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Radiative characteristics of opacifier-loaded silica aerogel composites

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A B S T R A C T

Radiative characteristics of opacifier-loaded silica aerogel composites such as specific spectral extinction coefficient and Rossland mean extinction coefficient were usually calculated by the Fourier infrared spectral experiment and the Beer law. For the composites, it needs lots of experiments to find the proper opacifier categories, contents, and sizes, hence, the optimal design becomes difficult. Based on this reason, this work proposes a theoretical method with four sub-models to evaluate the radiative characteristics of opacifier-loaded silica aerogel composites. First, the Fourier infrared spectral experiment and the modified Kramers–Krönig (K–K) relation are used to calculate the basic optical constants of the opacifier (complex refractive index). Second, the extinction efficiency of a single opacifier particle is calculated based on its complex refractive index. Third, the spectral and Rossland extinction coefficients of opacifier particle assemble are calculated by using extinction efficiency and mass fraction of opacifier. Finally, the spectral and Rossland extinction coefficients and radiative heat conductivity of the composite are obtained. The radiative characteristics of six kinds of opacifiers with various particle diameters are investigated by using the present models. The results show that optimal opacifier and its diameter are strongly temperature-dependent. The optimal diameter of opacifier reduces with increased temperature, and SiC is the best choice due to its high-temperature stability. A gradient design of composite is proposed based on the temperature-dependent optimal opacifier and its diameter, which significantly reduces radiative heat transfer compared to the traditional design.

1. Introduction

Silica aerogels are open-cell, transparent, and nanoscale porous thermal insulation materials, which have high porosity (85%–99%), small average pore diameters (2–50 nm), large specific surface area (500–1300 $m^2\ g^{-1}$), low density (30–150 $kg\ m^{-3}$) and lower thermal conductivity (0.01–0.02 $W\ m^{-1}\ K^{-1}$) than air in room temperature, so they are also called super thermal insulation materials [1–7]. With these advantages, silica aerogels are regarded as promising thermal insulation materials for aerospace, chemical engineering, metallurgy, energy saving and other applications [8–15]. Pure silica aerogels are almost transparent for radiation wavelengths of 3–8 μm, when they are used at high temperature conditions, the radiative heat transfer is significantly enhanced, which limits their utilization as promising insulation materials. In order to improve the performance of silica aerogels at high temperatures, some mineral powders, such as SiC, TiO_2, ZrO_2, coal ash, Al_2O_3, carbon black, $K_2Ti_6O_{13}$, BN, Fe_3O_4, B_4C and $ZrSiO_4$ (referred as to opacifiers) are loaded into the aerogels to form opacifier-loaded silica aerogel composites [16–25].

Generally, the extinction coefficient is used to represent the radiative performance of materials, a high extinction coefficient can significantly reduce radiative heat transfer through materials. The extinction coefficient of opacifier is closely related to its usage temperature, as well as its category, shape, and size, hence, selecting a proper opacifier is very important to reduce the radiative heat transfer of opacifier-loaded aerogel composites. The extinction coefficient of composites can be calculated by Beer law based on the infrared spectral experiment data [20–30]. Kuhn et al. [20] tested the specific spectral extinction coefficient of opacifier-loaded (carbon black, SiC, TiO_2, Fe_3O_4 and B_4C) silica aerogel composites with different particle sizes within wavelength range of 2.5–8.0 μm. Wang et al. [21] tested the Rossland mean extinction coefficient of TiO_2-loaded silica aerogel composites with different TiO_2 mass fractions. Feng et al. [25] tested the specific spectral extinction coefficient of opacifier-loaded silica aerogel composites with different particle sizes and opacifier mass fractions, where opacifiers were selected as BN, SiC, $K_2Ti_6O_{13}$ and $ZrSiO_4$ and the wavelength was varied from 2.5 μm to 7.0 μm. These experiments measured the extinction coefficient of the opacifier-loaded aerogel composite only with the specific opacifier category, size, and mass (or volume) fraction, so that once the component or structure of the composite changes, new test

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is needed. Thus, in order to predict the extinction coefficient of opacifier-loaded aerogel composites with various opacifier categories, sizes, and mass fractions more effectively, a theoretical method is necessary indeed [25,30]. However, due to the lack of complex refractive index data of opacifiers, such theoretical model has not been established yet.

The complex refractive index $m = n - \mathrm{i}\kappa$ is also referred to as optical constant. The real part, n, accounts for the radiation refraction and determines the phase velocity in the medium. The imaginary part, κ, accounts for the absorption and determines the radiation attenuation through the medium [31]. For transparent materials, the absorption effect can be ignored with $\kappa = 0$ [32–36], however, for opacifiers and opacifier-loaded aerogel composites, both n and κ are larger than zero.

Several methods to calculate the complex refractive index have been proposed by previous researches [4,29,32,34]. Lu et al. [4] calculated the imaginary part of complex refractive index of pure aerogel directly through its effective extinction coefficient. Zeng et al. [32] calculated the complex refractive index by measuring the reflectance and transmittance of silica aerogel, due to low measurement accuracy of reflectance caused by the surface roughness of aerogel sample, the complex refractive index cannot be calculated accurately. Zeng et al. [32] proposed that complex refractive index can also be solved through the dielectric function, but the dielectric function is also not easy to get for opacifiers. Ruan et al. [29] and Liu et al. [34] calculated the complex refractive index based on Mie theory and K–K relation, in which only the transmittance of materials needs to be measured, but the theoretical calculation is too complicated and hard to obtain the exact solution of the complex refractive index. The above investigations mainly focused on the aerogels, however, to our best knowledge, theoretical predictions for the complex refractive index of opacifiers have not been reported in the open literatures.

