EXAMINATION OF THERMAL CONDUCTIVITY ESTIMATION MODEL OF CNT DISPERSED WATER

YAMADA Shinya[1], MORITA Shin-ichi[2], HANIU Toshihiro[3], TAKAI Kazunori[4], YAMADA Takanobu[2], HAYAMIZU Yasutaka[5] and GONDA Takeshi[5]
[1]Graduate student, Mechanical Engineering Course, Graduate School of Kitami Institute of Tech.
(Koencho 165, Kitami, Hokkaido 090-8507, Japan)

[2]Professor, [3]Assistant Professor, [4]Associate Professor, Div. of Mechanical and Electrical Eng., Kitami Institute of Tech.
(Koencho 165, Kitami, Hokkaido 090-8507, Japan)
E-mail:s-morita@mail.kitami-it.ac.jp
[5]Associate Professor, National Institute of Technology, Yonago College,
(4448 hikona-cyo, Yonago-shi, Tottori 683-8502. Japan)

A dispersion system having a liquid continuous phase can maintain fluidity regardless of the phase state of the dispersoid. It is considered that the heat exchange performance of the heat medium fluid can be significantly improved by using the dispersoid as a fine material with high thermal conductivity. This study reports the results of comparative evaluation of the measured and theoretical values of the thermal conductivity of a carbon nanotube-dispersed fluid in which multi-walled carbon nanotubes, MWCNT, with extremely high thermal conductivity are dispersed in distilled water. The thermal conductivity of MWCNT dispersed water was measured by the wire heating method with the mass composition ratio and temperature as parameters. The ratio of thermal conductivity of the dispersoid to the continuous phase of this test sample is unprecedentedly large, which is a range that has never been evaluated in other study. The test MWCNT has a very thin and long shape, and is considered to be dispersed in the continuous phase in a deformed and interlaced state. Therefore, a model suitable for estimating the thermal conductivity of MWCNT dispersed water was examined by comparing the experimentally measured values with the theoretically calculated values. The thermal conductivity of the MWCNT dispersed water was measured to be higher than that of the single-phase water, and the results were in good agreement with the values estimated by the Rayleigh model with a cylindrical arrangement.

Key Words : *thermal conductivity, CNT, hot wire method, Rayleigh model, Maxwell model*

1. INTRODUCTION

The thermal conductivity of carbon nanotube (CNT) reaches 3.5 to 7.5 times the value of copper. In the case of multi-wall carbon nanotube (MWCNT), it is reported to be 1400 to 3000 W/(m・K)[1,2]. The thermal conductivity of single-walled carbon nanotube (SWCNT) is even higher[3]. The carbon nanotubes are dispersed fluid is expected to increase the thermal conductivity of the entire system and improve the heat exchange performance.

This report shows the experimental results of thermal conductivity measured by the hot wire method. Furthermore, the suitable estimation equation of theoretical dispersion model for thermal conductivity is evaluated by comparing the experimental results with the theoretical values. The Maxwell's model[4] of the spherical dispersion model and the Rayleigh's model[4] of the cylindrical arrangement model are adopted as the theoretical dispersion phase model for estimating the thermal conductivity. The results of this research will contribute to increase the heat storage rate by improving the thermal conductivity.

2. TEST SAMPLES AS HEAT MEDIUM

The dispersoid used in this study is multi-walled carbon nanotubes. Multi-walled carbon nanotube (MWCNT) is carbon nanotube in which CNT are laminated in a nested manner. Fig.1 shows the transmission electron micrograph of the MWCNT as dispersoid used in this study. The average size of the test MWCNT is 17 nm in diameter and 5 μm in length. The thermal properties are thermal conductivity 3000 W/(m・K), true density 1350 kg/m^3, and specific heat 0.6691 kJ/(kg・K). These values are provided by the manufacturer.

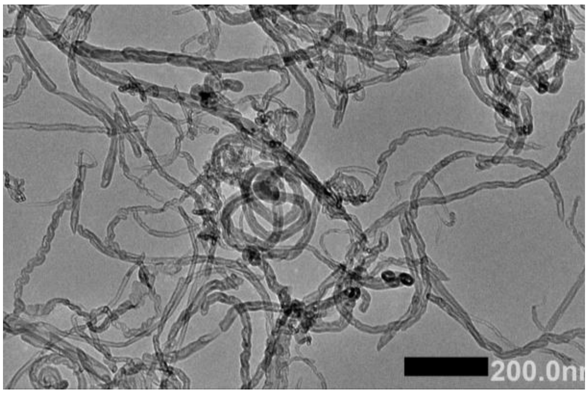


Fig.1 Transmission electron micrograph of MWCNT.

