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PHYSICAL PROPERTIES OF LATENT HEAT STORAGE MICROCAPSULE – WATER SLURRY

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ABSTRACT This paper has dealt with thermal properties of microcapsule water slurry as a latent heat-storage material having a low melting point. The measured results of the physical properties of the test microcapsule water slurry, that is, thermal conductivity, specific heat, latent heat, and density, were discussed for the temperature region of solid and liquid phases of the dispersion material (paraffin). It was clarified that Eucken's equation could be applied to the estimation of the thermal conductivity of the microcapsule water slurry. Useful correlation equations of the thermal properties for the microcapsule water slurry were proposed in terms of temperature and concentration ratio of the microcapsule water slurry constituents.

Keywords: Thermophysical property, cold heat storage, latent heat, microcapsule slurry, paraffin

1. INTRODUCTION

Recently, much attention has been paid to investigations of the usage of slurry-type latent heat-storage (phase-change material) systems [1]. This type of latent heat-storage system can take the place of the traditional sensible (water) heat-storage system. The benefit of a low-temperature phase-change material (solid-liquid phase) in water is to yield an increase of the amount of the heat transmitted, and to increase the heat-transfer coefficient by the churning effect [2]. There are some dispersion-mixing methods between latent heat-storage material and water, for example, microencapsulation [3] and emulsification. There are few studies of the thermal properties of phase-change microcapsules since this type of phase-change microcapsule has a complex construction. The present study deals with microcapsule (paraffin, freezing point T_m=278.9K, latent heat L=164kJ/kg as the phase-change material) water (continuous phase) slurry as the experimental latent heat-storage material.

The measurements of density, specific heat, latent heat, and thermal conductivity of the microcapsule water slurry have been carried out by using a specific-gravity meter, a water calorimeter, a differential scanning calorimeter (DSC), and a transient hot-wire method [4,5], respectively, in the temperature range over the solid-liquid phase change. Eucken's model was applied to estimate thermal conductivity of the microcapsule water slurry.

2. FEATURE OF TEST MICROCAPSULE WATER SLURRY

Paraffin as a cold latent heat-storage material is an insoluble oil [6]. This type of insoluble oil is dispersed in water by using capsulating, that is, a microencapsulation is used to obtain a homogeneous microcapsule water slurry [8].

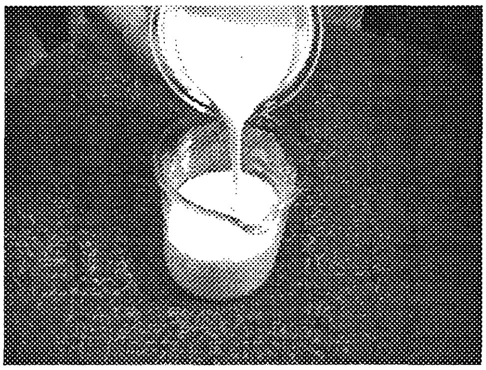

Fig. 1 (a) Appearance of microcapsule water slurry

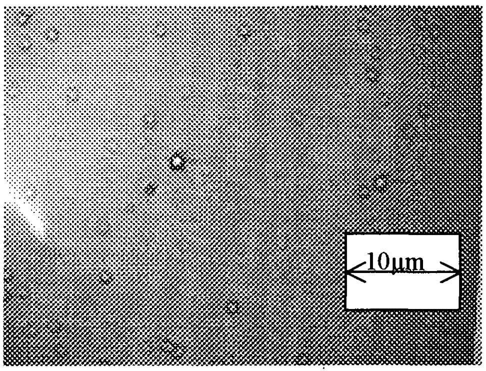

Fig. 1 (b) Microphotograph of microcapsule water slurry

Figure 1(a) shows the external appearance of the test microcapsule water slurry (C_{mi}=40.8wt%). The microcapsule water slurry has a white color and good fluidity. A microphotograph (2000 magnification of microcapsule water slurry) is shown in Fig. 1(b). Figure 1(b) illustrates the homogeneous dispersion of spherical microcapsules in water.

