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Thermal Properties of a Supercooled Synthetic Sand–Water–Gas– Methane Hydrate Sample

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S Supporting Information

ABSTRACT: Understanding the thermal properties of methane hydrate (MH)-bearing sediments is important to develop future energy resources. Thus, in this study, we measured the thermal properties of synthetic hydrate-bearing sediment samples comprising sand, water, methane, and MH using the hot-disk transient plane source technique. The melting heat of MH possibly affects the measurements; thus, the experiments were performed at supercooled conditions during MH formation in the sediment pores. The results show that thermal conductivity and diffusivity of the samples slightly increased as hydrate saturation increased from 0 to 0.3. We also performed thermal conductivity calculations using simple thermophysical models. The distribution model (geometric mean model) shows a relatively good agreement with the experimental data; however, it underestimates the thermal conductivity of the four-component sample. Thus, better prediction models are required to accurately determine the thermal properties of four-component systems.

1. INTRODUCTION

Gas hydrates consist of a network of hydrogen-bonded water molecules containing guest molecules in cavities.¹ Large amounts of methane hydrates (MHs) are known to exist in sediment layers under the sea floor and in permafrost regions on land.² To develop future energy resources, understanding the physical properties of MH-bearing sediments while minimizing the geohazard potential and carbon contributions to global climate is important.^{2–5}

In March 2013, Japan Oil, Gas, and Metals National Corporation performed the first gas production test on MHbearing sediment layers in the Nankai Trough by depressurizing the MH-bearing sediments. To evaluate the economics of gas hydrate production, understanding the thermal properties, such as thermal conductivity, heat capacity, and heat of dissociation of gas-hydrate-bearing sediments is critical.

Konno et al.⁸ studied the performance of depressurizationinduced gas production from MH deposits using the Nankai Trough MH reservoir model. For accurate gas production prediction using the MH reservoir model, it is important to determine accurate thermal properties of the hydrate-bearing sediment.

Waite et al.⁴ reviewed studies that dealt with the thermal properties of gas-hydrate-bearing sediments. Few studies have measured the thermal conductivity^{7,8} or other thermal properties⁹ of pure MH. The thermal conductivity^{10,11} and diffusivity¹² of synthetic MH-bearing sediments comprising sand, methane, and MH have been measured. Huang and Fan¹¹ and Cortes et al.¹³ measured the thermal conductivity of tetrahydrofuran hydrate-saturated sediment. Kim and Yun¹⁴ measured the thermal conductivity of synthetic MH-bearing sediments saturated with MH and brine under the vertical effective stress. Henninges et al.¹⁵ indirectly estimated the *in situ* thermal conductivity of hydrate-bearing sediments in

permafrost and suggested that the geometric mean model is suitable for estimating the thermal conductivity of MH-bearing sediments.

Muraoka et al.¹⁶ measured natural hydrate-bearing sediment cores recovered from Nankai Trough wells. They tested simple thermophysical models and concluded that the distribution model (geometric mean model) is suitable for estimating the thermal conductivity of hydrate-bearing sediments comprising sand, water, and MH. They also concluded that the thermal diffusivity, estimated by dividing the thermal conductivity obtained from the distribution model by the specific heat obtained from the arithmetic mean model, could be used to estimate the thermal diffusivity of hydrate-bearing sediments.

The above-mentioned studies report the effective thermal conductivity of three-component samples (sand-gas-MH or sand-water-MH). However, during gas production, the number of components in gas-hydrate-bearing sediments changes from three (sand, water, and MH) to four (sand, water, MH, and gas) because MH dissociates to water and methane. The thermal conductivity of gas is much lower than that of the other components (sand, water, and MH). Hence, the thermal properties of hydrate-bearing sediments could be significantly affected by MH dissociation.

During gas production, water and gas flow toward the production well. The behavior and morphology of MH in the sediment during gas production is not sufficiently clarified. Thus, clarifying the relative contribution of heat transport gains from the thermal conductivity of each component and heat transfer by fluids is important. However, at this stage, we thought that the measurement of the thermal properties of an

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Figure 1. Schematic of the experimental setup.

artificial four-component (sand, water, MH, and gas) closed system is important.

