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	(ナノ粒子コーティングによるふく射制御に関する研究)
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	論 文 内 容 要 旨

Chapter 1: General introduction and background

In this chapter, the background of this study was presented. A brief discussion about the necessity of radiative heat transfer control and its wide area of applications has been presented.

In large scale phenomena, the temperature of the earth is determined by the balance of the energy though radiative transfer. The sun's energy travels to the earth in the form of electromagnetic waves, is selectively absorbed, and scattered as it goes through atmospheric layer. The global warming problem is due to thermal balance of the earth brought by participating media such as carbon dioxide and it is thought that the propagation of radiative energy in participating media can be the core of solving these problems. Therefore, radiative transfer in large scale systems such as environmental problems must be discussed as the conjunction of nano-scale phenomena.

In engineering applications, this nano-scale phenomenon of radiation is important. Thermal radiation is affected by participating media or particulate media. Many systems contain particulates that actively participate in the radiative transfer processes. In the systems, the scattering and absorption of thermal radiation by particles plays an important role in the overall energy transfer, and its understanding is central to the prediction and evaluation of system performance. Therefore, nano-scale radiation must be considered in these systems.

When an electromagnetic wave interacts with a medium containing small particles, the radiative intensity should be changed by absorption and/or scattering. Therefore, controlling in the radiative transfer can be also achieved by controlling nano-scale effect of radiation by particle. This thesis concentrates on achievement of control the radiative transfer by the coating containing particulate which controls nano-scale effect of radiation.

Chapter 2: Fundamentals of Radiative Transfer in Nano-Particle Coating

In this chapter, fundamentals of the radiative transfer were studied for controlling it. The methods of evaluating the radiative properties of pigment particles were described. All radiative properties of a single spherical particle, interacting with an electromagnetic wave could be calculated using Mie theory.

For modeling the radiative transfer in pigmented coatings, the radiation element method by ray emission model (REM²) was used. It simplified for radiative heat transfer analysis in a one-dimensional plane parallel system which is for modeling the pigmented coatings. In this method, both diffuse and specular boundary conditions can be considered.

For simulating the solar irradiance, Bird's model was introduced. This model can simulate the spectral distribution of direct and diffuse solar irradiation on a horizontal surface.

For evaluating the color of the coating, the CIE (international commission on illumination) colorimetric system was introduced. In this color system, a color can be defined using three parameters including two color coordinates which show a

color on chromaticity diagram and brightness.

For deriving the radiative properties of surfaces for homogeneous, optically smooth media, the electromagnetic wave theory was introduced. It gives us spectral or total radiative properties of surfaces. By the electromagnetic wave theory, the specular reflectivity and the spectral emissivity for the pigment coating can be derived.

To find the real and imaginary parts of complex index of refraction of unknown opaque material, inverse analysis was introduced. Inverse analysis gives us the unknown data from the experimental data.

Chapter 3: Development of UV Barrier Coating

In this chapter, a method of optimizing of UV barrier coatings by optimizing the size, volume fraction of particles and coating thickness was introduced. The UV barrier performance was studied both experimentally and numerically.

The radiative properties of single pigment particles in a wide range of particle size and wavelength were calculated based on Mie theory. To design the UV barrier coating, the sum of the absorption and back scattering efficiencies was important. For the zinc oxide (ZnO) coating, the best diameter for our purpose was about 0.1 μ m. For the titanium dioxide (TiO₂) coating, the best diameter for our purpose was about 0.07 μ m.



Fig. 1 Measured and calculated transmittance

Theoretical calculation was conducted to evaluate the

spectral transmittance. The effects of particle size, the volume fraction of the coating and the coating thickness were discussed. Additionally, total UV and visible (VIS) transmittance were calculated from the numerical spectral transmittance. From the total UV and VIS transmittance, optimization parameter was defined and calculated. Optimized particle diameter was could be found from this new parameter.

For experimental part, the transmittance of the coating was measured. The measured transmittance of the ZnO coating when the nominal particle size $d_p = 100$ nm was low in UV region and high in VIS region. It meant the coating can protect the industrial products from UV attack without changing the appearances of the products. The effect of the particle size, the volume fraction of the coating and the coating thickness were discussed. By choosing the appropriate particle type, coating thickness, volume fraction, and particle size, the radiative properties of the coating could be controlled. Finally, the calculated transmittance showed the similar spectral tendency with the measured one as shown in Fig. 1. The optimum coating could be designed by the numerical calculation.