3. ESTIMATION OF DENSITY

A specific-gravity meter method was selected for the measurement of the microcapsule water slurry density. The specific-gravity meter was mounted in the cylinder, which is filled up with the microcapsule water slurry, in order to prevent supercooling of the paraffin as the dispersion phase-change material by stirring. The data below the freezing point of the paraffin was obtained after stirring the microcapsule water slurry in order to avoid the supercooling of the paraffin.

3.1 Measuring Device and Procedures For Density Measurement

Figure 2 shows the experimental apparatus for the microcapsule water slurry measurements. The temperature of the microcapsule water slurry was controlled by the temperature control bath (temperature range of T=253~373K, temperature control accuracy ±0.1 K). The test microcapsule water slurry (170cm^3) filled an acrylic cylinder (inner diameter D_i=30mm, height H=300mm), which was mounted in the temperature control bath. The temperatures of the microcapsule water slurry was measured by T-type thermocouples (0.1mm in diameter), which were located in the acrylic cylinder. The microcapsule water slurry density measurements were carried out at a constant temperature. Test microcapsule water slurry was mixed with the stirrer in the case of the temperature range of below freezing point (T_m=278.9 K) in order to solidify the dispersed paraffin as the phase-change material without the supercooling. The measurement range of the specific-gravity meter was ρ =700~1000[kg/m^3], and the division of its scale is 1[kg/m^3]. The accuracy of the specific-gravity meter becomes within ±0.5 percent.

3.2 Measuring Results and Discussion of Density

The variation of the densities of the microcapsule water slurry ρ_{mi}, paraffin ρ_p, and water ρ_w with temperature T are shown in Fig.3. The density of paraffin (purity 99.99 percent) has almost a constant value (ρ_{pl}=770 kg/m^3) in the liquid phase. The paraffin density in the solid phase of the dispersion material shows a higher value (ρ_{ps}=810 kg/m^3) than the one of the liquid phase.

The dashed line shown in Fig.3 indicate the calculated values of the microcapsule water slurry density by the additional properties law which is defined by the density and constituent of wall material, water, and paraffin as follows:

$$\rho_{mi} = \frac{\rho_{me} \times C_{me} + \rho_w \times C_w + \rho_p \times C_p}{100} \tag{1}$$

The water density ρ_w (from the published water-steam table) [7] and paraffin density ρ_p (measured in the present study) are used for Eq.(1). The density of the wall material is a constant value ρ_{me}=1490 kg/m^3 from the reference [9]. The calculated values of the microcapsule water slurry density from Eq.(1) are almost equal to the measured values within ±1.0 percent (application temperature range is T=273.0 ~ 293.0 K). It is understood that the additional properties law equation can apply to the estimation of the microcapsule water slurry density in both the liquid and solid phases of paraffin as the dispersed phase-change material.