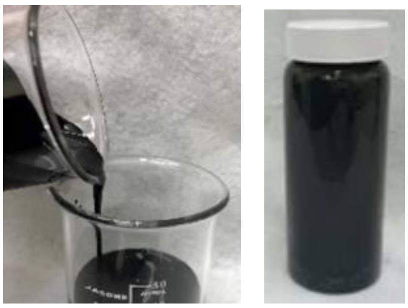


Fig.2 External appearance of MWCNT dispersed Water.

Table 1 Mass composition ratio of test samples [mass%].

MWCNT φ_d	Surfactant Nonion φ_{sn}	Surfactant Anion φ_{sa}	Distilled water φ_w
1.00	0.10	0.10	1.00
4.30	0.40	0.40	4.30
7.00	0.70	0.70	91.60

Fig.2 shows the photographs of the appearance of multi-walled carbon nanotubes dispersed water sample. The sample is black in color and has fluidity.

Table 1 is shown the composition mass ratios of the three measured samples. Two types surfactants are used to disperse MWCNT in water. The first one is nonionic surfactant (polyoxyethylene alkyl ether NIKKOL BT-7) as a wetting agent, and the second one is anionic surfactant (linear alkylbenzene sulfonate, Kao Co.,Ltd. Neoperex G-15) for dispersion in distilled water. The composition mass ratio of the two types of surfactants is as small as 10 mass% of MWCNT, respectively. The dispersion medium of the dispersion model described later is calculated as water because the surfactant content is very little. The thermophysical property value of water is used for the calculation by equation of theoritical dispersion model.

Carbon nanotubes are dispersed in water using an ultrasonic homogenizer (Sonics VCX-500, 20kHz, 500W) according to the following procedure.

1. Mix the nonionic surfactant with the carbon nanotubes.
2. Put the mixture of 1 and the anionic surfactant in distilled water and add ultrasonic waves for 180 seconds to disperse.

It has been confirmed that MWCNT separation and aggregation in the sample do not occur by observing at room temperature for 100 days or more.

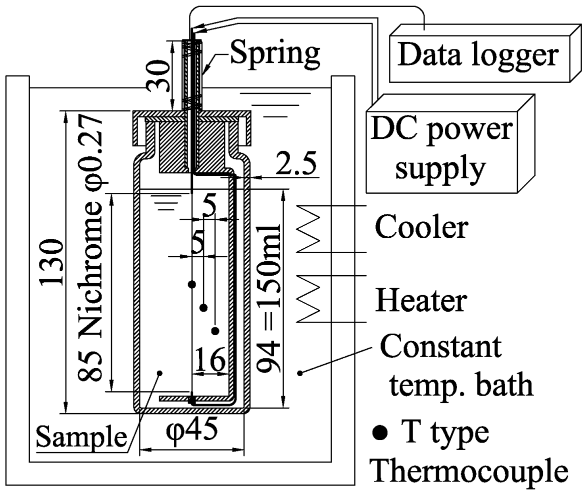


Fig.3 Thermal conductivity measurement apparatus: Transient hot wire method

3. EXPERIMENTAL APPARATUS AND METHOD

Fig.3 shows the schematic diagram of the experimental equipment using the unsteady hot wire method. The devices consisted of a measurement test section, a constant temperature bath, a regulated DC power supply for supplying power to the hot wire, and a data logger for temperature measurement. The measurement sample was filled in test section that is a glass vessel, inner diameter of 45 mm and a height of 130 mm. A nichrome wire (diameter 0.27 mm, length 85 mm, electrical resistance 1.7 Ω) as a heat source wire was installed in the center of the test section. The nichrome wire was always kept straight and vertical during the experiment by the tension of the spring. The temperature is measured by a T-type thermocouple with a wire diameter of 0.1 mm set on the surface of the wire and in the sample. The sample temperature was set by installing a glass vessel in a constant temperature bath. The experiment was started by passing a current of 0.6A through the nichrome wire.

