11]:

$$\phi_a = -\frac{8\pi r^3}{3a^3} + \frac{3\pi r^2}{a^2} - \frac{\pi}{4} \tag{4}$$

The specific surface area of nano-porous aerogels can be determined by the nitrogen adsorption and desorption measurement. In the present paper, we determine the specific surface area by [10,11]:

$$S_a = (324.3/\rho_a + 5.03) \times 10^5 \tag{5}$$

The definition of porosity is:

$$\phi_a = 1 - \rho_a/\rho_{bulk} \tag{6}$$

here, S_a is the specific surface area (m^2/kg), ϕ_a is the porosity (a dimensionless variable), ρ_a is the density of the pure aerogels and it has different values for different samples which can be obtained by measuring its mass and volume; ρ_{bulk} is the bulk density of the silicon dioxide, ρ_{bulk} = 2200 kg/m^3.

The gas thermal conductivity in nano-porous aerogels is expressed as [16,26]:

$$\lambda_g = \frac{60.22 \times pT^{-0.5}}{0.25 S_a \phi_a + 4.01 \times 10^4 \times pT^{-1}} \tag{7}$$

where λ_g is the gas thermal conductivity($W \cdot m^{-1} \cdot K^{-1}$), p is the pressure (Pa), and T is the temperature (K). The solid thermal conductivity of bulk SiO_2 λ_{bulk} ($W \cdot m^{-1} \cdot K^{-1}$) is a function of temperature [10]:

$$\lambda_{bulk} = 0.75264 + 3.1286 \times 10^{-3} T - 4.5242 \times 10^{-6} T^2 + 3.5253 \times 10^{-9} T^3 \tag{8}$$

The nanoscale size effects on the gas thermal conduction should be considered because the size of the aerogel skeleton is of the same order as the mean free path of phonons [27]. As shown in Fig. 3(b), $Q1$ is the heat transfer flux directly through the solid skeleton and mainly determine the solid heat conduction. Then, the solid thermal conductivity of this part should be modified. Considering the additional thermal resistances due to the scattering of the phonons at the boundary surface and the interface, the solid thermal conductivity of solid skeleton can be modified as follows [27]:

$$\lambda_s = \lambda_{bulk} \frac{3/l_v}{3/l_v + 3/\left(\sqrt{2}a - 2r\right) + 4/a} \tag{9}$$

where l_v is the mean free path of phonons.

2.2. Theoretical mixing model for λ_c of composite materials

In general, three phase materials, namely aerogel matrix, fibers and opacifiers, coexist in the aerogel composites doped with fibers and opacifiers. Many studies have been conducted on predicting the effective conductive thermal conductivity for multi-phase materials [28,29]. In the present paper, a modified mixing model based on the two-phase fundamental models is adopted. First, two of the multiple phases are mixed and regarded as a single homogeneous phase with their own effective thermal conductivity. Then, this equivalent phase is mixed with another new phase to obtain the total effective thermal conductivity of three-phase materials. In the present paper, the aerogel matrix and opacifiers are first mixed and then mixed with fibers to obtain the effective conductive thermal conductivity of silica aerogel composites.

For homogeneous and non-interacting solid spheres randomly distributed in a continuous matrix, Maxwell derived the exact solution of the effective thermal conductivity [25,28]:

$$\lambda_{op,c} = \lambda_{a,c} \frac{2(1-\phi_{op}) + \alpha(1+2\phi_{op})}{(2+\phi_{op}) + \alpha(1-\phi_{op})} \tag{10}$$

where α is the thermal conductivity ratio of the opacifiers to pure aerogels, ϕ_{op} is the volume fraction of opacifiers. The Maxwell model can be applied to the case that the volume fraction of the opacifiers is below 0.1. For the case that the volume fraction of opacifiers is larger than 0.1, a modified Maxwell model should be applied [30]:

$$\frac{\lambda_{op,c}}{\lambda_{a,c}} = 1 + 3\beta\phi_{op} + K{\phi_{op}}^2 \tag{11}$$

The coefficient K considers the interaction between the particles, and is expressed as follows [30]:

$$K = a + b{\phi_{op}}^{3/2} \tag{12}$$

where the coefficient a and b are the functions of β [30]:

$$a = -0.002254 - 0.123112\beta + 2.93656\beta^2 + 1.6904\beta^3$$
$$b = 0.0039298 - 0.803494\beta - 2.16207\beta^2 + 6.48296\beta^3 + 5.27196\beta^4 \tag{13}$$

here β is defined as $\beta = (\alpha - 1)/(\alpha + 2)$.

As for the fibrous materials, their effective thermal conductivities can be obtained by the model proposed by Davies [31]. The distribution orientations of fibers have an important influence on the heat transfer in aerogels. If the fibers are randomly distributed in space, the effective thermal conductivity can be approximately calculated as [31]:

$$\lambda_c = \lambda_{op,c} + \frac{\phi_f\left(\lambda_f - \lambda_{op,c}\right)\left(5\lambda_c + \lambda_f\right)}{3\left(\lambda_c + \lambda_f\right)} \tag{14}$$

If the fibers are randomly distributed in the plane vertical to the heat flux, the effective thermal conductivity can be approximately obtained by [31]:

$$\lambda_c = \lambda_{op,c} + \frac{2\phi_f\left(\lambda_f - \lambda_{op,c}\right)}{\lambda_c + \lambda_f} \tag{15}$$

where $\lambda_{op,c}$ is the effective thermal conductivity of pure aerogels doped with opacifiers, λ_f is the thermal conductivity of fibers, and ϕ_f is the volume fraction of fibers.

In the present paper, we assume that fibers are randomly distributed in the plane vertical to the heat flux, as shown in Fig. 1 (b). The reinforced fibers are made up of SiO_2. The opacifiers are SiC, TiO_2 and C, and their thermal conductivities varying with the temperature can be obtained from reference [32].