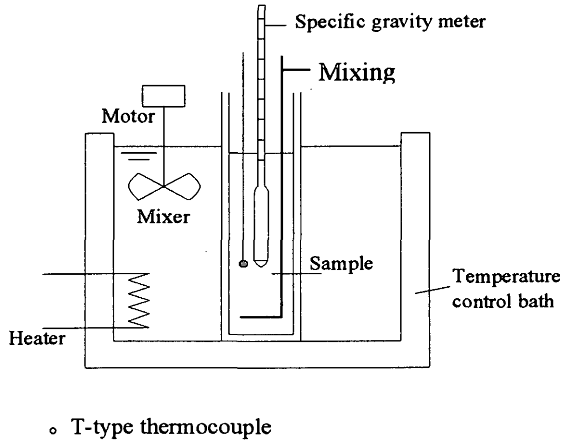

Fig. 2 Schematic diagram for the density measurement by Specific-gravity meter

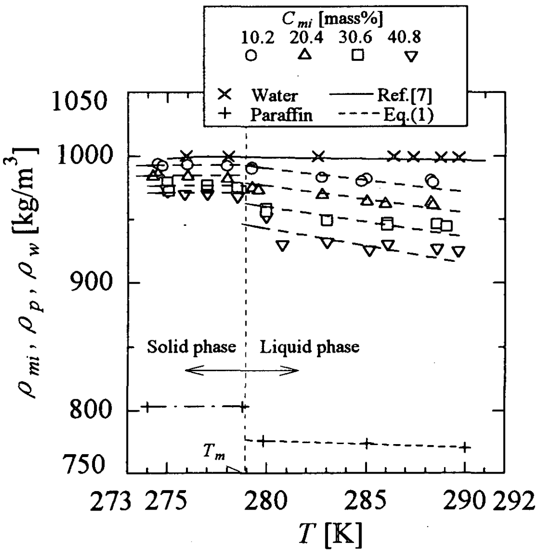

Fig. 3 Relationship between density and temperature

4. ESTIMATION OF SPECIFIC HEAT AND LATENT HEAT

Figure 4 indicates the water calorimeter used for the measurement of specific heat because of the ease of the release of the supercooling condition for the paraffin. The latent heat of the microcapsule water slurry was measured by a differential scanning calorimeter (DSC), which can also measure the melting point of the microcapsule water slurry at the same time.

4.1 Measuring Device and Procedures For Specific Heat and Latent Heat Measurement

The measurement of specific heat of microcapsule water slurry Cp_{mi} was carried out using the water calorimeter as mentioned above. The measuring process was as follows. The temperature of the water (M_w=80g) in the calorimeter (copper vessel M_c=80.96g, mixing rod M_m=12.53g) was controlled by the temperature control bath. Subsequently, the test microcapsule water slurry at a temperature 5.0~6.0 K higher than the initial water temperature in the calorimeter was put into the water calorimeter. The specific heat of the microcapsule water slurry was calculated from the following Eq.(2) which is derived from the heat capacities of water ($M_w \times Cp_w$), copper vessel W_c, mixing rod W_m, and the heat loss Q_l resulting from the temperature difference between the test sample and the environment temperature.

$$Cp_{mi} = \frac{(M_w \times Cp_w + W_c + W_m) \times (T_{fi} - T_{ws}) - Q_l}{M_e \times (T_{es} - T_{fi})} \qquad (2)$$

where, T_{fi} is the equilibrium temperature of the microcapsule water slurry and the water mixture, T_{ws} is the initial temperature of the water in the calorimeter, and Q_l is the heat loss from the water calorimeter. The heat loss Q_l was estimated from the temperature variation of the cold water in the water calorimeter [5]. The accuracy of the mass weight and temperature measurements were within ±0.1 percent and ±0.4 percent, respectively. The ratio of the heat loss Q_l to total heat transfer in the calorimeter was less than 4.0 percent, so that the total accuracy of the water calorimeter is estimated within ±5.0 percent. The data of specific heat of water measured by the present water-calorimeter show good agreement with the reference value [7] within ±5.0 percent.

A differential scanning calorimeter (DSC) was used for the measurement of the latent heat and melting point of paraffin (dispersion phase-change material). The test section of the DSC measurements was mounted into the temperature control bath (capacity 50 × 50 × 50cm, temperature range T=253~298 K, temperature control accuracy ±0.1 K). The test microcapsule water slurry temperature was decreased to 263 K by the temperature control bath, in order to completely freeze the paraffin. After that, the DSC measurement was started when the microcapsule water slurry temperature reached at 274 K in order to melt the water as a continuous phase.