The purpose of this paper is to develop a theoretical model to predict radiative characteristics of opacifier-loaded aerogel composites. Firstly, a new and simple approach is developed to predict complex refractive index of opacifiers. Then the complex refractive index is used to calculate the extinction efficiency of a single opacifier particle based on Mie theory. Finally, a predictive model is proposed to calculate the specific extinction coefficient, and the radiative thermal conductivity of opacifier-loaded silica aerogel composite based on the extinction efficiency and mass fraction of the opacifier. Based on the developed model, radiative characteristics of the six kinds of opacifiers are investigated systematically, and the optimal opacifier size and category in the composite are obtained under different temperatures. Furthermore, to reduce the radiative heat transfer further, a novel material design of opacifier-loaded aerogel composite is proposed, in which the optimal opacifier and its size are varied according to the internal temperature gradient of the composite.

2. Model

2.1. Complex refractive index of opacifiers

Opacifier particles have both scattering effect and absorption effect to light, therefore, they are regarded as absorbing medium, hence, both the real part and the imaginary part of the complex refractive index should be calculated for opacifier particles.

The transmittance of opacifier particles, τ, can be measured by Fourier infrared spectral experiment [29,32,34]. In the experiment, opacifier particles with the specific size and mass fraction are uniformly mixed with KBr particles. The mixture is dried in the oven and then is pressed about 10 s under pressure of 50–100 MPa by the pressure machine to form a thin circle disk (sample A). Another disk (sample B) with the same radius and thickness is also pressed using pure KBr particles. Two disks are put in the Fourier infrared spectrometer, respectively, to measure their transmittances. Since the volume fraction of opacifier particles in the sample A is very low, the transmittance of opacifier particles can be obtained by subtracting the transmittance of sample B from the transmittance of sample A.

Based on the Beer law, the transmittance and specific extinction coefficient of opacifier meet the following relation [3,20,22,25,30]:

$$\tau(\lambda) = e^{-e^{*}(\lambda)\rho h} \tag{1}$$

where λ is the wavelength, e^{*} is the specific extinction coefficient of opacifier, ρ is the density of the sample A, and h is the sample thickness. It is noted that τ and e^{*} are the transmittance and specific extinction coefficient, respectively of opacifier particles with specific volume fraction and size, so they are not the universal parameters. However, Zeng et al. proposed that for an absorbing homogeneous medium, such as opacifier in the opacifier-loaded aerogel composite, the imaginary part of complex refractive index can be derived from e^{*} as follows [32]:

$$e^{*}(\lambda) = \frac{4\pi\kappa(\lambda)}{\lambda\rho_{opa}} \tag{2}$$

where ρ_{opa} is the density of opacifier. Combining Eqs. (1) and (2), we have,

$$\kappa(\lambda) = \frac{\lambda\rho_{\mathrm{opa}}\ln\left(\frac{1}{\tau(\lambda)}\right)}{4\pi\rho h}. \tag{3}$$

The real part and the imaginary part of complex refractive index meet the classic K–K relation [25,29,32,34]:

$$n(\lambda) = 1 + \frac{2\lambda^2}{\pi}P\int_0^{\infty}\frac{\kappa(\lambda_0)}{\lambda_0\left(\lambda^2-\lambda_0^2\right)}d\lambda_0. \tag{4}$$

Ruan et al. [29] and Dombrovsky et al. [37] used a more accurate modified K–K relation originally proposed by Ahrenkiel [38]:

$$n(\lambda) = n(\lambda_1) + \frac{2\left(\lambda_1^2-\lambda^2\right)}{\pi}P\int_0^{\infty}\frac{\lambda_0 k(\lambda_0)}{\left(\lambda^2-\lambda_0^2\right)\left(\lambda_1^2-\lambda_0^2\right)}d\lambda_0 \tag{5}$$

where $\lambda_1 = 0.4358$ μm, is the wavelength at the triple blue mercury line, the refractive coefficient $n(\lambda_1)$ was measured using a Hilger Watts Abbe refractometer [37], and P is the Cauchy principal value of the integral.

There is a Cauchy integral over all the wavelengths in Eq. (5), however, we can only get a finite wavelength range [λ_{min}, λ_{max}] through the experiment, so that the finite experimental data must be extrapolated into both long wavelength [λ_{max}, $+\infty$] and short wavelength [0, λ_{min}] regions. Ruan et al. [29] used the following extrapolation method:

$$\begin{aligned} &\lambda \le \lambda_{\mathrm{min}}, \kappa(\lambda) = C_L\lambda^3 \\ &\lambda \le \lambda_{\mathrm{max}}, \kappa(\lambda) = C_H/\lambda \end{aligned} \tag{6}$$

where C_{L} and C_{H} are expressed by:

$$\begin{aligned} C_{\mathrm{L}} &= \kappa(\lambda_{\mathrm{min}})\lambda_{\mathrm{min}}^3 \\ C_{\mathrm{H}} &= \kappa(\lambda_{\mathrm{max}})/\lambda_{\mathrm{max}} \end{aligned}. \tag{7}$$

After the extrapolation, the K–K relation can be expressed by [29]:

$$n(\lambda) = n(\lambda_1) + \frac{2\left(\lambda_1^2-\lambda^2\right)}{\pi}\int_{\lambda_{\mathrm{min}}}^{\lambda_{\mathrm{max}}}\frac{\lambda_0 k(\lambda_0)}{\left(\lambda^2-\lambda_0^2\right)\left(\lambda_1^2-\lambda_0^2\right)}d\lambda_0 + N_{\mathrm{H}} + N_{\mathrm{L}} \tag{8}$$