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A Novel Thermal Insulation Coating with SiO_2@TiO_2 Core-shell Particles and Its *In-situ* Characterization at High Temperature

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Abstract: A novel type of SiO_2@TiO_2 core-shell particles were fabricated as pigments for high-temperature thermal insulation coatings using a Sol-Gel method. TEM images of SiO_2@TiO_2 core-shell particles indicated that TiO_2 shell with a thickness about 50 nm was deposited well on the surface of SiO_2 particles. The thermal insulation properties of the products obtained were characterized by a developed apparatus in the temperature range from 1300℃ to 1500℃. The results show that, using SiO_2@TiO_2 particles as a radiant barrier, the heat flux from radiation sources is successfully reduced by about 50% and the temperature difference reaches 260℃ when radiation heater temperature is 1500℃. The effectiveness of SiO_2@TiO_2 core-shell particles on high-temperature thermal insulation is obvious. The work suggests that SiO_2@TiO_2 core-shell particles are very promising pigments for high-temperature thermal insulation coatings.

Key words: Sol-Gel method; core-shell; thermal insulation; coating

Thermal insulation materials have been the subject of interest and importance to protect metal parts and ceramic components in high temperature applications such as hypersonic cruise missile and turbine vanes[1-3]. Since the effects of thermal radiation transfer increases rapidly with temperature[4], high-temperature insulation properties can be effectively improved by reducing the thermal radiation heat transfer. For example, thermal radiation can be degraded through depositing high reflective index on the surface of fibers[5], and also radiator heat transfer can be reduced by adding metallic foils(as reflective foils) into multilayer thermal insulation materials[6-7]. But the addition of metals can generally affect the physical properties of thermal insulation materials, such as wave-transparent property. Fortunately, the advent of particles with core-shell structure, which have attracted considerable attention due to their potential application in optical, electronic, magnetic and catalytic materials, may solve this problem[8-11]. Although particles with core-shell structure are propitious to exhibit excellent scattering properties due to the interfaces between core and shell, few were reported about their applications in thermal insulation materials for high temperature. Recently, some researchers started to focus on modifying the thermal insulation properties of certain material by coating it with another type of material. Wang *et al*[12] optimized core-shell particles using Kubelka-Munk theory and Mie model, and found that SiO_2@TiO_2 core-shell particles present great thermal insulation properties. Also, limited experimental data are available on their thermal insulation properties at high temperature (≥1000℃)[13-15]. However, due to the present characterization means of thermal insulation coatings (such as determination of infrared transmittance and reflectance) are always performed at room temperature, the data obtained cannot completely reflect real properties at high temperature. Therefore, it is necessary to perform characterization in appropriate conditions which thermal insulation materials are really applied in.

In this letter, SiO_2@TiO_2 core-shell particles were synthesized through a simple Sol-Gel process and their capacities for reducing radiation heat transfer were experimentally characterized by a developed apparatus in the temperature range from 1300℃ to 1500℃. The results show that the heat flux from radiation sources was successfully reduced by about 50% and the effectiveness of thermal insulation was obvious, indicating that SiO_2@TiO_2 core-shell particles are very promising pigments for high-temperature thermal insulation coatings.

1 Experimental

All chemicals were analytical-grade reagents and used as received without further purification. All experiments were conducted in air.

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1.1 Titania coating on silica particles

To prepare the $SiO_2@TiO_2$ core-shell particles, 2.0 g commercial SiO_2 with 10 μm diameter core particles were initially dispersed in a mixture solution of 25 mL ethanol and 0.5 mL tetrabutyl titanate(TBOT) by ultrasonicator in reactor. A mixture solution of 25 mL ethanol, 10 mL deionized water and 0.25 mL nitric acid was then slowly injected into the reactor in 0.5 h, and then was stirred for 12 h and sealed in autoclaves for 24 h at 180℃ to complete the Sol-Gel process. Thereafter, the product suspension was filtered out, washed with deionized water, dried at 90℃ and calcined at 550℃ for 1 h.