In this study, the thermal properties of synthetic MH-bearing sediment samples comprising sand, water, methane, and MH were measured using the hot-disk transient method, and these samples were supercooled to minimize the effect of the heat of fusion of MH. In addition, we used a large multiprobe cell to understand the dependence of the thermal properties upon the local conditions within the cell. The hot-disk method enables us to simultaneously measure thermal conductivity, thermal diffusivity, and specific heat. Then, the thermal conductivities of synthetic samples were calculated using simple thermophysical models, similar to the models used by Henninges et al.¹⁶ and Muraoka et al.¹⁶ to evaluate the experimental data for four-component hydrate-bearing sediment specimens.

2. EXPERIMENTAL SECTION

2.1. Experimental Apparatus. Figure 1 shows the experimental setup, which consists of a high-pressure vessel, a thermal properties analyzer, temperature and pressure control units, and a gas cylinder. The thermal properties of the samples were measured using a hot-disk thermal probe (sensor design 7577, with a sensor radius of 2.001 mm, Hot Disk AB Co., Sweden; the sensor is shown in Figure S1 of the Supporting Information) and a hot-disk thermal properties analyzer (TPS 2500, Hot Disk AB Co., Sweden). The hot-disk sensor is connected to the hot-disk thermal properties analyzer as shown in Figure S2 of the Supporting Information. The principle of the hot-disk transient method is described by Gustafsson.¹⁷ The inner parts of the lid and the bottom of the high-pressure vessel have a circulation channel for cooling water. The cooling water is circulated from the chiller to the channel at the bottom of the vessel, then to the channel at the lid of the vessel, and finally to the chiller. The temperature in the vessel is measured by a sheath-type platinum resistance temperature detector (Pt100), as shown in Figure S3 of the Supporting Information. The pressure is measured using a pressure gage (PG-200 KU, Kyowa Electronic Instruments).

Figure 2 shows the layout of the hot-disk probe. Nine hot-disk probes were arranged inside the pressure vessel. The upper panel shows the top view, and the lower panel shows the horizontal view. The filled circles mark the positions of the hot-disk sensor probes in the vessel. The hot-disk sensors were numbered from 1 to 9, as shown in Figures 1 and 2. Each hot-disk sensor probe is fixed on a stainless-steel plate, and the horizontal plane faces the vertical (gravitational) direction, as shown in Figure S3 of the Supporting Information. The fixed stainless-steel plate around the sensor probe is circularly bored to



Figure 2. Layout of the hot-disk probes in the pressure vessel.

make contact with the sensor probe and test specimen and to prevent heat conduction from the probes to the plates during the measurements, as shown in Figure S1b of the Supporting Information. Preliminary experiments using a standard specimen (silicon rubber plate, R2-2, Kyoto Electronics Manufacturing Co., Ltd.) confirmed that the fixed stainless-steel plates around the sensor do not affect the measurements. Preliminary measurements with the nine hot-disk sensors inside the high-pressure vessel were performed using sensor probes sandwiched in the silicon rubber plates.

2.2. Sample Preparation. Sand specimens were placed in the high-pressure vessel (cylindrical stainless-steel cell, with an internal diameter of 140 mm and a height of 140 mm). The inner volume of the vessel with the dead volume removed is 2110 cm³. Toyoura

standard test sand was used (Iwamoto Kousan Co., Ltd.). The mean diameter d_{50} of the sand is 234 μ m, which was determined by laser diffraction scattering analysis (Microtrac MT3000II Nikkiso Co., Japan). The mean diameter of the Toyoura standard test sand is slightly larger than that of the sand grains of the MH-bearing sandy layer in the Nankai Trough.^{16,18} Toyoura sand consists of quartz (92.6%), and its density ρ_s according to the manufacturer is 2630 kg m⁻³. Sand specimens were prepared by pouring water in the cell and then pouring the sand particles at a constant rate using a funnel held near the water surface, as shown in Figure S5a of the Supporting Information. The stainless-steel cell was vibrated to achieve uniform packing; then the vibration was stopped; and the excess pore water was removed when the sand reached a height of 140 mm, as shown in Figure S5b of the Supporting Information. Finally, the cell was covered with a stainless-steel lid, as shown in Figure S6a of the Supporting Information.