2.3. Radiative thermal conductivity

Aerogels doped with fibers and opacifiers can be treated as optical thick materials, and the radiative transport equation can be simplified as the Rosseland equation. According to the Rosseland equation, the radiative thermal conductivity can be obtained by [11,33]

$$\lambda_r = \frac{16n^2}{3\beta_T}\sigma T^3 \tag{16}$$

where n is the refractive index of the medium, n = 1.04 [33], β_T is the Rosseland mean extinction coefficient, σ is the Boltzmann constant, T is the mean temperature of materials.

The temperature-dependent Rosseland mean extinction coefficient can be obtained from the spectral extinction coefficient [9]:

$$\frac{1}{\beta_T} = \int_0^\infty \frac{1}{\beta_{e\lambda}} \frac{\partial E_{b\lambda}}{\partial E_b} d\lambda \tag{17}$$

where $\beta_{e\lambda}$ is the spectral extinction coefficient of the aerogels doped with fibers and opacifiers, including the spectral extinction coefficient of pure aerogels, fibers and opacifiers [25]:

$$\beta_{e\lambda} = \beta_{e\lambda,a} + \beta_{e\lambda,op} + \beta_{e\lambda,f} \tag{18}$$

where $\beta_{e\lambda,a}, \beta_{e\lambda,op}, \beta_{e\lambda,f}$ are the spectral extinction coefficients of pure aerogels, opacifiers and fibers, respectively. In the present paper, the spectral extinction coefficient of pure aerogels is obtained from Reference [9], while the spectral extinction coefficients of fibers and opacifiers are obtained according to the Mie theory described below.

Mie scattering occurs when the size of obstacles is of the same order as the incident wavelength. Mie theory can be applied to calculate the extinction coefficients of the spherical particles or infinite cylinders. Assuming that the opacifiers are spherical particles, the extinction efficiency for the single particle can be obtained according to Mie theory [34,35] through the computation of Q_{ext}:

$$Q_{ext} = \frac{2}{x^2}\mathrm{Re}\left[\sum_{n=1}^{\infty}(2n+1)(a_n+b_n)\right] \tag{19}$$

where Re is the real component, x is the particle size parameter, defined as $x = \pi Dn/\lambda$, D is the diameter of opacifiers, λ is the wavelength of incident light, a_n and b_n are the coefficients dependent on the complex refractive index. The real part of complex refractive index is the refractivity, and the imaginary part is the absorptivity. As for the expressions of a_n, b_n, Reference [35] can be referred. For a certain volume fraction of opacifiers, their total extinction coefficient can be expressed as [35]:

$$\beta_{e\lambda,op} = \frac{3}{2}Q_{ext}\frac{f_{op}}{D_{op}} \tag{20}$$

Assuming that fibers are infinite long cylinders, the extinction efficient for one single fiber can be obtained according to Mie theory [34]:

$$\begin{aligned} Q_{ext}(\xi) &= \frac{1}{2}(Q_{ext,I} + Q_{ext,II}) \\ Q_{ext,I}(\xi) &= \frac{2}{\chi}Re\left(b_{0I} + 2\sum_{n=1}^{\infty}b_{nI}\right) \\ Q_{ext,II}(\xi) &= \frac{2}{\chi}Re\left(a_{0II} + 2\sum_{n=1}^{\infty}a_{nII}\right) \end{aligned} \tag{21}$$

For fibers randomly distributed in the plane vertical to the heat flux, namely $\xi = 90^\circ$, the coefficients, $b_{0I}, b_{nI}, a_{0II}, a_{nII}$, can be simplified. For details, Reference [34] can be referred. For a certain volume fraction of fibers, their spectral extinction coefficient can be expressed as [25]:

$$\beta_{e\lambda,f} = \frac{4f_v}{\pi D_f}Q_{ext} \tag{22}$$

where f_v is the volume fraction of the opacifiers.

Once the spectral extinction coefficient of pure aerogels, fibers and opacifiers are determined, the Rosseland mean extinction coefficient for aerogel composites can be obtained from Eq. (17). Then according to Eq. (16), one can determine the radiative thermal conductivity. The complex refractive indexes ($m = n + ik$) are important for determining the spectral extinction of fibers and opacifiers, and their values can be found in [36,37,38].

3. Experimental measurement

3.1. Hot Disk method

In the present paper, the Hot Disk method based on the transient plane source method is adopted to measure the effective thermal conductivity of aerogel composites at different temperature. The detailed measurement theory and process can refer to [39]. The Mica 4922 which can withstand the temperature up to 1050 K is adopted, shown in Fig. 4. And the measurement time is set to be 160 s, and the output power is 0.005 W.

3.2. Comparisons with the experimental results

In Section 2, we have developed a complete engineering model for the calculation of the effective thermal conductivity for aerogel composites. To validate the accuracy of the present model, some corresponding experimental measurements are conducted. The comparisons between the calculations and measurements are made at different temperature.

The effective thermal conductivities of two aerogel composites within the temperature range from room temperature to 1000 K have been measured by our experimental system. For material one, the porosity is 0.8591, the fiber volume fraction is 0.51%, the opacifier volume fraction is 1%, the opacifier is SiC with diameter 3.5 μm and the fiber is SiO_2 with diameter 6 μm. For material two, the porosity is 0.8731, the fiber volume fraction is 0.51%, the opacifier volume fraction is 3.75%, the opacifier is SiC with diameter 3.5 μm and the fiber is SiO_2 with diameter 6 μm. The comparisons of effective thermal conductivities between the theoretical predicted results and experimental data at the different temperature are shown in Fig. 5. It can be seen that the predicted results agree well with the theoretical predicted results, and their deviations were within ±10%, which validates the accuracy of the theoretical model developed in the present paper.

As mentioned above, to predict the effective thermal conductivity by this model a number of parameters are required, some of which are closely related to manufacturing process and the material composites. For the two aerogels studied we are able to obtain all the required parameters. Although some other aerogels can be found in the market, however, the required input data cannot be

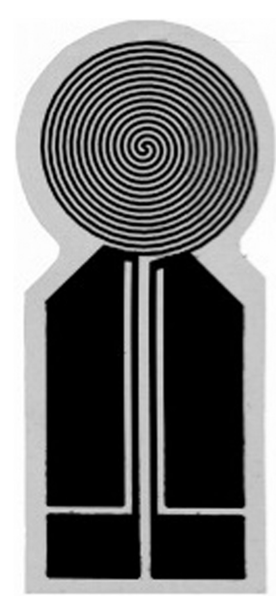


Fig. 4. Hot Disk probe Mica 4922.