1.2 Preparation of films adding $SiO_2@TiO_2$ particles

In order to prevent films from cracking, 3 g SiO_2 with 30 μm diameter particles were added into 0.17 g $SiO_2@TiO_2$ particles and the mixture was dispersed in 2 mL silica sol. The mixture was deposited on the surface of 30 mm×30 mm×2 mm quartz plates, dried at room temperature and calcined at 800℃ for 1 h.

1.3 Characterization

Transmission electron microscope (TEM, JEM-2100, JEOL) was used for studying the morphology of coatings on the surface of SiO_2. The samples were dispersed in absolute ethanol and were ultrasonicated before observation. The transmittance of reflective coatings was recorded in Fourier transform spectroscope (FT-IR, AVATAR) in the range from 4000 cm^{-1} to 2000 cm^{-1} as films deposited on quartz plates. The reduction of the heat flux passing through the film was measured by a radiant heat flux sensor (TS-10, K_s=0.367 μV/(W•m^2), Captec) deposited below samples with 100 mm distance and the IR radiation heater of heating rate 1 ℃/s was installed above the upper surface of samples with 10 mm range. Two type-B thermocouples were used to monitor the temperature difference between upper and lower surfaces of film. These pieces of equipment were insulated from surroundings and connected to a data logger (DaqPRO 5300, Fourier). The samples were deposited in this apparatus when radiation heater temperature achieved 1000℃ until 1500℃. The data were collected every second as radiation heater temperature raised from 1300℃ to 1500℃.

2 Results and discussion

Figure 1 shows the low- and high- magnification TEM micrographs of $SiO_2@TiO_2$ particles calcined at 550℃ for 1 h. Considering the commercial SiO_2 size, it was not appropriate to observe the shell clearly with low magnifycation. Therefore, in order to obtain the thickness of TiO_2 shell, part of a $SiO_2@TiO_2$ particle was chosen to be magnified. As shown in Fig. 1(a), the core-shell structure and the interface were clearly observed from the typical individual $SiO_2@TiO_2$ particles. It is clear that the TiO_2 shell with a thickness of about 50 nm was deposited well on the surface of SiO_2 particles. The lattice fringes of TiO_2 shell were observed from Fig. 1(b), where the size of grains were found to be 5−10 nm. The refraction index of SiO_2 is 1.54 and crystalline titanium dioxide turns into anatase whose refraction index is about 2.6 after sintered at 550℃. Therefore, obvious refraction index difference lies between core and shell. According to Tran[5], the interface formed between SiO_2 core and TiO_2 shell could scatter and reflect radiation effectively, which is the main reason of the radiation reduction.

In order to evaluate the effectiveness of the $SiO_2@TiO_2$ on blocking radiation heat transfer, the optical properties of $SiO_2@TiO_2$ were examined using films of 50–80 μm thick, with the quartz substrate attached. The transmittance of $SiO_2@TiO_2$ and SiO_2 films for spectral range of 1000 to 4000 cm^{-1} are displayed in Fig. 2, where it can be found that the transmittance of $SiO_2@TiO_2$ film was lower than SiO_2 film nearly in the wave number range except the 3250–3500 cm^{-1} range. To obtain the effectiveness of radiation blocking directly, areas under each curve were calculated by integration algorithm. Assuming the amount of infrared radiation passing through pure SiO_2 film as 100%, the transmittance of film with $SiO_2@TiO_2$ particles was 83.34%. Calculated results showed that infrared radiation reduced by $SiO_2@TiO_2$ was 16.66%, more than

