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OPTIMIZATION OF THE THERMAL RADIATION EXTINCTION OF SILICON CARBIDE IN A SILICA POWDER MATRIX

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Abstract

In order to optimize the infrared extinction of a SiC-powder in a silica powder matrix, Mie scattering calculations for spherical SiC-particles have been performed. A single oscillator-model was applied to calculate the optical constants of SiC. Taking into account the particle size distribution of a commercially available SiC-powder, its wavelength dependent extinction coefficient was calculated. The result is in very good agreement with the extinction spectrum of the powder derived by infrared optically measurements. Mie scattering theory also was used to find the optimum mean SiC-particle diameter of a mixture of 20% SiC-powder and 80% silica powder.

Keywords: silicon carbide, specific extinction, thermal conductivity, thermal radiation

Introduction

Evacuated thermal insulations have been proved to be very efficient for insulation of refrigerators [1], latent heat storage devices [2] and high temperature batteries [3]. They can be 10 to 20 times more efficient than conventional insulations with thermal conductivities λ in the range of 0.002 to 0.008 W m^{-1} K^{-1} at room temperature. Possible filler materials for the vacuum insulation are fibres, open pore foams and powders. Microporous powders have the advantage that a relatively high residual gas pressure is tolerable (up to 50 mbar) without a significant increase of the total thermal conductivity. Fine precipitated silica or fumed silica powders, however, have a transmission window for infrared (IR) radiation at wavelengths below 7 μm. Therefore IR-opacifiers like TiO_2-powder or carbon black are usually added, which scatter or absorb thermal radiation and reduce the radiative heat transfer [4]. Here we discuss the properties of silicon carbide as an efficient IR-opacifier for silica powders.

The powder mixture investigated in this work consists of 80% (mass percentage) precipitated silica (Sipernat 22LS, Degussa, Hanau, Germany) and of 20% silicon carbide. The mixture was prepared with an ultra high revolution mill (10000/15000 rpm). Therefore an excellent dispergation of the SiC-powder within the silica powder matrix could be achieved.

The aim of these investigations is to find the optimum SiC particle diameters for maximum reduction of thermal radiative heat transfer in silica powders used for vacuum insulations.

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Heat transfer in vacuum insulations

We consider only evacuated insulations where the heat transfer due to residual gases can be neglected. Then heat is only transported by thermal conduction via the powder fill or by thermal radiation. The total thermal conductivity λ is the sum of the thermal conductivity λ_{rad} due to thermal radiation and the thermal conductivity λ_s of the solid skeleton:

$$\lambda(T,\rho) = \lambda_s(T,\rho) + \lambda_{rad}(T,\rho) \tag{1}$$

with ρ density of the powder which is a function of the external pressure load p_{ext} and T temperature. In a first approximation the particles of the powders can be regarded as hard spheres. Then the solid thermal conductivity λ_s is proportional to $p_{ext}^{1/3}$ [5]. Real powders may deviate in their dependence considerably from this model. Therefore in general only qualitative statements about the solid thermal conductivity λ_s of powders can be made. The temperature dependence of the solid conductivity $\lambda_s(T)$ can be assumed as being proportional to the solid conductivity of silica glass. The thermal radiative conductivity λ_{rad} of an optically thick powder is [6]:

$$\lambda_{rad} = \frac{16}{3}\sigma n^2 \frac{T^3}{E(T)} \tag{2}$$

with σ Stefan Boltzmann constant ($5.67 \cdot 10^{-8}$ W m^{-2} K^{-4}), $E(T)$ extinction coefficient and n effective index of refraction. The square of the effective index of refraction of the powder matrix with a density of about 200 kg m^{-3} is approximately $n^2=1.1$.

The extinction coefficient E usually is proportional to the density ρ. Thus, a specific extinction coefficient $e=E/\rho$ is defined. The specific extinction coefficient e can be determined by three different methods: temperature dependent measurement of the total thermal conductivity, IR-optical measurements of the reflection and transmission [4] and calculation of the scattering and absorption cross section of the radiation by Mie theory [7].

Here we apply especially the third method because only the complex index of refraction of the material (SiC) and the diameter of the powder grains is necessary to calculate the extinction coefficient e. The results are compared with extinction coefficients obtained by IR reflection and transmission measurements and with calorimetric measurements.