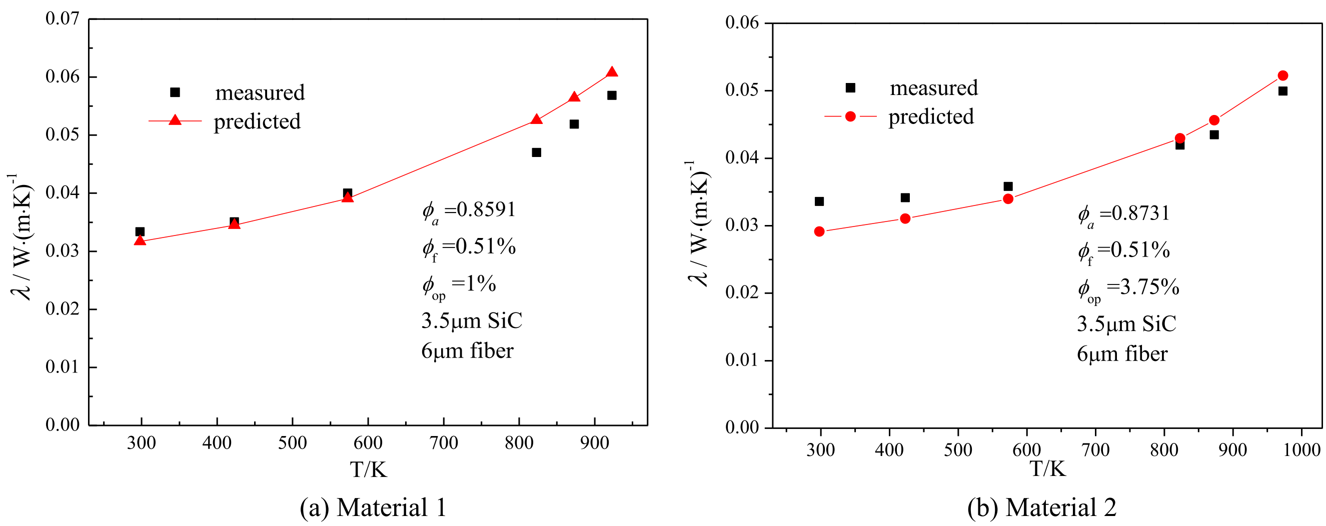


Fig. 5. Comparison of effective thermal conductivity at different temperature.

completely obtained. Thus for the time being only the comparison of the two aerogels are provided.

4. Results of parameter influences and discussion

After validations, the influences of the porosity, temperature and pressure on the effective thermal conductivity of pure aerogels are investigated. The influences of doped additives on the thermal insulation performance of aerogel composites are also investigated.

4.1. Pure aerogels

As discussed in Section 2, the effective thermal conductivity of aerogels is the superposition of the radiative thermal conductivity and the coupled conductive thermal conductivity of the gas and solid. The contribution of gas heat conduction, solid heat conduction and thermal radiation to the total effective thermal conductivity can be decomposed as [11]:

$$\lambda_e = \lambda_c + \lambda_r = \lambda_{g,0} + \lambda_{s,0} + \lambda_{r,0} \tag{23}$$

where $\lambda_{g,0}, \lambda_{s,0}, \lambda_{r,0}$ are the contributions of the gas conduction, solid conduction and radiation to the total effective thermal conductivity, respectively. Here, $\lambda_{r,0}$ equals λ_r because the thermal radiation is not coupled in the whole calculation process, and the $\lambda_{s,0}$ can be obtained by:

$$\lambda_{s,0} = \lambda_{e,\mathrm{evc}} - \lambda_r \tag{24}$$

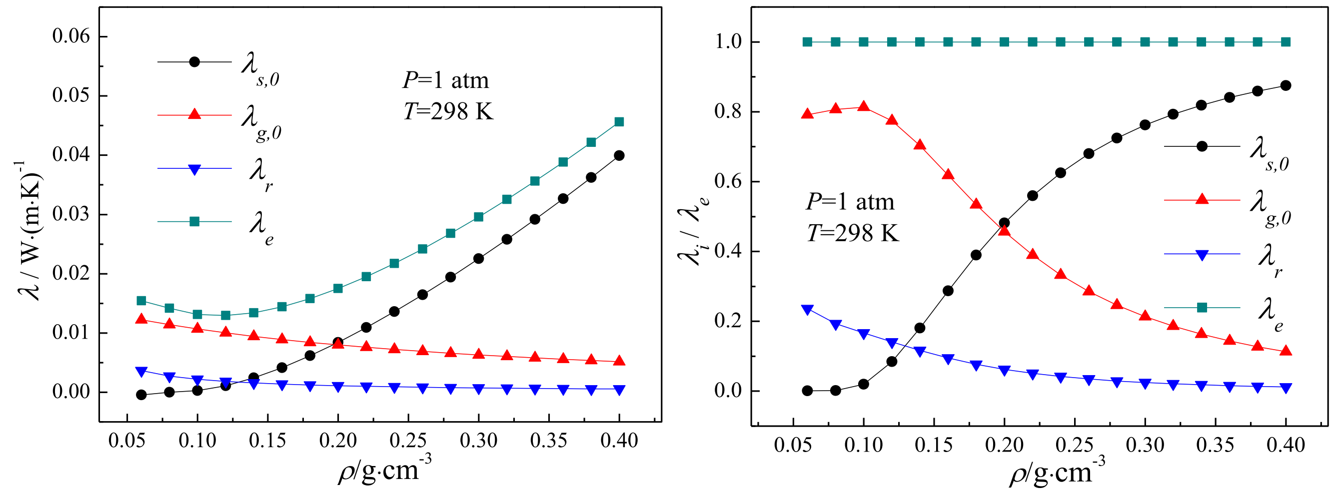
where $\lambda_{e,evc}$ is the effective thermal conductivity of aerogels after being evacuated to vacuum, and it does not include the contribution of the gas heat conduction. In the present model, we can set the gas thermal conductivity λ_g in Eq. (2) to be zero to obtain the $\lambda_{e,\mathrm{evc}}$. Finally, the contribution of the gas heat conduction to the total effective thermal conductivity can be obtained by subtracting $\lambda_{g,0}$ and $\lambda_{s,0}$ from the total effective thermal conductivity. Their numerical results will be presented later.