We formed MH directly in the high-pressure vessel by injecting methane into the vessel. Methane injection continued until no excess water was observed to discharge into the trap (Figure 1). Then, the pore methane pressure in the vessel was raised to approximately 12.1 MPa at room temperature (31.6 °C). The coolant circulated from the bottom to the lid of the vessel to control the temperature. Hence, the bottom portion was cooled relatively faster than the middle and top of the test specimen. Finally, to form MH, the vessel was cooled to 2.0 °C. During the experiments, the pressure and temperature in the vessel were recorded continuously. The mass of Toyoura sand and water were 3385 and 360.6 g, respectively, and the initial specimen porosity ψ was 0.39. The specimen porosity was determined by the formula 1 – $V_{\text{sand}}/V_{\text{cell}}$, where V_{sand} is the volume of the sand determined by the inner volume of the vessel.

On the basis of the grain size (medium or fine sand), the hydrate morphology is of the disseminated type, $^{19-21}$ which is the same as in the MH-bearing sediments of the Nankai Trough.^{22,23}

2.3. Thermophysical Models for Estimating Thermal Properties. We used simple thermophysical models to evaluate the experimental data in the four-component hydrate-bearing sediment specimens. The series model is based on the harmonic mean and yields minimum values. The parallel model is given by the arithmetic mean and produces maximum values. The distribution model is based on the geometric mean and yields intermediate values between the other two models. The effective properties of a random combination of components can be estimated using the geometric mean model, which was empirically derived for a two-component system (water and sand).²⁴ Subsequently, the model was expanded and used for estimating the properties of hydrate-bearing sediments.^{15,16} In this study, to estimate the thermal properties of the specimens, we used the model equations as follows:

series model

$$\lambda = \frac{1}{\frac{S_{h}\psi}{\lambda_{h}} + \frac{S_{w}\psi}{\lambda_{w}} + \frac{S_{g}\psi}{\lambda_{g}} + \frac{(1-\psi)}{\lambda_{s}}}$$
(1)

parallel model

$$\lambda = S_{\rm h}\psi\lambda_{\rm h} + S_{\rm w}\psi\lambda_{\rm w} + S_{\rm g}\psi\lambda_{\rm g} + (1-\psi)\lambda_{\rm s} \tag{2}$$

distribution model

$$\lambda = \lambda_{\rm h}^{S_{\rm h}\psi} \lambda_{\rm w}^{S_{\rm w}\psi} \lambda_{\rm g}^{S_{\rm g}\psi} \lambda_{\rm s}^{1-\psi} \tag{3}$$

In the above equations, λ is the effective thermal conductivity and $\lambda_{\rm h\nu}$, $\lambda_{\rm g\nu}$, and $\lambda_{\rm s}$ are the thermal conductivities of MH, water, methane, and sand, respectively. The specimen porosity is represented by ψ . $S_{\rm h\nu}$, $S_{\rm g\nu}$, and $S_{\rm g}$ represent the MH, water, and methane saturation, respectively, and $S_{\rm h} + S_{\rm w} + S_{\rm g} = 1$.

The specific heat ρC_p may be closely approximated as^{24,25}

$$\rho C_{\rm p} = (S_{\rm h}\psi)\rho_{\rm h}C_{\rm ph} + (S_{\rm w}\psi)\rho_{\rm w}C_{\rm pw} + (S_{\rm g}\psi)\rho_{\rm g}C_{\rm vg} + (1-\psi)\rho_{\rm s}$$

$$C_{\rm ps}$$
(4)

where $\rho_{\rm h}$, $\rho_{\rm w}$, $\rho_{g'}$ and $\rho_{\rm s}$ are the densities of MH, water, methane, and sand, respectively. $C_{\rm ph'}$, $C_{\rm yw}$, $C_{\rm vg}$, and $C_{\rm ps}$ are the specific heats of MH, water, methane, and sand, respectively.

The thermal diffusivity α is given by

$$\alpha = \frac{\lambda}{\rho C_{\rm p}} \tag{5}$$

Goto and Matsubayashi²⁵ proposed the estimation of the thermal diffusivity of marine sediments using eq 5, the distribution model for λ , and the arithmetic mean model for ρC_{p} .