Fig.4 shows the time history of the wire temperature using distilled water as a sample. The temperature rise of the wire was delayed due to the heat capacity of the wire in the range from the start of the experiment to the time t_1. After time t_2, the temperature rise was observed to slow down due to the occurrence of convection in the sample. The range excluding the effects of wire heat capacity and convection is the range of heat flow by heat conduction. The thermal conductivity was calculated by the following equation using the temperature difference of the temperatures θ_1 and θ_2 corresponding to the time t_1 and t_2. In which, q is the generate heat amount per length of wire. The accuracy of the thermal conductivity measuring device was tested using distilled water, and the result was within ± 1.75% of the reference value of water.

$$\lambda = q\frac{\ln(t_2/t_1)}{4\pi(\theta_2 - \theta_1)} \tag{1}$$

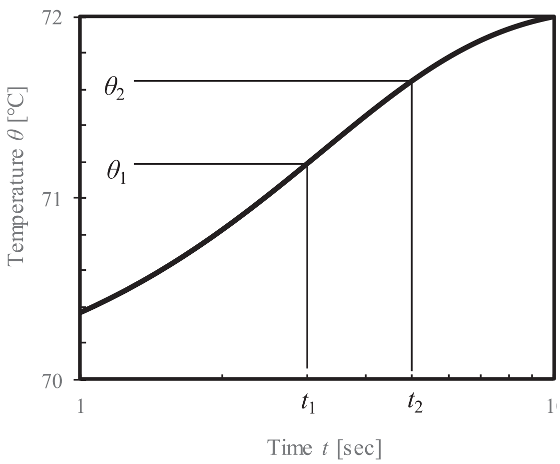
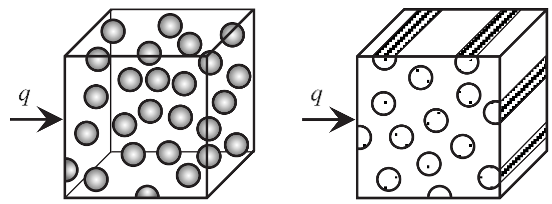


Fig.4 Variation of the wire temperature with time.

Fig.5 shows the distributed layout images of the Maxwell model and the Rayleigh model. The Maxwell model is a theoretical model in which fine spheres were dispersed in continuum phase. The Rayleigh model is a theoretical model in which cylinders were distributed in dispersion medium and heat flows in the direction perpendicular to the axis. In the case of electrical conduction[6)], heat is considered to flows parallel to the axis, but in this paper, the Rayleigh model is used, so the axial direction is not considered. The thermal conductivity of the theoretical model λ_{th} was calculated using the following equation. λ_c and λ_d are the thermal conductivity of the continuous phase and the dispersed phase, respectively. The physical properties of MWCNT as dispersoid were used the manufacturer provided values, the thermal conductivity λ_d = 3000 W/(m・K) and the density ρ_d = 1350 kg/m^3. The volume fraction V_d of the dispersoid was calculated by the following equation using the composition mass ratio φ_d, the dispersed phase density ρ_d, and the continuous phase density ρ_c. x is a value that includes the shape of the dispersed phase substance. The Maxwell model (spherical shape) is x = 2, and the Rayleigh model (cylindrical shape and heat flow to the axis direction) is x = 1.

$$\lambda_{th} = \frac{(x\lambda_c + \lambda_d) - x(\lambda_c - \lambda_d)V_d}{(x\lambda_c + \lambda_d) + (\lambda_c - \lambda_d)V_d}\lambda_c \tag{2}$$

$$V_d = \frac{\varphi_d}{\varphi_d + (100 - \varphi_d)\dfrac{\rho_d}{\rho_c}} \tag{3}$$



Maxwell's model : x =2 Rayleigh's model : x =1

Fig.5 Dispersion image.

4. RESULTS AND DISCUSSION

Fig.6 shows the relationship between thermal conductivity and temperature of the measured and calculated values of MWCNT dispersed water. The experimentally measured values show the average value of the values measured 7 times at each temperature for each sample of MWCNT composition mass ratio. The dotted line in the figure shows the reference value[7)] of water. The absolute value of the experimentally measured thermal conductivity increases with increasing of the mass composition ratio of MWCNT. Dispersion of MWCNT is observed to result in an increase in thermal conductivity. The measurement results show the thermal conductivity raise up to about 10% compared to water at the mass composition ratio of MWCNT 7.00 mass%.