4.1.1. Porosity effects

The porosity of aerogels, namely the ratio of the gas and the entire volume, has a significant influence on the effective thermal conductivity. The porosity of aerogels can be directly obtained from the density of pure aerogels according to Eq. (6). The variations of effective thermal conductivity with the density of aerogels are shown in Fig. 6(a), while the ratios of contributions of each part to the total effective thermal conductivity varying with the density are shown in Fig. 6(b). As shown in Fig. 6(a), the contribution of the solid heat conduction to the total effective thermal conductivity increases with the density, while the contributions of gas heat conduction and radiation decrease when the density increases. As a result, there exists an optimal density (porosity) to minimize the effective thermal conductivity of aerogels. The optimal density (porosity) is the function of temperature because the ratios of the contributions of each part to the total effective thermal conductivity change with temperature. In Fig. 6(b), we can see that the solid conduction is significant and even becomes a dominant factor at a relatively high density. Fig. 7 shows the variation of the optimal density with temperature. At high temperature, a larger density value is needed to minimize the effective thermal conductivity. Therefore, the density of aerogels can be set as a function of the temperature during the manufacturing process to improve the thermal insulation performance if the aerogels serve under different temperature condition.

4.1.2. Temperature effects

The gas thermal conductivity, solid thermal conductivity and radiative thermal conductivity are all related to temperature. The influences of temperature on the effective thermal conductivity of pure aerogels are shown in Fig. 8. It can be seen that the radiative thermal conductivity increases dramatically with temperature. At ambient temperature, the contribution of the radiation to the total effective thermal conductivity is small enough to be neglected. While at higher temperature, the radiative thermal conductivity becomes the dominant contribution factor. This is because the pure aerogels are almost transparent to the infrared wavelength within 3–8 μm. As indicated above to improve the high temperature thermal insulation performance of aerogels, some additives should be doped to enhance the effect coefficient to limit the radiative thermal conductivity. In addition, pure aerogel has low strength and poor toughness, so embrittlement of the bulk material is easy to take place when an external force is imposed on them. During the measurement, an bolt of the experimental apparatus is employed to bring force on the specimen which can ensure the excellent contact between the sensor and the specimen to get accurate results. So embrittlement was always happen during the measurement and for the same specimen after several times of measurements we even could not get an accurate thickness of the specimen. Thus we could not obtain the thermal



(a)The contributions of each part (b)The ratios of each part

Fig. 6. Effective thermal conductivity vs the density.

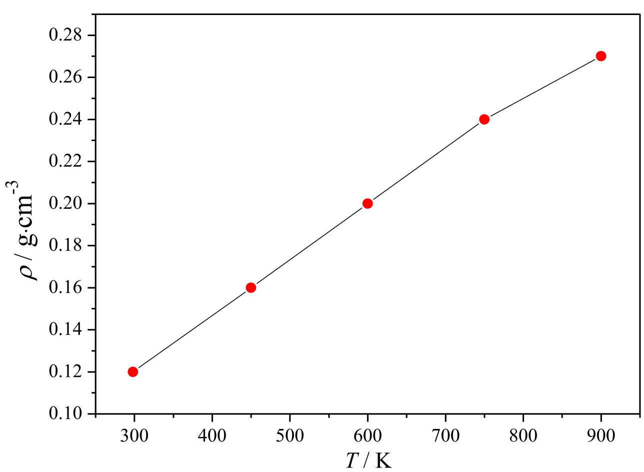
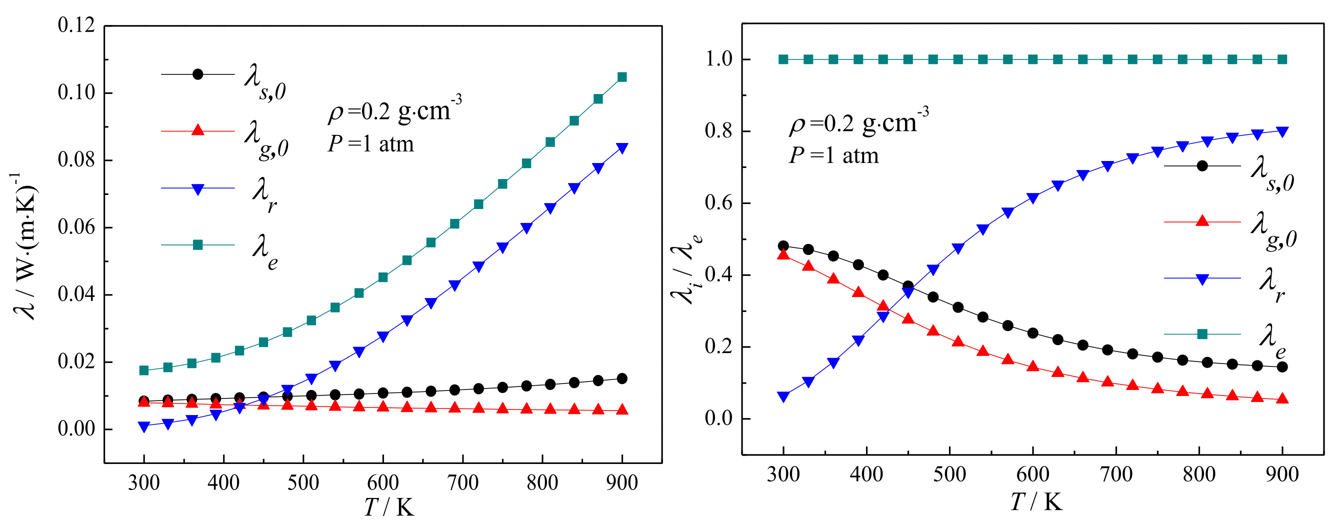


Fig. 7. Variation of the optimal density with temperature.

conductivity for the pure aerogel by the present measurement method.