3. RESULTS

3.1. Thermal Properties versus Time. Figure 3 shows the pressure, temperature, and degree of supercooling of MH



Figure 3. (a) Pressure, temperature, and degree of supercooling in the pressure vessel as a function of time. (b) Saturation of methane hydrate, water, and methane as a function of time.

(Figure 3a) as well as the saturation of MH, water, and methane as a function of time (Figure 3b). The initial time *t* corresponds to the initialization of coolant circulation in the cooling jackets. The degree of supercooling ΔT is calculated with the function

$$\Delta T = T_{\rm eq}(P) - T \tag{6}$$

 $T_{eq}(P)$ is the equilibrium temperature of MH as a function of pressure *P*. $T_{eq}(P)$ is calculated using the CSMGem software of Slone et al.¹

Figure 3a shows that the temperature decreased from 31.6 to 2 °C during the experiments. Temperature *T* decreased from 31.6 to 2.5 °C as time *t* changed from 0 to 500 min. After t = 500 min, the temperature *T* gradually decreased and

approached the coolant temperature (2 °C). Pressure P decreased from 12.1 to 3.2 MPa during the experiments. From t = 0 to 170 min, the pore methane pressure decreased gradually from 12.1 to 10.7 MPa because the gas volume decreased with a decreasing temperature. After t = 170 min, significant pressure change was observed because of MH nucleation and methane consumption. Then, pressure P decreased and approached 3.2 MPa, which corresponds to equilibrium conditions for MH at T = 2 °C. The degree of supercooling ΔT was lower than 0 °C up to t = 140 min. Afterward, ΔT was greater than 0 °C and reached the maximum value $\Delta T = 9.3$ °C at t = 380 min. Subsequently, ΔT decreased gradually and reached 0 °C at t = 2500 min because pressure and temperature converged toward the equilibrium conditions. The double-headed arrows show the range of $\Delta T \ge 2$ °C. To minimize the effect of the melting heat of MH on the measurements, we measured the thermal properties within 150-2200 min by keeping the temperature increase of the hot-disk sensor below 2 °C.

From 150 to 300 min, the average temperature change rate is -0.0011 °C s⁻¹. The thermal drift did not affect the measurement of the thermal properties because the temperature increase of the hot-disk sensor is between 1 and 1.5 °C and the data are collected within 5 s. After 300 min, the effect of the temperature drift is negligible because the average temperature change rate is very small.

Figure 3b shows the degree of saturation for MH, water, and gas in the specimen as a function of time t. Each degree of saturation was calculated using the equation of state of the gas. The initial conditions are as described in section 2.2, and the temperature and pressure conditions are as shown in Figure 3a. The calculation details are described by Sakamoto et al.²⁶ The degrees of saturation S_h for MH, S_w for water, and S_g for gas were constant up to t = 170 min. After t = 170 min, the MH nucleation began and $S_{\rm h}$ increased drastically from 0 to 0.1 up to t = 300 min. Simultaneously, with the formation of MH, S_w decreased from 0.43 to 0.36 and S_g decreased from 0.56 to 0.54. For t = 300-2500 min, S_h increased gradually from 0.10 to 0.32, $S_{\rm w}$ decreased gradually from 0.36 to 0.18, and $S_{\rm g}$ decreased gradually from 0.54 to 0.50. After t = 2500 min, each saturation converged to a constant value. The effect of the heat of formation of MH on thermal property measurements is discussed below.

3.2. Measurement of Thermal Properties. Figure 4 shows the thermal conductivity λ as a function of the MH saturation S_h . As shown in Figure 3b, the latter increases with time *t*. The plotted data show an overlap within the range $S_h = 0.07-0.18$. For clarity, the plotted data represent the average of three measurements from the same sensor within this range. The solid line in the middle represents the best fit to all data. Thermal conductivity λ fluctuates for $S_h = 0-0.1$, but this is not attributed to the averaging. For $S_h = 0.1-0.3$, the thermal conductivity slightly increased. The calculation results using the series, parallel, and distribution models are shown in Figure 4. Details of the calculations are described in the Discussion.

Figure 5 shows the specific heat ρC_p as a function of the MH saturation S_h . For $S_h = 0.07-0.18$, the data represent averages of three measurements for the same sensor. The specific heat ρC_p fluctuates between $S_h = 0$ and 0.1 and is nearly constant between $S_h = 0.1$ and 0.3. The lower solid line represents the best fit to all data for all sensors. The upper line was calculated with the arithmetic mean model using eq 4. Calculation details are also described in the Discussion.