Spectral extinction coefficient of SiC-powder

A particle can scatter and/or absorb electro-magnetic radiation. If we assume spherical geometry of the powder particles we can calculate the spectral extinction coefficient $E(\Lambda)$ with Λ wavelength by Mie theory. Silicon carbide is nonmagnetic, thus, the complex index of refraction m is related to the dielectric function $\varepsilon=\varepsilon'+i\varepsilon''$ by the Maxwell relation:

$$m = \sqrt{\varepsilon} = n + ik \tag{3}$$

where n is the real part and k is the imaginary part of the index of refraction. The lattice vibrational modes in α-SiC are well described by a single oscillator model [8]:

$$\varepsilon = \varepsilon_{oe} + \frac{\omega_p^2}{\omega_t^2 - \omega^2 - i\gamma\omega} \tag{4}$$

with $\omega_p = e(N/(m\varepsilon_0))^{1/2} = 2.08 \cdot 10^6$ cm^{-2} plasma frequency, $\omega_t = 793$ cm^{-1} frequency of the transverse optical mode of SiC, $\gamma = 4.76$ cm^{-1} damping constant and $\varepsilon_{0e} = 6.7$ dielectric function at frequencies which are low compared with electronic excitation frequencies. The optical constants of SiC calculated by the oscillator model (Eqs (3) and (4)) are shown in Fig. 1.

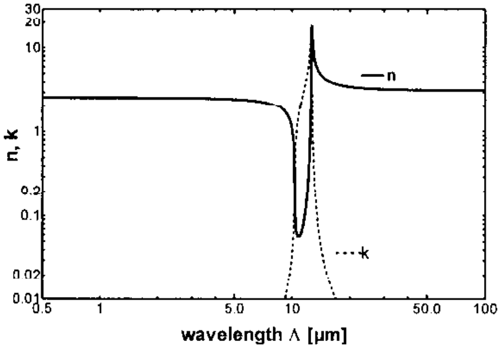

Fig. 1 Complex index of refraction of silicon carbide: n – real part; k – imaginary part

From the known complex index of refraction the extinction and scattering cross section C_{ext} and C_{scat}, respectively, and the scattering phase function can be calculated. The influence of forward scattering on the diffusive process of thermal radiation is taken into account if instead of the extinction cross section C_{ext} the cross section of the radiation pressure C_{pr} is considered [8]:

$$Q_{pr} = \frac{C_{pr}}{r^2\pi} = Q_{ext} - Q_{sca}\langle\cos\theta\rangle \tag{5}$$

with Q relative cross section, $\langle\cos\theta\rangle$ asymmetry factor of scattering phase function and r particle radius. The cross-sections can be derived by summing up the scattering coefficients. Then the specific extinction coefficient e of a sheet of identical spherical particles for incident light of wavelength Λ can calculated with [8]:

$$e(\Lambda) = \frac{E}{\rho} = \frac{3}{2}\frac{1}{\rho_s}\frac{Q_{pr}(x, m(\Lambda))}{D} \tag{6}$$

with D diameter of the spherical particle, $x = \pi D/\Lambda$ and ρ_s bulk density of SiC (=3200 kg m^{-3}). In Fig. 2 the effective specific extinction $e(\Lambda)$ for three diameters D of spherical SiC particles are shown.

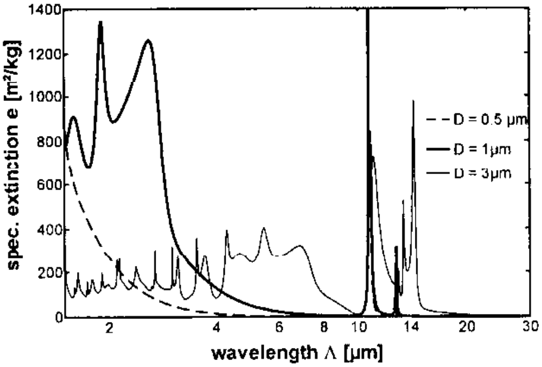

Fig. 2 Specific extinction e of spherical silicon carbide particles as a function of wavelength Λ for three different particle diameters D

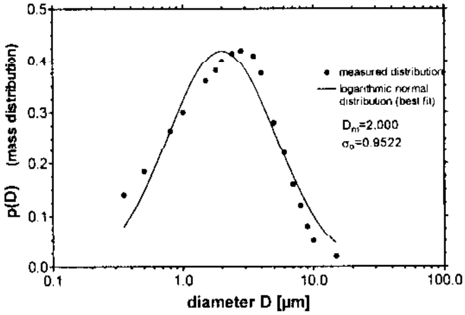

Fig. 3 Typical mass distribution $p(D)$ of the investigated silicon carbide powder as measured by the producer and the resulting fit according to Eq. (7)