4.1.3. Pressure effects

Pressure has an influence on the gas thermal conductivity but no influence on the solid and radiative thermal conductivity. The influence of the pressure on the effective thermal conductivity is investigated. Fig. 9(a) and (b) shows the variations of the effective thermal conductivity with pressure at the aerogel density of 0.1 g/cm^3 and 0.2 g/cm^3, respectively. As shown in Fig. 9, the total effective thermal conductivity increases with pressure as 'S' curve. For the aerogels density of 0.1 g/cm^3, when the pressure is lower than1000 Pa, the contribution of gas conduction is almost zero due to the restriction of nano-porous structure, and when the pressure is larger than 10 MPa, the contribution of gas conduction approaches a maximum value and then remains constant. The contribution of gas conduction becomes the dominant factor affecting the thermal conductivity when the pressure is larger than 10 kPa



(a)The contributions of each part (b)The ratios of each part

Fig. 8. Variation of effective thermal conductivity with temperature.

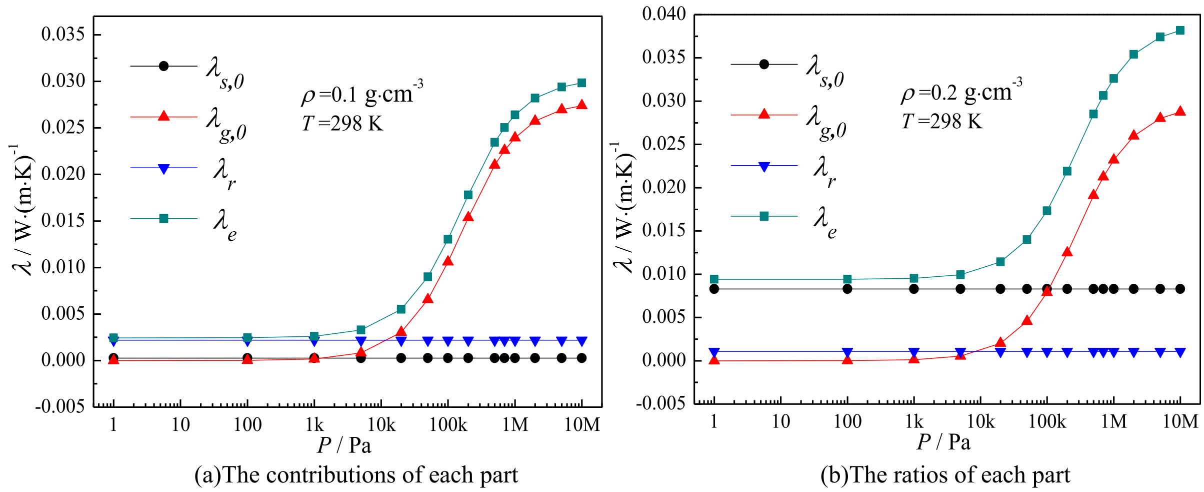


Fig. 9. Variation of effective thermal conductivity with pressure.

for the case of the aerogel density being 0.1 g/cm^3, and 100 kPa for the case of 0.2 g/cm^3. The pressure value at which the contribution of gas conduction becomes dominant factor changes with the aerogel density.

4.2. Aerogels doped with opacifiers

In applications, some opacifiers are doped in aerogels to restrain the radiative thermal conductivities. Following results are obtained by Mie theory assuming that the doping opacifiers are spherical particles. The diameters, doping concentrations and the types of opacifiers have different effects on the thermal insulation performance of aerogel composites, which are discussed below.

4.2.1. Diameter effect

The size of the opacifier impacts the radiative thermal conductivity while almost has no influence on the heat conduction. The spectral extinction coefficient of opacifier-loaded aerogel composites is shown in Fig. 10(a). The opacifier is chosen as SiC with a diameter of 3 μm, and its doping concentration is 1%. The extinction coefficient of pure aerogels is obtained from Reference [9]. As shown in Fig. 10(a), the spectral extinction coefficients of opacifiers within the wavelength of 3–8 μm are much higher than that of pure aerogels, and therefore the total Rosseland mean extinction coefficient of aerogel composites increases especially for high temperature if the opacifiers are doped. The comparisons of the Rosseland mean extinction coefficient between the opacifier-loaded aerogels and the pure aerogels are shown in Fig. 10(b). We can find that the optimal diameter of doping opacifiers varies with temperature. When temperature is larger than 450 K, aerogels doped with a diameter of 2 μm have a highest Rosseland mean extinction coefficient; when temperature is less than 450 K, the optimal diameter is 3 μm. According to Wien's law, the peak wavelength of the emitted light moves to the short wavelength direction when temperature increases, thus resulting in a smaller corresponding optimal diameter of doping opacifiers.