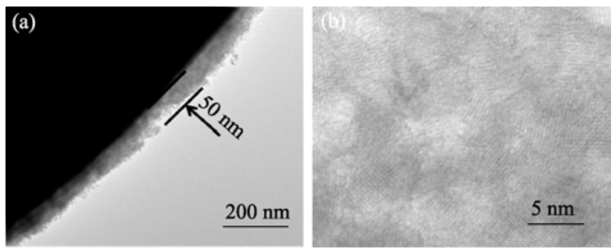

Fig. 1 TEM images of SiO_2/TiO_2
(a) Low-magnification; (b) High-magnification

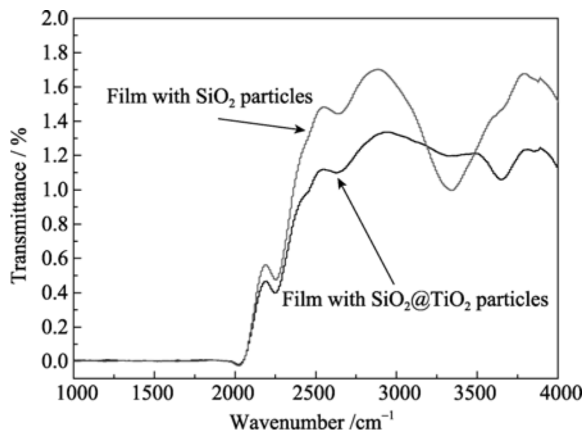

Fig. 2 FI-IR spectra of films with SiO_2/TiO_2 and SiO_2

that by pure SiO_2. Therefore, it is concluded that the capacity of SiO_2@TiO_2 to reduce radiation is improved, but not so more evidently compared with that of pure SiO_2 (obtained by FT-IR at room temperature).

In order to resemble the high-temperature conditions where pigments would be applied, an apparatus was developed to measure the heat flux through films and the temperature difference between upper and lower surfaces of films at high temperature. It is clear from Fig. 3(a) that the heat flux passing through coatings increases with radiation heater temperature, revealing that the reduction of heat flux induced by SiO_2@TiO_2 particles is more obvious than that caused by SiO_2 particles. In order to compare the rate of heat flux increase, the dots of each curve were fitted into lines with the least square method. The upper (representing SiO_2 film) and lower (corresponding to SiO_2@TiO_2 film) dots were fitted into two lines with slopes of about 6.71 and 4.17, respectively. Apparently, the heat flux increase rate of the former is higher than that of the latter at high temperature, which suggests that at high temperature the films with SiO_2@TiO_2 particles exhibit better thermal insulation properties than those with uncoated SiO_2.

Figure 3(b) shows the heat flux reduction percentage

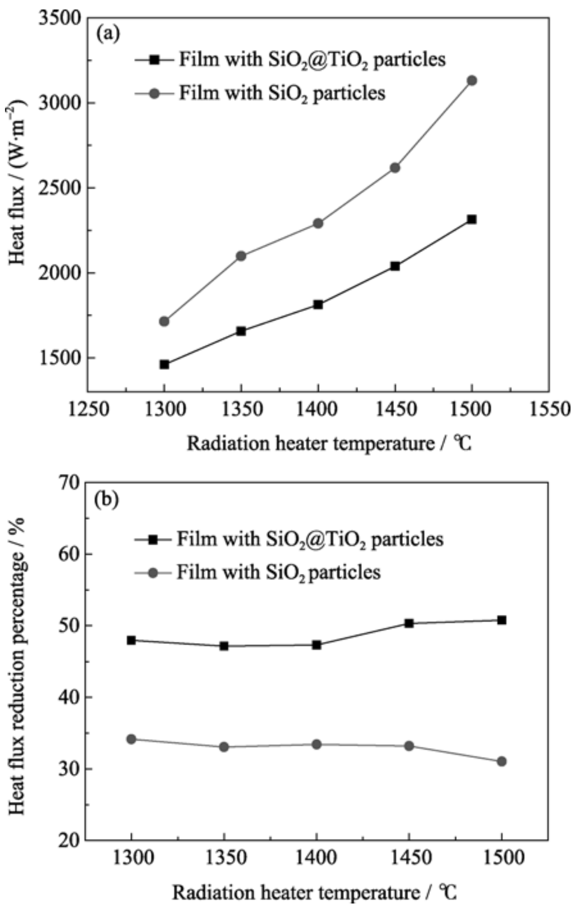

Fig. 3　(a) Heat flux passing through films with SiO_2@TiO_2 and SiO_2; (b) Heat flux reduction percentage of SiO_2@TiO_2 and SiO_2

passing through coatings and the base case is a bare quartz plate. It is clear that the heat flux increases with the temperature of IR radiation heater and nearly 50% radiation heat flux could be decreased by SiO_2@TiO_2, thus the film with SiO_2@TiO_2 particles exhibits excellent scattering ability compared to film with uncoated SiO_2. Moreover, the heat flux reduction percentage induced by SiO_2@TiO_2 seems to be nearly 30% more than that by SiO_2. Figure 3(b) also shows that, the heat flux reduction percentage of film with SiO_2@TiO_2 increases slightly whit the temperature of radiation heater, distinctively different form the case of the film with pure SiO_2. Therefore, the SiO_2@TiO_2 particles possess a better capacity than SiO_2 to reduce thermal radiation transfer at high temperature, which indicates that SiO_2@TiO_2 exhibits better radiation insulation properties than SiO_2 at high temperature.