The values calculated by equation of Maxwell's theoretical model are indicated by double solid lines and broken lines. The solid and dashed lines show the values calculated by Rayleigh's theoretical model formula. The calculated values by the Maxwell model, which is a sphere dispersion model, are higher than the experimental values. The difference between calculated values of the Maxwell model and experimental values are -1.925 to + 0.885% (absolute mean deviation 0.007 W/(m·K)) at the mass composition ratio of 1.00 mass%, +2.596 to + 5.072% (Absolute average deviation 0.019W/(m･K)) at the mass composition ratio of 4.30 mass%, +6.836 to +8.731% (absolute average deviation 0.043W/(m･K)) at the mass composition ratio of 7.00 mass% and the overall absolute average deviation is 0.023W/(m･K). The calculated values by Maxwell model are estimated higher value than the experimental values. The differece between calculated values and experimental values are increased with the increasing of mass composition mass ratio of MWCNT.

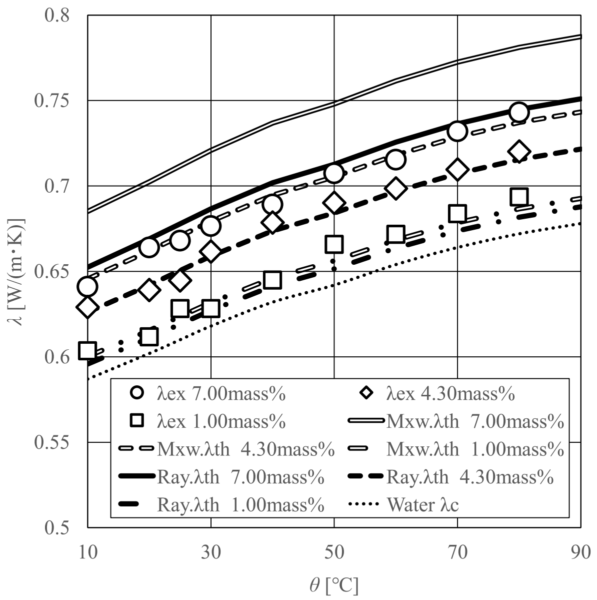


Fig.6 Variation of thermal conductivity with temperature.

The measured thermal conductivity values are in good agreement with the theoretically calculated values by the equation of Rayleigh model of the cylindrical arrangement. It is considered that the slender and long shape ot MWCNTs brings the increasing of the placement ratio of acrossing the heat flux. As a result, it is presumed that Rayleigh's calculated value and experimental value were in good agreement. The agreement between the experimental measured value and the Rayleigh's theoretical value is -2.646 to + 0.143% (absolute mean deviation 0.007 W/(m·K)) at the mass composition ratio of 1.00 mass%, and -0.597 to the measured value at the mass composition ratio of 4.30 mass%. + 1.802% (absolute average deviation 0.004W/(m・K)), + 1.492 to + 3.291% (absolute average deviation 0.008W/(m･K)) at the mass composition ratio of 7.00 mass%, and the overall absolute average deviation 0.006W/(m･K). It is considered effective to apply the Rayleigh model to estimate the thermal conductivity of MWCNT dispersed water.

5. CONCLUSIONS

The actual measurement of thermal conductivity of MWCNT dispersed water by the hot wire method was performed. Furthermore, the optimal dispersed model evaluation was carried by Maxwell and Rayleigh model, and the following conclusions were obtained.

1. It was observed that the measured thermal conductivity increased by up to about 10% from the value of water at the composition mass ratio of MWCNT 7.00 mass%.
2. The estimated thermal conductivity by the equation fo Maxwel's sphere dispersed model is up to 8.7% higher than the measured value (absolute mean deviation 0.023 W/(m·K)).It was suggested the difference between calculated value and experimental value was increased with increasing of the mass composition ratio of WMCNT.
3. . The equation of the heat flow in the radial direction of the cylinder model was shown the good agreement between the calculated value and the measured value by the hot wire method within ± 3.3% (absolute average deviation 0.006 W/(m·K)).It was clarified that Rayleigh model was useful for estimation of the thermal conductivity of the MWCNT dispersed water.

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NOMENCLATURE

q	: calorific value per unit length, W/m
t	: time, sec.
x	: values that include the shape of the dispersoid, -
V_d	: volume fraction of the dispersoid, -
λ	: thermal conductivity, W/(m･K)
ρ	: density, kg/m^3
θ	: temperature, °C
$\Delta\theta$	: temperature difference, K
φ	: mass composition ratio, mass%

Subscripts

1	: at the start
2	: at the end

c : continuous phase
d : dispersoid
sa : anionic surfactant
sn : nonionic surfactant
th : theory

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