4.2.2. Effects of doping concentrations

The doping concentration of opacifiers has impacts on the heat conduction and thermal radiation. The influences of the opacifier doping concentration on the effective thermal conductivity are shown in Fig. 11(a). As can be seen there the combination of thermal conductivity of the gas and solid, λ_c, increases with the doping concentration because the thermal conductivity of opacifiers is

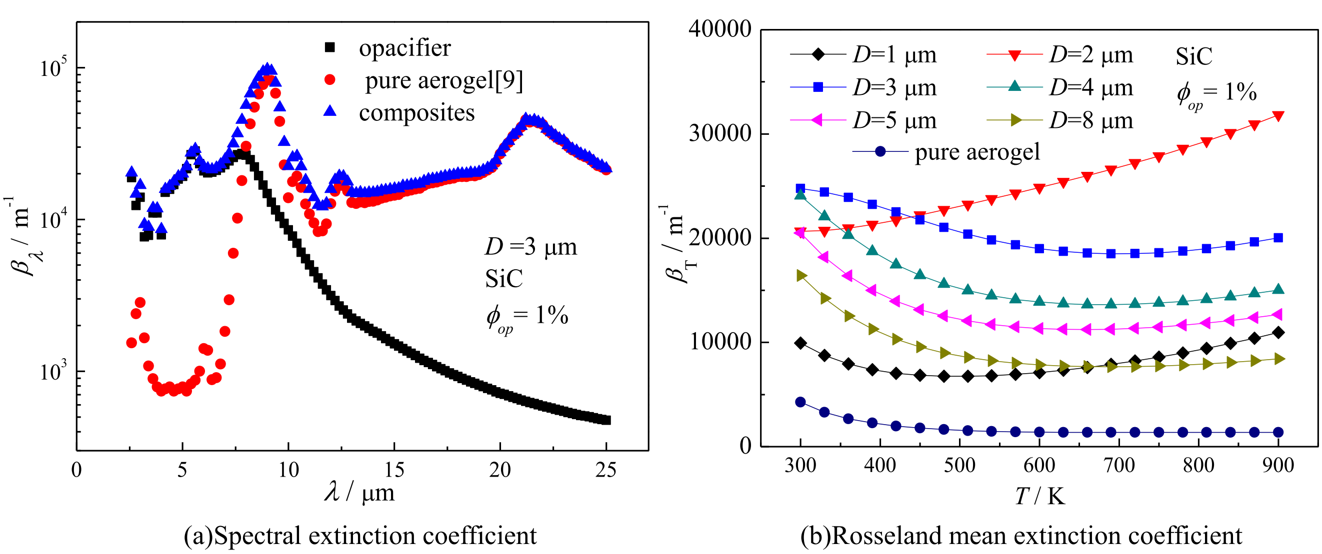
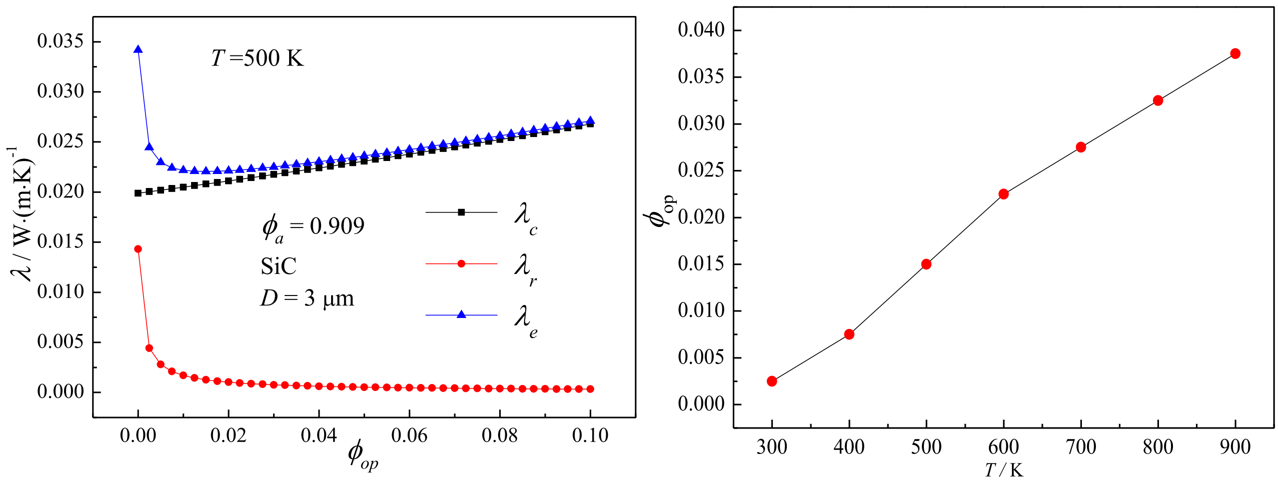


Fig. 10. The influence of opacifier diameters on the extinction coefficients.



(a)The effective thermal conductivity

(b) Variations of the optimal doping concentration

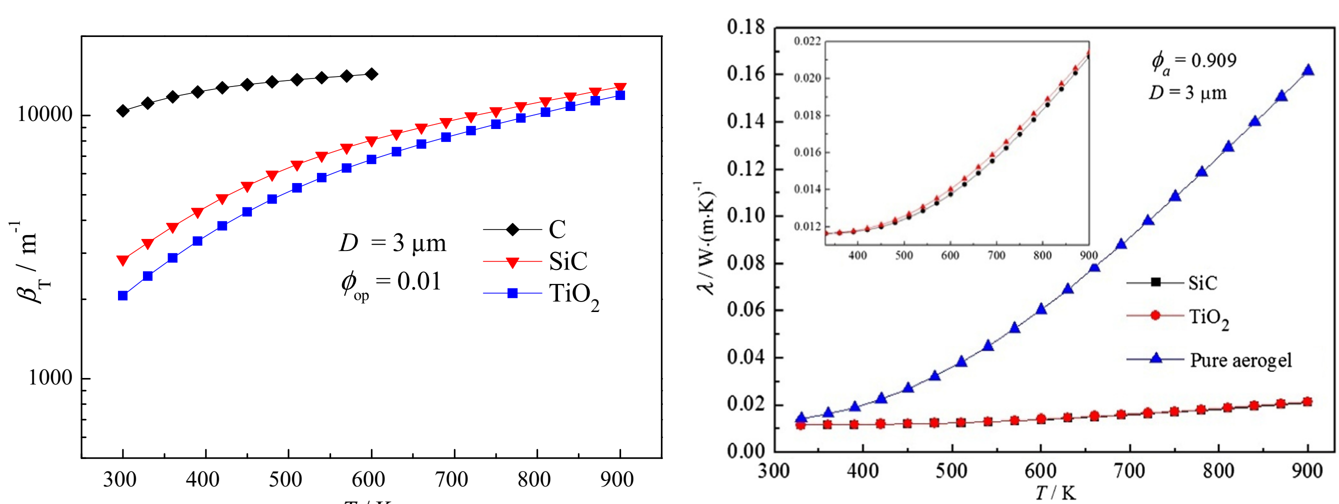
Fig. 11. The influences of opacifier doping concentrations.