Chapter 4: Optimization and Evaluation of Thermal Barrier Coatings

In this chapter, a method of designing and optimizing of thermal barrier coating was introduced. As the pigment particle, copper (II) oxide (CuO) was focused. CuO particles are highly absorbing in UV and VIS regions and non-absorbing at near infrared (NIR) region. It can be predicted this material is available for black-colored cool coating.

The databases for radiative properties of CuO particles in a wide range of wavelength and particle size were constructed. For the CuO pigment particles with $d_p = 0.4 \mu m$, the maximum backscattering efficiency and hence maximum reflectance is observed in NIR region.

Theoretical calculation was conducted to evaluate the spectral reflectance. The effects of particle size, the volume fraction of the coating and the coating thickness were discussed. Additionally, total VIS and NIR reflectance were calculated from the numerical spectral transmittance. From the total VIS and NIR reflectance, optimization parameter was defined and calculated. Optimized particle diameter was could be found from this new parameter. For a CuO pigmented coating on the white paper, the optimization parameter peak occurs at about 15.6, where the optimum pigments size is 0.57 μ m and the optimum value of parameter *b* is 10 μ m. This is the maximum theoretical value for a CuO pigmented coating.

For experimental part, the coatings pigmented were made by three different types of CuO pigment powders with 0.050 μ m, 0.89 μ m and 3.0 μ m nominal average particle sizes. The measured spectral reflectance of CuO pigmented coating on white paper when the nominal particle size $d_p = 0.89 \mu$ m is quite low in the VIS and high in the NIR, while the coating color is black-color as shown in Fig. 2. It is possible to control the spectral behavior of pigmented coating by controlling the size of the pigment particles. The performance of CuO pigment is much higher than that of other pigment materials (white TiO₂ pigment and red Fe₂O₃ pigment), though the CuO coating shows a black-color.

Finally, the results of numerical simulation were validated using experimental data. The results of experiment show a reasonable agreement with numerical calculation. The



Fig. 2 Measured reflectance of CuO coating

difference between calculated and measured reflectances is due to some simplifications in numerical analysis, an uncertainty in the size distribution of pigment particles and the uncertainty in the complex refractive index about CuO material. Additionally, the theoretical calculation suggests that the average particle size of the CuO powder used in the experiment is smaller than that indicated in the catalogue. More accurate particle size control enables us to achieve better performance.

By using CuO particles, a cool black-color coating with high reflectance against NIR in solar irradiation can be obtained. By choosing the appropriate particle type, substrate, thickness, volume fraction and particle size, the radiative properties of the coating can be controlled. By using the proposed cool black-color coating, the interior temperature decreases and the cooling load can be reduced while keeping the dark tone of the object.

Chapter 5: Emissivity Evaluation for Cool Coatings

In this chapter, the emissivity evaluation was conducted for cool coatings. First, the emissivity measurement was conducted by infrared camera. About pure acrylic resin samples and CuO coatings, the emissivity increases with the increment of coating thickness.

To find spectral emissivity, it evaluated from the transmittance and reflectance measurement. Evaluated emissivity from the transmittance measurement had good agreement with the measured one by infrared camera. Evaluated emissivity from the reflectance measurement had good agreement with the measured one by infrared camera. Pigment particles affected the radiative property of the coating in IR region.

The emissivity was calculated from the quoted complex refractive index by electromagnetic theory. Calculated emissivity by electromagnetic theory had good agreement with the measured one by infrared camera.

Chapter 6: Thermal Evaluation and Analysis for Cool Coatings

In this chapter, the thermal behavior of the spectral-selective coatings pigmented with CuO particles was discussed. The temperature measurement and analysis was conducted to evaluate thermal barrier performance of the cool coatings.

Exposure experiment was conducted in sunny days to measure the temperature of the coating. The coating was observed by infrared camera as shown in Fig. 3. CuO pigmented coating on white paper when the nominal particle size $d_p = 0.89 \,\mu\text{m}$ is the coolest in all black coating. The effects of particle size, coating thickness and the substrate on thermal and esthetic behaviors were discussed. The temperature of the CuO coating with the volume fraction $f_v = 0.05$ and the coating thickness $t = 10 \,\mu\text{m}$ was the lowest in all black coatings.