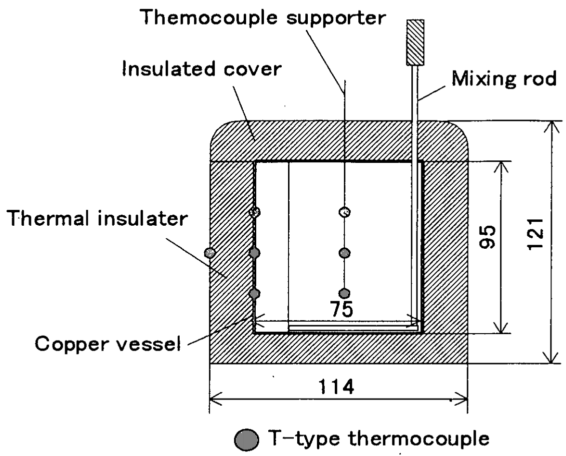

Fig. 4 Cut view of water calorimeter

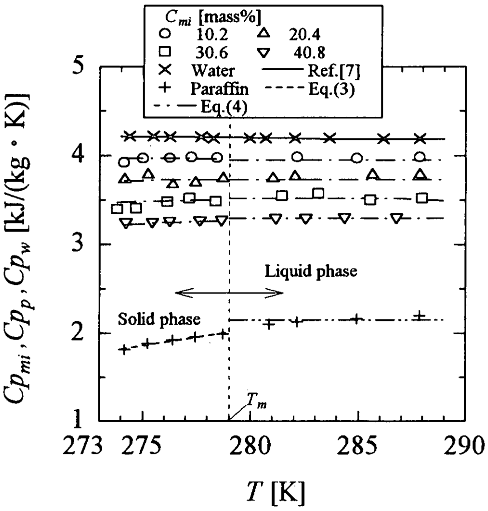

Fig. 5 Relationship between specific heat and temperature

The latent heat measurements of the microcapsule water slurry were performed under the conditions of a heating rate V_h=5.0 K/min, mass of sample M_e=5.0~6.0 mg. The total accuracy of the measurement was estimated to be within ±2.0 percent in consideration of the heat supply of the electric heater, a temperature measurement accuracy of ±0.1 percent and a measurement accuracy of the mass weight of the sample of ±0.5 percent. The latent heat of water and indium (purity 99.99 percent) were measured by the present DSC, and these measured values coincide with the reference values [9] within ±2.0 percent.