Through comparing data obtained in different experimental conditions, it is found that SiO_2@TiO_2 pigments exhibit much better insulation property at high-temperature than at room temperature, indicating that data obtained at room temperature cannot completely reflect real thermal insulation properties at high temperature. Moreover, SiO_2@TiO_2 particles could reduce nearly 50% radiation heat flux with only 5% pigment volume fraction, which shows that SiO_2@TiO_2 can effectively improve insulation properties of coatings with the low pigment volume fraction. Therefore, the influence of SiO_2@TiO_2 on other physical properties is expected to be minimized.

Figure 4 demonstrates the effect of radiation heater temperature on temperature difference of two types of films. Here, the temperature difference of SiO_2@TiO_2 film was found to rise slightly up to 260℃, evidently higher than that of SiO_2 film. In addition, the temperature difference of pure SiO_2 film decreases slightly with the radiation heater temperature above 1400℃. Accordingly, SiO_2@TiO_2 particles exhibit much better thermal insula-

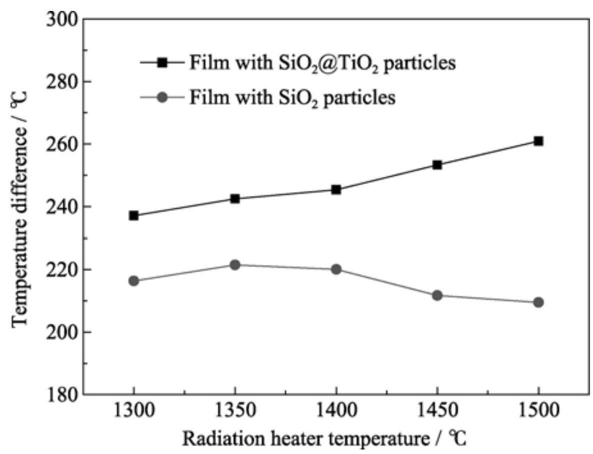

Fig. 4　Temperature difference between upper and lower surfaces of SiO_2@TiO_2 film and uncoated SiO_2 film with the temperature of radiation heater

tion properties than uncoated SiO_2 due to their excellent scattering ability at higher temperatures.

3 Conclusion

TiO_2 was coated on the surface of SiO_2 spheres by Sol-Gel method in order to obtain the pigments with excellent scattering ability. The results show that TiO_2 can be deposited on the surface of SiO_2 spheres with a thickness about 50 nm and the radiation heat transfer has been obviously declined by SiO_2@TiO_2 particles at high temperature. Therefore, SiO_2@TiO_2 with core-shell structure is expected to be a promising thermal insulating pigment through reduction of radiation heat transfer in the environment temperature ranging from 1300℃ to 1500℃.

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SiO_2@TiO_2核壳结构及其在高温下的隔热性能表征

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摘 要: 以SiO_2@TiO_2核壳结构粒子为新型功能填料，采用旋涂方法制得了高温隔热涂层. TEM照片显示通过溶胶–凝胶法，成功在 SiO_2 核上包覆上厚度为 50 nm 的 TiO_2 壳层. 通过自开发的测试设备表征了填料加入前后涂层在1300~1500℃的隔热性能. 结果表明: SiO_2@TiO_2 核壳结构粒子加入后，隔热涂层能将从热源辐射出的热流减少50%，在热源温度达1500℃时涂层试样的表背温度差为260℃. 加入SiO_2@TiO_2核壳粒子的涂层在高温下隔热效果明显，是一种很有前景的高温隔热涂层填料.

关 键 词: 溶胶–凝胶法; 核壳结构; 隔热; 涂层

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