Figure 4. Thermal conductivity λ as a function of the MH saturation and thermal conductivity model estimates.



Figure 5. Specific heat ρC_p as a function of the MH saturation and the arithmetic mean model estimates.

Figure 6 shows the measured thermal diffusivity α as a function of the MH saturation $S_{\rm h}$. For $S_{\rm h} = 0.07-0.18$, the plotted data represent averages of three measurements from the same sensor. The average value line is the best fit to all data from all sensors. Thermal diffusivity α fluctuated for $S_{\rm h} = 0-0.1$ and then slightly increased for $S_{\rm h} = 0.1-0.3$. The thermal diffusivity was estimated using eq 5. Details are given in the Discussion.

4. DISCUSSION

4.1. Effect of the Formation Heat of MH on the Thermal Measurements. The formation heat of MH was estimated from S_h with time t, as shown in Figure 3b. We used an enthalpy of formation H = 52.9 kJ mol⁻¹ for MH.²⁷ The heat capacity of the entire sample was estimated using the volume fractions of each component (sand, water, MH, and gas) based on the initial conditions and Figure 3b. Because of the formation heat, the temperature change rate of the sample ΔR_H was sufficiently smaller than the temperature increase during



Figure 6. Thermal diffusivity α as a function of the MH saturation and estimates using the thermal conductivity models.

the measurements. The average $\Delta R_{\rm H}$ was 0.0010 °C s⁻¹ from t = 170 to 300 min. The formation rate of MH peaked in this period. After t = 300 min and between t = 300 and 2500 min, $\Delta R_{\rm H}$ was 0.000 15 °C s⁻¹. The effect of the formation heat of MH on the thermal constants was apparently very small because the temperature increase of the hot-disk sensor during the measurements was between 1 and 1.5 °C and the measurement interval was 5 s. The reason for the low formation rate of MH is as follows: After MH nucleation, a thin gas hydrate film preferentially forms on the water-gas interface because the solubility of methane in water is extremely low. Thus, the continuous formation of gas hydrate was prevented because the film does not allow for contact between water and gas.²⁸⁻³⁰ The gas hydrate can form dissolved gas with a concentration smaller than that when gas bubbles are present.³¹ However, the solubility of methane in water is much lower than the gas concentration in the hydrate. The hydrate formation stops once the dissolved gas in water is depleted. As a result, the gas diffusion in the hydrate is very slow. The supercooling method is clearly very helpful in determining the thermal properties of the gas hydrate-water-guest gas system because the characteristic low formation rate of the gas hydrate is not unique for MH.

4.2. Thermal Property Estimations. The calculation results using the thermophysical models given by eqs 1, 2, and 3 are shown in Figure 4. In the calculations, we used $\lambda_h = 0.619$,⁹ $\lambda_w = 0.565 \text{ W m}^{-1} \text{ K}^{-1}$ (NIST Chemistry WebBook, Gaithersburg, MD), and a variable λ_g that decreased from 0.049 to 0.034 W m⁻¹ K⁻¹ as the pressure decreased from 12.1 to 3.2 MPa (NIST Chemistry WebBook, Gaithersburg, MD). In the preliminary experiments, the thermal conductivity of Toyoura sand λ_s was determined from the thermal conductivity measurements of the sand and water mixture (two-component system). Sand-water specimens were similarly prepared by following the procedure reported in section 2.2. The specimen porosity was determined using the density and mass of sand and water. Then, the thermal conductivity λ was measured, and the measurements from all sensors were averaged. Finally, the value $\lambda_s = 5.93 \text{ W m}^{-1} \text{ K}^{-1}$ was estimated using the distribution model formula

$$\lambda_{\rm s} = \exp\left(\frac{\ln\lambda - \psi \ln\lambda_{\rm w}}{(1-\psi)}\right) \tag{7}$$

In addition, we used the saturation $S_{\rm h}$ for MH, $S_{\rm w}$ for water, and $S_{\rm g}$ for gas, which were obtained from Figure 3b. Considering the effect of local conditions on the measurements, the calculations were performed using the distribution model. We assumed that $S_{\rm g} = 0$ and $S_{\rm w} = 1 - S_{\rm h}$. Most of the pore space in the sand was saturated with water. This is shown by the upper line, which represents the distribution model, in Figure 4.