4.2 Measuring Results and Discussion of Specific Heat and Latent Heat

Figure 5 shows the relationship between the specific

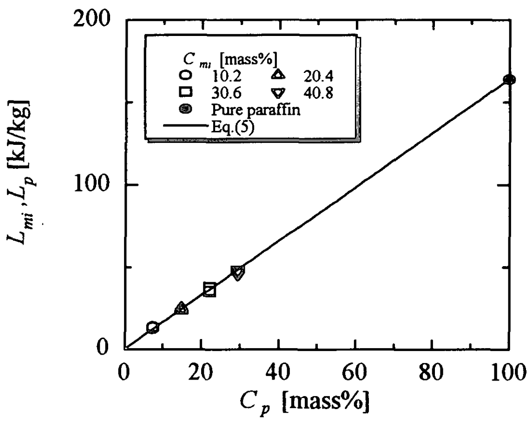

Fig. 6 Relationship between latent heat and concentration of paraffin

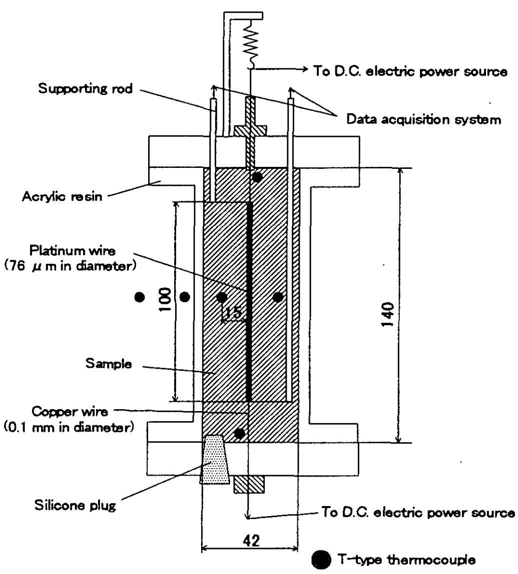

Fig. 7 Cut view of measuring device of thermal conductivity

heat of the microcapsule water slurry Cp_{mi}, water Cp_w, and paraffin Cp_p, and temperature T. The specific heat of the paraffin has almost a constant value Cp_p=1.8 [kJ/kg · K] in the temperature region of the solid phase (T<278.9 K). On the other hand, the specific heat of the paraffin in the liquid phase (T>278. K) increases with temperature T, and its value is larger than in the solid phase (T<278.9 K). The specific heat of the microcapsule water slurry Cp_{mi} shows the difference between the solid and liquid phases (melting point T_m=278.9 K). The specific heat of the microcapsule water slurry in the liquid phase is larger than that in the solid phase. The specific heat of the microcapsule water slurry Cp_{mi} decreases with an increase in paraffin concentration C_p. This tendency of the specific heat of the microcapsule water slurry could be caused by the fact that the specific heat of paraffin Cp_p has the smaller value than that of water Cp_w. The specific heat of the wall material has a constant value Cp_{me}= 1.67 [kJ/(kg · K)] in the temperature range of T=273~293 K [9]. An additional properties equation can be applied to the calculation of the specific heat of the microcapsule water slurry as shown in Eq.(4) by using the reference values of the specific heat of water Cp_w [8], the specific heat value of the paraffin in the solid phase Cp_p=1.8 [kJ/(kg · K)] and the specific heat value in the liquid phase which can be calculated from Eq.(3).

$$Cp_{ps} = -5.85\times10^{-3}T + 3.69 \quad (273\ \mathrm{K} < T < 278.9\ \mathrm{K}) \quad (3)$$

$$Cp_{mi} = \frac{Cp_p C_p + Cp_w C_w + Cp_{me}(100 - C_p - C_w)}{100} \quad (4)$$

The values calculated by Eq. (4) are shown in Fig.5 as one point chain lines. These calculated values agree with the measurement values within ±4.0 percent, so that the additive property law is applicable to apply for the estimation of the specific heat of the microcapsule water slurry. Fig.6 shows the measurement values of the latent heat of the microcapsule water slurry and the calculated values from Eq.(5) which is expressed by the mass weight ratio of the paraffin to the microcapsule water slurry and the latent heat of the paraffin. The measured latent

$$L_{mi} = \frac{C_p}{100}\times L_p \quad (5)$$

heat of the microcapsule water slurry is consistent with the calculated one L_{mi} from Eq.(5) within ±3 percent. It is clarified that the latent heat of the microcapsule water slurry is proportional to the mass weight ratio of the paraffin to the microcapsule water slurry. The measured melting point T_m of the paraffin as a dispersion material coincides with proposed value [9] within ±2 percent considering the standard deviation.

5. ESTIMATION OF THERMAL CONDUCTIVITY

A transient hot-wire method, by using an electrically insulated platinum wire [5,6], was used for the thermal conductivity measurement for the microcapsule water slurry, because (1) the test emulsion is an electrolyte, (2) the transient hot-wire method enables us to measure the thermal conductivity of the microcapsule water slurry even if the paraffin changes phase (solid and liquid phase) and (3) this transient method can be used to measure the thermal conductivity in the required temperature range without natural convection induced from the temperature increase of the hot wire.