larger than that of the aerogel matrix, while the radiative thermal conductivity of aerogel composites decreases. As a result, there exists an optimal doping concentration to minimize the effective thermal conductivity of aerogel composites. The variation of the optimal doping concentration with the temperature is shown in Fig. 11(b). Here, the porosity of aerogels is 0.909 and the diameter of the opacifier (SiC) is 3 μm. It can be seen that the optimal doping concentration increases with temperature. This is because the radiative thermal conductivity becomes significant when temperature is high, thus requiring a larger doping concentration to restrain the radiative thermal conductivity.

4.2.3. Effects of opacifier types

Some mineral materials, such as C, SiC and TiO_2, are often doped in aerogels as opacifiers to restrain the radiative thermal conductivities at high temperature. The radiative properties dependent on complex refractive index will impact the radiative thermal conductivities of opacifier-loaded aerogels. The Rosseland mean extinction coefficients of different opacifiers are shown in Fig. 12(a). It can be seen that black carbons have the best extinction property than others, but tend to oxidize at high temperature. The extinction effect of the SiC is better than that of TiO_2. The comparisons of the effective thermal conductivity between the aerogel composites and the pure aerogels are shown in Fig. 12(b). And the deviation of the effective thermal conductivity of aerogel doped with SiO_2 and TiO_2 is shown in the top left corner of Fig. 12(b). It can be seen that the effective thermal conductivity of aerogels will drastically decrease at high temperature if the opacifiers are doped. Aerogels doped with SiC will have a better thermal insulation performance than that doped with TiO_2.

As discussed above, both the optimal doping diameters and the optimal doping concentrations vary with temperature. When the aerogels are exposed to a great temperature difference environment, it is expected that aerogel composites with opacifier-gradient-loaded structure would have a better insulation performance. At the high temperature side, a smaller diameter and a bigger doping concentration are expected compared with the low temperature side. The SiC and C can be chosen as the best opacifiers at the high temperature and at the low temperature side, respectively.



(a)Rosseland mean extinction coefficient

(b) The effective thermal conductivity

Fig. 12. The influence of opacifier types.

4.3. Aerogels doped with fibers

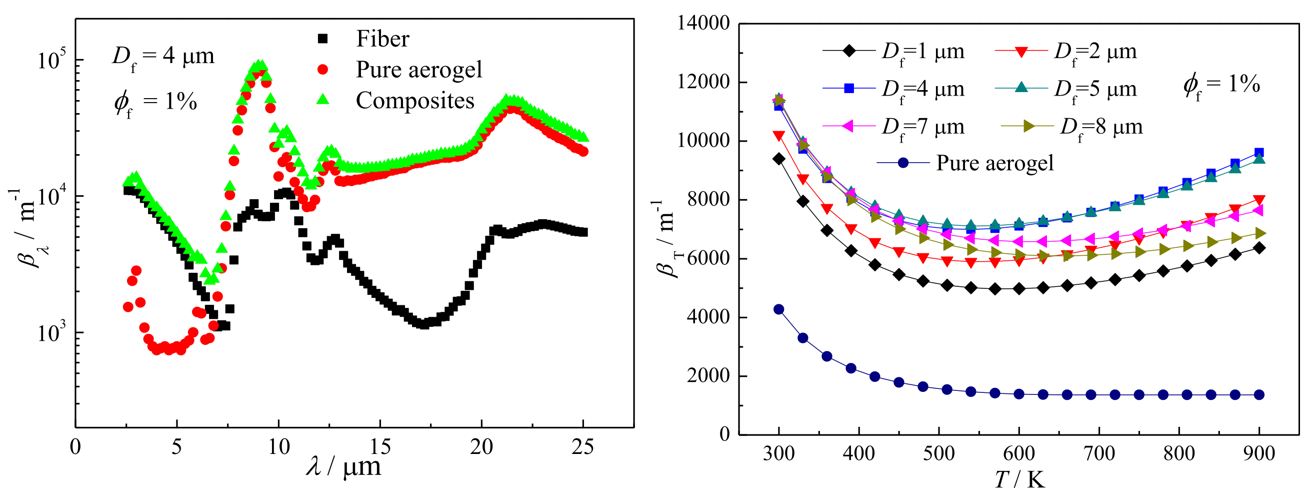
In practical applications, fibers are loaded in aerogels to improve the mechanical property. The reinforced fibers also improve the extinction effect. Mie theory can be applied to theoretically calculate the extinction efficiency of doping fibers if we assume that the loaded-fibers are infinite long cylinders. The fibers are assumed to be randomly distributed in the plane vertical to the heat flux direction. And only the influences of diameters and doping concentrations of fibers on the thermal insulation performance are discussed below.

4.3.1. Diameter effects

The size of fibers can impact the radiative thermal conductivity while almost has no influence on the heat conduction. The spectral extinction coefficients of fiber-loaded aerogel composites are shown in Fig. 13(a). It can be seen that the spectral extinction coefficients of fibers within the wavelength of 3–8 μm are larger than that of pure aerogels, and therefore the total extinction effect of aerogels will be improved if the fibers are loaded. The comparisons of the Rosseland mean extinction coefficients between the aerogels doped with different diameters and pure aerogels are shown in Fig. 13(b). All the aerogels doped with fibers have a higher Rosseland mean extinction coefficients than the pure aerogels, but the increase of extinction effect is lower than the aerogels doped with opacifiers when they are at the same doping concentrations. The influence of fiber diameters on the Rosseland mean extinction coefficient is not as significant as that of the opacifiers. The fiber-loaded aerogels with diameter of 5 μm and 4 μm have the best extinction effect among the six diameters studied. Thus diameter 4 μm or diameters 5 μm can be regarded as the optimal doping diameter.