The theoretical results of Mie theory are to be verified with experimental data. We used a commercially available SiC-powder. The particles have a specific mass distribution $p(D)$ depending on the production process. The specific particle size distribution of SiC was given by the producer of the powder (Fig. 3). A satisfactory representation of this distribution is a logarithmic normal distribution [9], where $\ln(D)$ is normally distributed rather than D:

$$p(D)\mathrm{d}(\ln D) = \frac{1}{\sqrt{2\pi}\sigma_g}\exp\left[-\frac{(\ln D - \ln D_m)^2}{2\sigma_g}\right]\mathrm{d}(\ln D) \qquad (7)$$

The maximum of the distribution is represented by D_m and the standard deviation of $\ln(D)$ by σ_g.

95% of the population is contained within the interval $D_m e^{-1.966\sigma_g} \leq D \leq D_m e^{1.966\sigma_g}$. The best fit of the measured curve yields the parameters D_m=2.00 µm and σ_g=0.95. This distribution is discretised into 100 logarithmically spaced diameters D_i and the effective extinction efficiencies Q_{pr} are calculated by Mie theory. The effective specific extinction is derived (Eq. (6)). A second calculation was done with the 25 discrete diameters and probabilities $p(D)$ according to the distribution given by the producer.

The resulting calculated specific extinctions based on the two different distributions are plotted in Fig. 4. Both theoretical spectra are compared to the infrared optically measured extinction spectrum of the SiC-powder. Especially in the wavelength range below 7 μm, where scattering dominates, there is a very good agreement between IR measurements and the two calculated spectra.

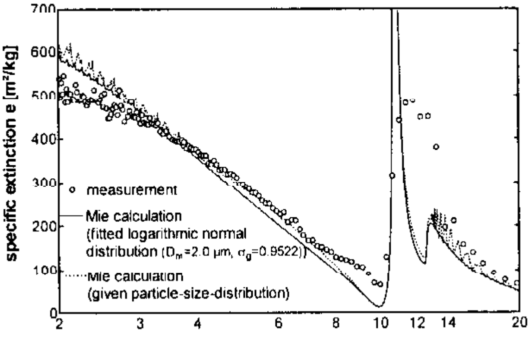

Fig. 4 Comparison of the IR-optically determined specific extinction of SiC-powder with two theoretical spectra based on Mie theory

The enhanced extinction measured between 8 and 10 μm wavelength is the result of a small amount of SiO_2 within the SiC-powder due to the production process. The calculations show a pronounced absorption peak between 10.5 and 11μm wavelength (e≈2000 m^2 kg^{-1}, not plotted), whereas the IR-measurement reveal a broadening of the absorption band between 10.5 and 14 μm wavelength. This broadening can be a consequence of the deviation of the real particle geometry from the assumed ideal spherical geometry [8]. The spectral extinction of the Mie calculations using the fitted logarithmic normal distribution is slightly less accurate, but it is nevertheless usable for questions of optimization of the powder.

The measured extinction spectrum between 1.4 up to 20 μm wavelength (Fig. 4) is derived from directional-hemispherical measurements of transmission and reflection on loose powders by using an integrating sphere [4, 7]. These data are compared in Fig. 5 with the specific extinction of the silica powders. The extinction of the silica powders above 20 μm wavelengths have been obtained without an integrating sphere by measuring the exponentially decaying transmission of the infrared beam. In non-grey media the mean effective specific extinction e_R is obtained by averaging the reciprocal spectral extinction with the Rosseland weight function $f_R(T,\Lambda)$ [6]. The Rosseland weight function f_R is plotted for the temperature T=300 K in Fig. 5, too. The effect of SiC as an IR-opacifier can be clearly seen: in the wavelength region below 7 μm the extinction of the silica is very low whereas the specific extinction of the silicon carbide powder is remarkably high. Without opacifier the thermal

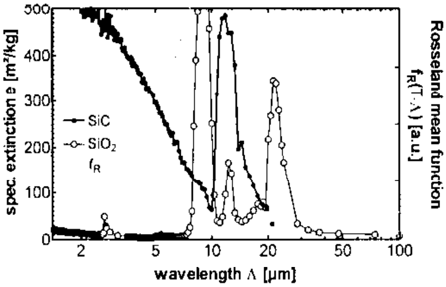

Fig. 5 Silicon carbide as an infrared-opacifier: comparison of the spectral effective extinction of a SiC-powder-sample and a silica powder; Rosseland weight function f_R for T=300 K

conductivity of precipitated silica usually is in the range of (4.5–7) 10^{-3} W m^{-1} K^{-1} depending on preparation like the applied load during pressing the powder board.