5.1 Measuring Device and Procedures For Thermal

Conductivity Measurements

The device consists of an acrylic cylinder (inner diameter D_i=42mm, height H=140mm, 3.5mm in thickness) and a platinum wire as the hot wire (purity 99.99 percent, wire diameter 76 μ m, length l=100mm), which is located in the center of the acrylic resin cylinder. The platinum wire was coated with Teflon (17 μ m in thickness) in order to eliminate any electric current leakage to the test sample. Both ends of the platinum wire are supported by enameled copper wires (0.1mm in diameter). The thermal expansion of the platinum wire is absorbed by the tension of the spring which is mounted on top of the acrylic resin cylinder. The electric insulation of the soldered joint between the platinum and copper wire was made by using acrylic paint. The relationship between the electric resistance of the platinum wire and temperature was calibrated by a standard thermometer and a precision electric-resistance measuring instrument, in the temperature range of T=273~313 K. The temperature increase of the hot wire was controlled within ΔT=1.0 K. The temperature difference between the upside and downside of the test sample in the wire direction was measured by the T-type thermocouples, and the temperature difference was controlled within 0.1 K. The thermocouples were calibrated by a standard thermometer, so that the accuracy of the thermocouples was ±0.05 K.

The measurement began by impressing an electric voltage to the hot wire after the temperature of the test sample layer reached a given temperature, which was controlled by a temperature control bath. The thermal conductivity was calculated from the following Eq.(6) [4,5] by using the temperature increase ΔT and the elapsed times t_1,t_2.

$$\lambda = q \times \frac{\ln(t_2/t_1)}{4\pi\Delta T} \qquad (6)$$

The total accuracy of the device was estimated to be ±2.5 percent, by considering the Teflon coating effect on the hot-wire temperature rise, the measuring accuracy of the electric voltage and the wire length, etc. An experimental check of the device's accuracy was carried out by using pure water. The results of the water coincide with the reference values [8] within ±2.5 percent.

5.2 Measuring Results and Discussion of Thermal Conductivity

The surfactant forms the melamine in the water solution, and it makes a wall around the dispersed paraffin in the microcapsule water slurry. At the beginning, the thermal conductivity of the spherical surfactant construction is complex in the test microcapsule water slurry. The thermal conductivity of the microcapsule water

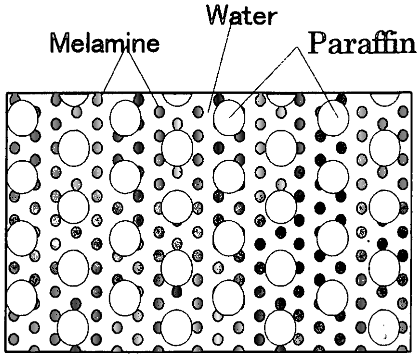

Fig. 8 Eucken's dispersion model

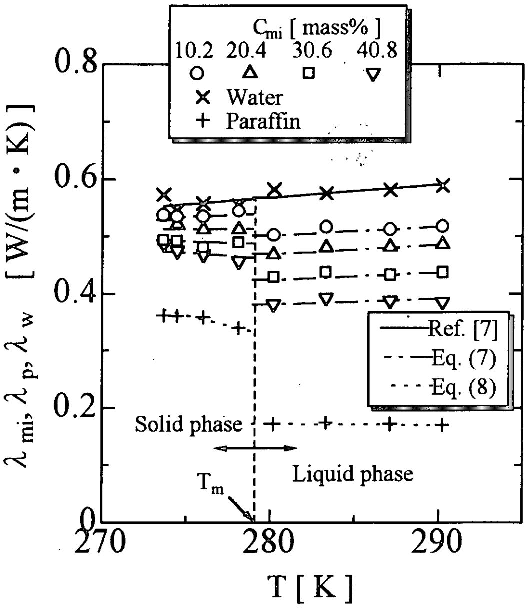

Fig. 9 Relationship between thermal conductivity and temperature

slurry was estimated by using the measured results of the two phase (melamine and water). Eucken's dispersion model [10] was then applied to estimate the thermal conductivity of the test microcapsule water slurry. An estimation of the thermal conductivity of the microcapsule water slurry is very difficult because the paraffin (phase-change material) is dispersed in the water and coated with the wall material. In this study, the spherical paraffin dispersed in water was assumed for the thermal conductivity model of the microcapsule water slurry, as shown in Fig.8. The thermal conductivity of the assumed microcapsule water slurry model (Eucken's model) was calculated by using thermal conductivity of water, paraffin, and microcapsule water slurry as follows:

$$\lambda_{mi} = \lambda_w \frac{1 - 2[\phi \dfrac{\lambda_w - \lambda_p}{2\lambda_w + \lambda_p} + (\varphi - \phi)\dfrac{\lambda_w - \lambda_{me}}{2\lambda_w + \lambda_{me}}]}{1 + [\phi \dfrac{\lambda_w - \lambda_p}{2\lambda_w + \lambda_p} + (\varphi - \phi)\dfrac{\lambda_w - \lambda_{me}}{2\lambda_w + \lambda_{me}}]} \qquad (7)$$

where, the thermal conductivity of the paraffin is calculated from Eq. (8). The calculated values in the solid phases are shown in Fig.9 as the doted lines.

$$\lambda_p = -9.03\times10^{-6}T^2 - 2.2\times10^{-3}T + 1.65$$

$$(273\ \mathrm{K} < T < 278.9\ \mathrm{K}) \qquad (8)$$

Figure 9 presents the variation of the thermal conductivity of the test microcapsule water slurry λ_{mi}, water λ_w, and paraffin λ_p with temperature T. The one point chain lines indicate the calculated values from Eq.(7). The thermal conductivity of the paraffin is plotted in Fig.8 as the plus. The thermal conductivity of the paraffin decreases with an increase in temperature in the solid phase. On the other hand, the thermal conductivity of paraffin in the liquid phase has an almost constant value. The thermal conductivity of the water becomes larger than that of the paraffin, and it increases slightly with temperature.

The thermal conductivity of the microcapsule water slurry shows a different behavior below and above the freezing point. The thermal conductivity of the microcapsule water slurry decreases with increasing paraffin concentration. The thermal conductivity for a low paraffin concentration is dependent on the thermal conductivity of water. The temperature dependence of the thermal conductivity of the microcapsule water slurry shows a decreasing tendency with an increase in the paraffin concentration. The calculated values from Eq.(7) are consistent with the measured results within ±0.9 percent. Therefore Eucken's dispersion model can be applied to the estimation of the thermal conductivity of this type microcapsule water slurry.

6. CONCLUSION

Measurements of thermal properties of a microcapsule water slurry have been performed which included the dispersed phase-change (latent heat-storage) material. The following conclusions were obtained.

(1) Measurements of the microcapsule water slurry density were carried out by using a specific-gravity meter. It was determined that an appropriate property law could be applied to estimate the microcapsule water slurry density with paraffin (dispersion phase), water (continuum phase), and melamine density.

(2) The specific heat of the microcapsule water slurry was measured by the water-calorimeter. The specific heat of the microcapsule water slurry could also be estimated using the property law mentioned above.

(3) A transient hot-wire method was used for the measurement of the thermal conductivity of the microcapsule water slurry in the solid and liquid phases of the dispersion material. It was clarified that a modified Eucken model could be applied to the estimation of the thermal conductivity of the microcapsule water slurry.

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NOMENCLATURE

C : mass concentration [wt%]
Cp : specific heat [kJ/(kg・K)]
D : diameter [mm]
H : height [mm]
L : latent heat [kJ/kg]
M : mass [g]
T : temperature [K]
t : time [sec]
q : heat flux of hot wire per length [W/m^2]

Greek Symbols
Δ : difference
λ : thermal conductivity [W/(m・K)]
ρ : density [kg/m^3]
ϕ : volume concentration of paraffin
ϕ : total volume concentration of paraffin and water

Subscripts
m : melting point
me : melamine resin
mi : microcapsule
p : paraffin
ps : solid phase of paraffin
pl : liquid phase of paraffin