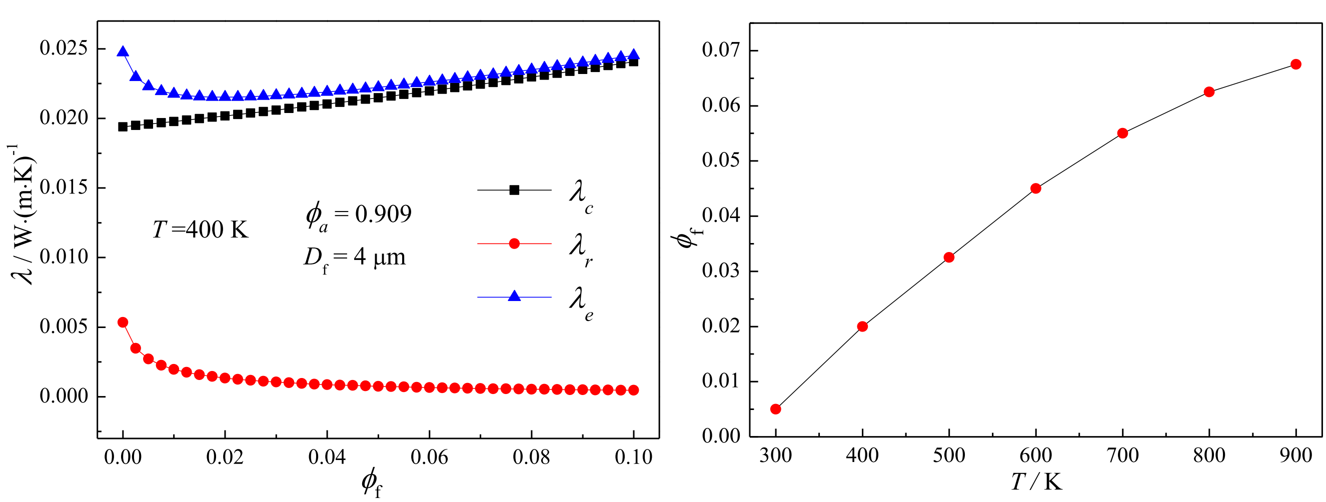
4.3.2. Effects of doping concentrations

The doping concentrations of fibers have impacts on the heat conduction and thermal radiation. The influences of the fiber doping concentration on the effective thermal conductivity are shown in Fig. 14(a). It can be seen that λ_c increases with doping concentration because the thermal conductivity of fibers is larger than that of aerogel matrix, while the radiative thermal conductivity decreases. Therefore, there exists an optimal doping concentration to minimize the effective thermal conductivity of aerogel composites. In addition, the optimal doping concentration of fibers is a function of temperature. The relationship of the optimal fiber



(a)Spectral extinction coefficient (b)Rosseland mean extinction coefficient

Fig. 13. The influence of fiber diameter on the effective thermal conductivity.



(a)The effective thermal conductivity (b) Variations of the optimal doping concentration

Fig. 14. The influence of fiber doping concentration on the effective thermal conductivity.

doping concentration and the temperature is shown in Fig. 14(b). We can find that the optimal fiber doping concentration increases with temperature. At high temperature, the radiation becomes the dominant contribution factor of the effective thermal conductivity, and a larger doping concentration is required to restrain the radiative thermal conductivity of aerogels.

5. Conclusion

In the present paper, an engineering model for fast evaluations of the effective thermal conductivity for aerogel composites is developed. The major steps are as follows: First, the spherical hollow model is adopted to calculate the conductive thermal conductivity of pure aerogels. Then, the modified Maxwell model and the Davies model are applied to consider the conduction enhancement effects of doped opacifiers and fibers. The Mie theory is used to calculate the temperature-dependent Rosseland mean extinction coefficient, and then the radiative thermal conductivity of aerogels can be obtained according to the Rosseland equation. Finally, the summation of the conductive thermal conductivity and radiative thermal conductivity is the total effective thermal conductivity of the aerogel composites. To validate the accuracy of the proposed model, the Hot Disk thermal constant analyzer based on the transient plane source method is adopted to measure the effective thermal conductivity of some aerogel composites, and the predicted and measured results are compared, showing a good agreement with the maximum deviation about ±10%. The influences of the environmental parameters, including temperature and pressure, and the structure parameters, including the porosity, additive sizes, additive doping concentrations and different types of opacifiers, on the effective thermal conductivity of aerogel composites are investigated. The contributions of the gas heat conduction, solid heat conduction and thermal radiation to the total effective thermal conductivities are decomposed to determine the dominant contribution factor of the effective thermal conductivities of the silica aerogel composites. Following conclusions can be made:

(1) The porosity of the aerogel matrix has a significant influence on the effective thermal conductivity of aerogels. There exists an optimal porosity to minimize the effective thermal conductivity, and the optimal porosity increases with temperature.
(2) For the pure aerogels, the radiative thermal conductivities increase drastically when temperature increases and become the dominant contribution factor at high temperature; the effective thermal conductivities of aerogels vary with pressure as 'S' curve. At relatively high pressure, the contribution of gas conduction becomes the dominant part.
(3) The effective thermal conductivity of aerogels will drastically reduce if the opacifiers are doped. The best doping opacifier diameter for opacifier-loaded aerogels varies with temperature. The aerogels doped with an opacifier diameter of 3 μm has the best extinction effect at low temperature and 2 μm at high temperature; There exists an optimal doping concentration of opacifiers to minimize the effective thermal conductivity, and the optimal doping concentration increases with temperature. The material of SiC has the best comprehensive performance among the opacifiers studied in the present paper.
(4) The doped fibers can improve the mechanical property and meanwhile enhance the extinction effect, but the extinction effect of fibers is not as significant as that of opacifiers. The best doping fiber diameter is about 4 μm; the optimal doping concentration of fibers that minimizes the effective thermal conductivity increases with temperature.

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