Mixture of silica powder with SiC-powder

A mixture of 20% SiC-powder and of 80% powder of precipitated silica (Sipernat 22LS) was prepared. The mixture was evacuated and the temperature dependent thermal conductivity λ was measured with a guarded hot plate apparatus [10].

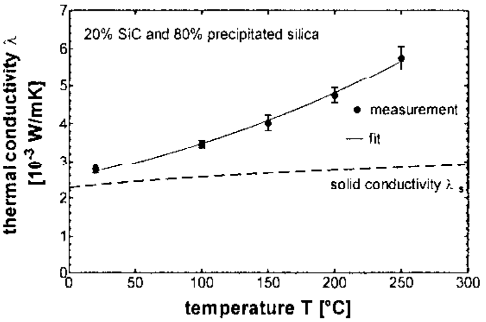

Fig. 6 Thermal conductivity λ of an evacuated mixture of 20% SiC and 80% precipitated silica at room temperature (external pressure load p_{ext}=1 bar) and derived solid conductivity λ_s

Figure 6 shows the graph of the temperature dependent total thermal conductivity of the evacuated mixture. The external pressure load p_{ext} during measurement was 1.0 bar, while it had been pressed before with 1.6 bar. At room temperature the thermal conductivity of the mixture is $\lambda=(2.8\pm0.1)\cdot10^{-3}$ W m^{-1} K^{-1}. A fit according to Eqs (1) and (2) of the data yields a caloric determined specific extinction of e_{cal}=67 m^2 kg^{-1} (e_{cal} is here assumed to be independent of temperature). At room temperature the solid conductivity is $\lambda_s=2.2\cdot10^{-3}$ W m^{-1} K^{-1}.

The measured IR-spectrum of the specific extinction e of the powder mixture at room temperature is shown in Fig. 7. For comparison a second spectrum was calculated by $e=0.2e_{SiC}+0.8e_{SiO_2}$ where the effective specific extinction e_{SiC} of the SiC-powder was determined by Mie theory using the particle size distribution of Fig. 3 and for e_{SiO_2} the measured data of precipitated silica according to Fig. 5 were taken.

The Rosseland averaged mean extinction of the measured spectrum for room temperature is $e_{IR}=72\ m^2\ kg^{-1}$ and the mean of the calculated spectrum is $e_{Mie}=70\ m^2\ kg^{-1}$. These results are in very good agreement and only a little higher than the extinction of $e_{cal}=67\ m^2\ kg^{-1}$ obtained from the caloric measurements.

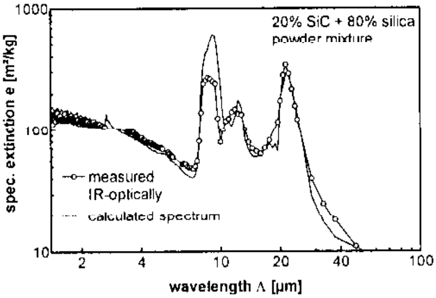

Fig. 7 Comparison of the IR-optically determined spectrum of the powder mixture (20% SiC+ 80% SiO_2) with the calculated spectrum

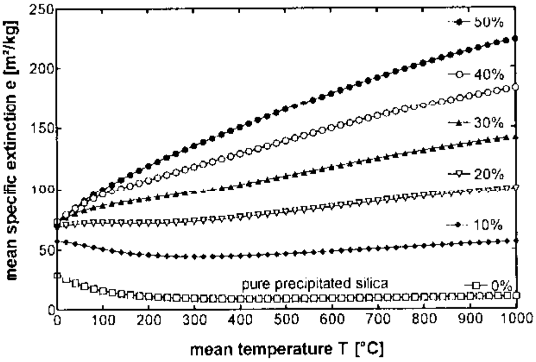

Fig. 8 Mie calculation of specific extinction $e(T)$ of a mixture of x% SiC and $(100-x)$% SiO_2-powder

Calculations of the mean specific extinction e_{Mie} depending on the temperature T for different mixtures of the SiC and silica powder are shown in Fig. 8. For applications at room temperature a 20% addition of the SiC-powder is satisfactory.