Temperature measurement was conducted in solar simulator. By the solar simulator, the meteorological factors (e.g. ambient temperature, wind) could be controlled. CuO coatings optimized theoretically are much cooler than the bare black paper and the black paint and maintain a low brightness. Coatings with high brightness have the best thermal performance because they reflect both of VIS and NIR radiations. However, high VIS reflectance produces a high glare, which is unpleasant

to the human eye. Thus, the visual and thermal performances need to be optimized together.

Using optimal-size CuO particles, a cool black coating with high NIR reflectance against solar irradiation could be obtained. By selecting the appropriate particle size, substrate color, coating thickness, and volume fraction, the visual and thermal performance of the coating could be controlled. The temperature of the optimized CuO coating was 10 °C lower than that of the bare black paper. Using such a cool black coating on an object such as a car, the interior temperature would decrease and the cooling load could be reduced.

(a) Visual image



Fig. 3 Visible and infrared images of the coating

Finally, the thermal analysis was

conducted to simulate the temperature measurement in the solar simulator. Thermal analysis effectively estimated the temperature measurement using the solar simulator. The temperatures of the coatings in the solar simulator were estimated from the measured reflectance.

Chapter 7: General conclusions

The founding in this thesis is concluded. In this study, following result and knowledge were obtained.

- 1. The fundamentals of the radiative transfer were studied for controlling it.
- 2. The UV barrier coating was developed theoretically. Its performance was evaluated experimentally. The coating can protect the industrial products from UV attack without changing the appearances of the products.
- 3. The thermal barrier coating was achieved theoretically. Its spectral reflectance shows quite low in the VIS and high in the NIR, while the coating color is black-color.
- 4. The emissivity evaluation was conducted for cool coatings. The emissivity can be controlled by coating thickness.
- 5. The thermal behavior of the cool coatings was discussed. Designed coatings are much cooler than the bare black paper and the black paint and maintain a low brightness.

論文審査結果の要旨

温暖化ガスなどのふく射の吸収や雲などの散乱媒体のふく射の散乱等の微小領域におけるふく射伝 達は地球温暖化現象やヒートアイランド現象の大規模現象の理解に重要である。また、この微小領域に おけるふく射伝達は様々な工学応用においても重要であり、この現象を応用・制御することで性能向上 が可能となる。本研究ではこの現象を応用することでナノ粒子コーティングによるふく射制御を行って いる。本論文は、これらの研究成果をまとめたものであり、全編7章からなる。

第1章は序論であり、本研究の背景、目的および構成を述べている。

第2章では、ナノ粒子コーティングに関するふく射伝達の理論を述べている。微粒子のふく射特性の 導出するため Mie 散乱理論を述べている。また、光線放射モデルによるふく射要素法を用い、ナノ粒子 コーティングのふく射伝達をモデル化している。これは、重要な成果である。

第3章では,紫外線遮蔽膜の開発を通して,紫外線及び可視光領域でスペクトル透過率を制御している。その結果,低い紫外線透過率及び高い可視光透過率を持つ紫外線遮蔽膜を実現している。これは, 有効及び重要な成果である。

第4章では,遮熱コーティングの設計及び最適化を通して,可視光及び近赤外領域の反射率を制御し ている。その結果,低い可視光反射率及び高い近赤外反射率を持つ遮熱コーティングを実現している。 これは,実用化に向けた重要な成果である。

第5章では、赤外領域において遮熱コーティングの放射率を評価している。全放射率を赤外線カメラ により測定している。また、スペクトル放射率を透過率測定及び反射率測定から評価している。これは、 重要な知見である。

第6章では、第4章で開発した遮熱コーティングの遮熱性能に関して評価している。実際の使用を想定し、曝露実験において温度測定を行っている。また、外的な気象の影響を無視した評価のため、ソーラーシミュレータを用いた温度測定を行っている。以上により、本研究で開発した遮熱コーティングの優位性を確認している。これは、実用化に向けた重要な成果である。

第7章は結論である。

以上要するに本論文は、微小領域におけるふく射伝達を応用することで、ナノ粒子コーティングによ るふく射制御を行ったものであり、機械システムデザイン工学および環境工学の発展に寄与するところ が少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。