The distribution model agrees with the lowest values, which were measured by sensor 5. On the other hand, the distribution model for water-saturated conditions agrees with the highest values, which were measured by sensor 1. The results suggest that the water distribution in the vessel was not uniform. The spatial variability of the measured thermal constants is as follows: the proving depth was approximately 4 mm, and the radius of the hot-disk sensor probe was 2 mm. The local water saturation around the sensors that record high thermal conductivity may be higher than that of the sensors that record low thermal conductivity.

The distribution model underestimates the thermal conductivity of the sand-water-MH-gas sample by approximately 30% relative to the average, possibly owing to the low thermal conductivity of methane. In contrast, the results of Henninges et al.¹⁵ and Muraoka et al.¹⁶ suggest that the distribution model (geometric mean model) is consistent with the thermal conductivity measurements of three-component hydrate-bearing sediment samples (sand-water-MH). Woodside and Messmer²⁴ performed experiments on a twocomponent system (solid and fluid phases) and showed that the distribution model (geometric mean model) could not reproduce the effective thermal conductivity when λ_s/λ_f exceeded 20, where λ_s and λ_f are the thermal conductivities of the solid and fluid phases, respectively. In this study, the values of λ_s/λ_f are $\lambda_s/\lambda_w \approx 10$, $\lambda_s/\lambda_h \approx 10$, and $\lambda_s/\lambda_g \approx$ 120-180. The four-component hydrate-bearing sediment sample consists of components with large differences in thermal conductivity. The gas phase complicates the thermal conductivity analysis. Therefore, studies to improve the thermal conductivity mixing model for the four-component (sand, water, MH, and gas) system are currently under way.

Figure 5 shows the specific heat ρC_p as a function of the MH saturation S_h . The upper line was calculated with the arithmetic mean model using eq 4 and $\rho_h = 915.2$ kg m⁻³. The density of MH was calculated using the formula E.S.2.1 by Slone et al.,¹ a unit cell edge length of 12 Å,¹ and small and large cavity occupancies of 0.91 and 0.98, respectively (CSMGem). In the calculation of ρC_p , we used $C_{ph} = 2172$ J kg⁻¹ K⁻¹,⁹ $\rho_w = 1001$ kg m⁻³, $C_{pw} = 4200$ J kg⁻¹ K⁻¹ (NIST Chemistry WebBook, Gaithersburg, MD), $\rho_s = 2630$ kg m⁻³, and $C_{ps} = 689$ J kg⁻¹ K⁻¹. In the preliminary experiments, the specific heat C_{ps} of Toyoura sand was established using differential scanning calorimetry (DSC-204, Netzsch Co., Germany). We varied $\rho_g C_{vgy}$ which decreased from 0.20 to 0.042 MJ m⁻³ K⁻¹ as pressure decreased from 12.1 to 3.2 MPa (NIST Chemistry WebBook, Gaithersburg, MD).

The spatial variability of the measured ρC_p is possibly owing to the bias introduced by the local water saturation because the ρC_p of water is the highest at 4.205 MJ m⁻³ K⁻¹. The local water saturation around the sensors that record high ρC_p may be higher than that of the sensors that record low ρC_p . This is consistent with the above-mentioned thermal conductivity results. As shown in Figures 4 and 5, sensor 1 recorded the highest λ and $\rho C_{\rm p}$ values, whereas sensor 5 recorded the lowest λ and $\rho C_{\rm p}$ values. Both trends suggest that water saturation was high around the sensors that recorded the highest values and low around those that recorded the lowest values. The arithmetic mean model may accurately reproduce the $\rho C_{\rm p}$ of the four-component system when the volume fraction of each component around the sensors is accurately determined. For these reasons, a method directly or indirectly to obtain the volume fractions of each component in the experiment cell is required.