Optimization of the mixture

For the above calculations the diameter distribution of the delivered SiC-powder has been used (Fig. 3). Also other diameter distributions may be used to maximize the extinction coefficients. The basis of the optimization remains the mixture of 20% SiC and 80% SiO_2. For SiO_2 the spectrum of precipitated silica is selected as shown in Fig. 5. The extinction of SiC is calculated by Mie theory with the logarithmic normal distribution of the diameters (Eq. (7)).

The first calculations concern the optimal diameter of the SiC-powder at room temperature. For comparison the mean extinction of an idealised powder with one fixed particle diameter was calculated. Then two distributions with logarithmic particle distributions with two different widths σ_g (Fig. 9) were considered.

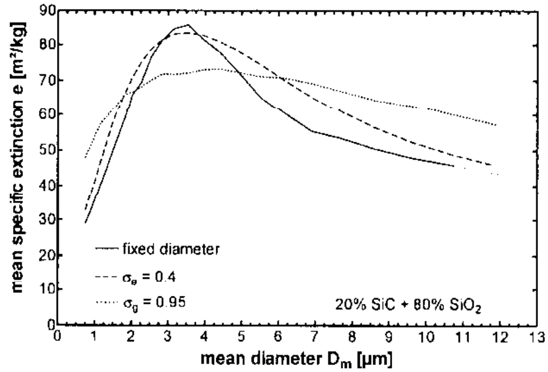

Fig. 9 Mean specific extinction of 20% SiC and 80% SiO_2 at room temperature for fixed diameters of the SiC particles and for two diameter distributions with different width σ_g

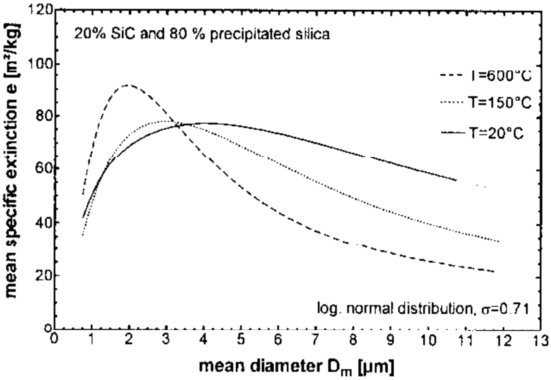

Fig. 10 Mean specific extinction of 20% SiC and 80% SiO_2 at different temperatures

The optimum for a fixed particle diameter D is about 3.5 μm. If the width of the particle distribution is broadened, the mean specific extinction e of the optimal diameter decreases. SiC-powders like the delivered one with a fitted logarithmic standard deviation σ_g of about 0.9 achieve an effective specific extinction e of about

72 m^2 kg^{-1} with a mean diameter D_m in a range from 3 to 5 μm. The mean diameter D_m of 2.8 μm of the commercially available SiC-powder provides a nearly optimal IR-extinction. Higher specific extinctions e of up to 82 m^2 kg^{-1} at room temperature would be possible by using a powder with smaller deviation around the optimal diameter D_m of 3.5 μm.

As can be seen in Fig. 8 the effective specific extinction e of the mixture increases with increasing temperatures. It is interesting to find the optimum mean diameter of SiC-powder also for higher temperatures. In Fig. 10 the mean specific extinction e of the mixture for different temperatures was calculated for a logarithmic normal distribution with different mean diameters D_m and σ_g=0.71.

At temperatures of 900 K the optimum mean particle diameter D_m for SiC is 1.8 μm with a specific extinction coefficient e of 92 m^2 kg^{-1}. If the deviation σ_g is reduced to 0.4, then the powder mixture can reach a specific extinction coefficient e of up to 105 m^2 kg^{-1}. Thus SiC-powder may be also an efficient opacifier for air-filled microporous powder boards, which are used as high temperature insulations.

Conclusions

Silicon carbide powders have shown to be very efficient opacifiers for silica based powder insulations, if the particle diameter is in the order of 3 to 5 μm. Vacuum insulations filled with precipitated or fumed silica and 10 to 20% silicon carbide reach thermal conductivities between 0.003 and 0.004 W m^{-1} K^{-1} at room temperature. Meanwhile powder boards with fumed silica and SiC mixtures have been produced in larger quantities. About 50 m^2 have been wrapped with laminated aluminum foil, evacuted and sealed and now serve as highly efficient wall insulation in a new office building of the ZAE Bayern Institute.

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