Figure 6 shows the thermal diffusivity α as a function of the MH saturation S_h . The thermal diffusivity is estimated using eq 5. λ was obtained from the corresponding model, as shown in Figure 4, while ρC_p was calculated using the arithmetic function, as shown in Figure 5. The distribution model underestimates α , probably because α is calculated from the underestimated λ and overestimated ρC_p . To accurately estimate α , a suitable thermal conductivity model for the four-component system (sand, water, MH, and gas) and a method for determining the distribution of volume fractions for each parameter in the cell are required.

The measured thermal conductivity, specific heat, and thermal diffusivity fluctuated for $S_h = 0-0.1$, possibly because of the marked change in the water distribution with MH formation in this S_h range. The range $S_h = 0-0.1$ corresponds to the high growth rate region of MH, whereas $S_h = 0.1-0.3$ corresponds to the relatively stable measured thermal constants for the same sensor. This may be attributed to the stable water distribution around the sensor. Generally, we only obtain data for the bulk marine sediment samples; however, local variations within the bulk samples are clearly important to estimate the accuracy of the thermal constants.

The measurements were in the MH saturation range of $S_h = 0-0.3$. However, gas production from the MH sediment with the depressurization method is defined as the dissociation process. Note that the sediment in the hydrate stability region is subject to overburden pressure by the overlying sediments. The measurements in this study were performed without overburden pressure for simplicity. Thus, in the future, we will measure the thermal properties of synthetic-gas-hydrate-bearing samples accompanied by dissociation with overburden pressure.

5. CONCLUSION

The thermal properties of synthetic-gas-hydrate-bearing sediment samples comprising sand-water-gas-MH were measured with the hot-disk transient plane source technique. MHbearing sediment samples were directly synthesized in a highpressure vessel. This is a novel method for obtaining the thermal properties of four-component hydrate-bearing sediment samples with coexisting water, MH, and methane in the sand pores.

To prevent the heat of fusion of MH from affecting the measurements, because of the power output from the transient plane source, the specimens were supercooled. The rate of the temperature variation of MH formation heat $\Delta R_{\rm H}$ in the specimens is sufficiently smaller than the temperature increase in the measurements, probably because the gas hydrate formation is very slow. Clearly, supercooling facilitates thermal measurements in a system consisting of gas hydrate, water, and guest gas.

Thermal conductivity λ slightly increased with MH saturation for $S_{\rm h} = 0-0.3$. Calculations of the thermal

conductivity with mixing models were also performed to examine their applicability in estimating the conductivity of four-component hydrate-bearing sediments. The distribution model (geometric mean model) underestimates the thermal conductivity of the four-component system. This suggests that the distribution model cannot accurately predict the thermal conductivity of samples containing sand and gas, which have large differences in thermal conductivity.

The measured specific heat ρC_p was nearly constant for $S_h = 0-0.3$. The arithmetic mean model underestimated the average specific heat. However, this model can accurately reproduce the ρC_p in a four-component system if the volume fractions of the components around the sensors are accurately determined. A method directly or indirectly to obtain the volume fractions of each component in the experiment cell is required.

Thermal diffusivity α slightly increased between $S_{\rm h} = 0$ and 0.3. The calculated α underestimates the measured average values because α is calculated from the underestimated λ and overestimated $\rho C_{\rm p}$. Accurate estimation of α requires a thermal conductivity model for the four-component system (sand, water, MH, and gas) and a method for measuring the local distribution of volume fractions for each parameter in the cell.

The measured thermal conductivity, specific heat, and thermal diffusivity fluctuated between $S_{\rm h} = 0$ and 0.1, probably because of the extreme variation in the local water distribution that accompanied the MH formation in this S_h range. The range $S_{\rm h} = 0-0.1$ corresponds to the high growth rate region for MH, while all of the recorded parameters in specific sensors were relatively stable between $S_{\rm h}$ = 0.1 and 0.3, possibly because of the stable water distribution around these sensors. The results suggest that local variations are important and affect the accuracy of the calculations of thermal properties. We have presented novel thermal properties measurements of a gashydrate-bearing sediment sample comprising sand, water, MH, and gas. However, the accurate estimation of the thermal properties of this four-component system requires better prediction models and a measurement method for determining the distribution of local volume fractions of each component in the experiment cell.

ASSOCIATED CONTENT

Supporting Information

Details of the experimental setup, process of specimen preparation, and particle size distribution of Toyoura sand. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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