Promotion of Methane Hydrate Dissociation by Underwater Ultrasonic Wave

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Promotion of Methane Hydrate Dissociation by Underwater Ultrasonic Wave

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The methane hydrate that exists in the abyssal floor is receiving attention as a nonconventional type of natural gas resource. An efficient dissociation technology is necessary and indispensable to achieve a steady supply of methane from methane hydrate because it does not easily dissociate in a stable environment of high pressure and low temperature. We consider that underwater ultrasonic wave irradiation may be a method of promoting the dissociation of methane hydrate on the basis of the facilitator effect. We carried out a preliminary examination using dry ice at various pressures, water temperatures, and input electric power. Methane hydrate was similarly examined. As a result, it was clarified that the dissociation time was shorted by the ultrasonic wave, and the wave was effective when the water temperature was low at the time of dissociation.
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KEYWORDS: underwater ultrasonic wave, pressure under, dry ice, methane hydrate, sublimation promotion, dissociation promotion

1. Introduction

A large amount of methane hydrate exists in the abyssal floor, including the waters neighboring Japan, and in the permafrost layer zone, both of which are high-pressure low-temperature environments, and it is receiving attention as one of the a nonconventional type of natural gas resource. An efficient dissociation technology is necessary and indispensable for the steady supply of methane from methane hydrate because it does not easily dissociate in the stable environment of high pressure and low temperature.[1–3)]

Reseachers have been studying the defrosting of frozen material using underwater ultrasonic waves at atmospheric pressure with the aim of using it in industry.[4)] When using a frozen sponge that contains water and ice as a sample, the water temperature and the input electric power were held constant, while as the position of the frozen material was changed. It is clear that the most effective position is at a node of the sound pressure of a standing sound wave, and the most ineffective position is at a loop. When the size of the sponge is $2 \times 2 \times 3\,\mathrm{cm}^3$ or larger, there is little difference in the defrosting time at the node of the sound pressure and at the loop because the length of the sponge is more than half the wavelength of the sound wave. In addition, the lower the water temperature, the more effective the ultrasonic wave is for defrosting. It has been understood that defrosting progressed from the outside of each sample, and it was promoted by heat transfer to the frozen material. The defrosting of frozen material is enhanced by applying underwater ultrasonic waves.[5,6)]

However, up to now, the dissociation of methane hydrate by underwater ultrasonic waves has not been studied. Here we report the promotion of the dissociation of methane hydrate by ultrasonic waves. Although heat stimulation, decompression, and inhibitor methods are available as technologies for the dissociation of methane hydrate, the technology which uses ultrasonic waves is applicable to both heat stimulation and decompression.

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First, as a preliminary examination, we used dry ice, because it sublimates.[7)] It is also cheap, easy to obtain, and harmless to the human body. We studied samples at constant frequency with water temperature, pressure, and input electric power for the transducer as variables. Then, we examined cases with both frequency and input electric power constant while pressure and water temperature were changed. We also studied the promotion of the dissociation of methane hydrate as a fundamental experiment.[8)] The methane hydrate is expensive, and its generation takes time.

2. Experimental Setup

Figure 1 shows an outline of the experimental apparatus. The size of the water tank is 30 cm long, 30 cm wide, and 40 cm high, and the water level is assumed to be 39 cm. About 36 L of water is used first to reduce the influence of cavitation. Water is circulated using a low-temperature circulator to keep the water temperature constant. The pressure vessel is made of stainless steel and has an inside diameter of 5 cm, a resisting pressure of 10 MPa, and a capacity of 500 mL. The maximum pressure of the back-pressure-regulating valve is 10 MPa. Nitrogen is used to pressurize the pressure vessel. The ultrasonic wave source is a throw type-ultrasonic transducer (13 cm long, 13 cm wide, and 9 cm high, MODEL 4329C, KAIJO) which generates resonance using a multifrequency ultrasonic wave generator (MODEL TA-4021, KAIJO) at 28 kHz. The ultrasonic wave is irradiated from the bottom of the pressure vessel.

3. Sound Pressure in Pressure Vessel

To examine of the effect of dissociation by the ultrasonic wave, the sound pressure in the pressure vessel was measured. For the convenience of measurement, the first sound pressure in the direction of the height in the pressure vessel was measured at atmospheric pressure for about four combinations of water levels of 22 and 26 cm in the pressure vessel and for distances of 7 and 15 mm between the vibration side of the transducer and the lower side of the pressure vessel. Measurements without the pressure vessel were also made. The frequency was 28 kHz, the input electric power to the transducer was 100 W, and the water

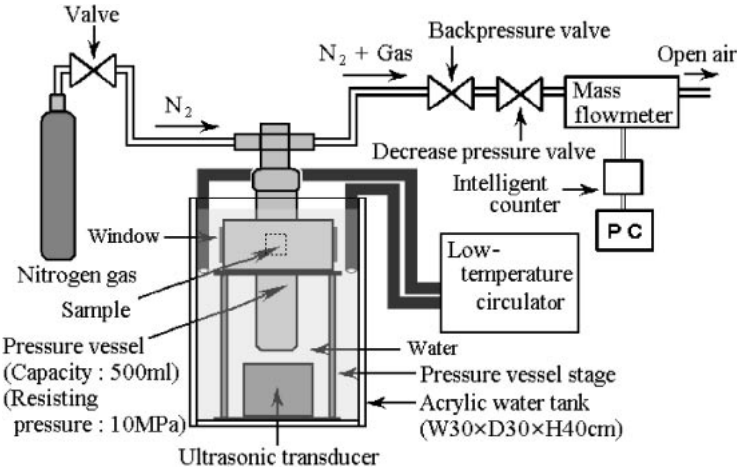

Fig. 1. Outline of experimantal setup.

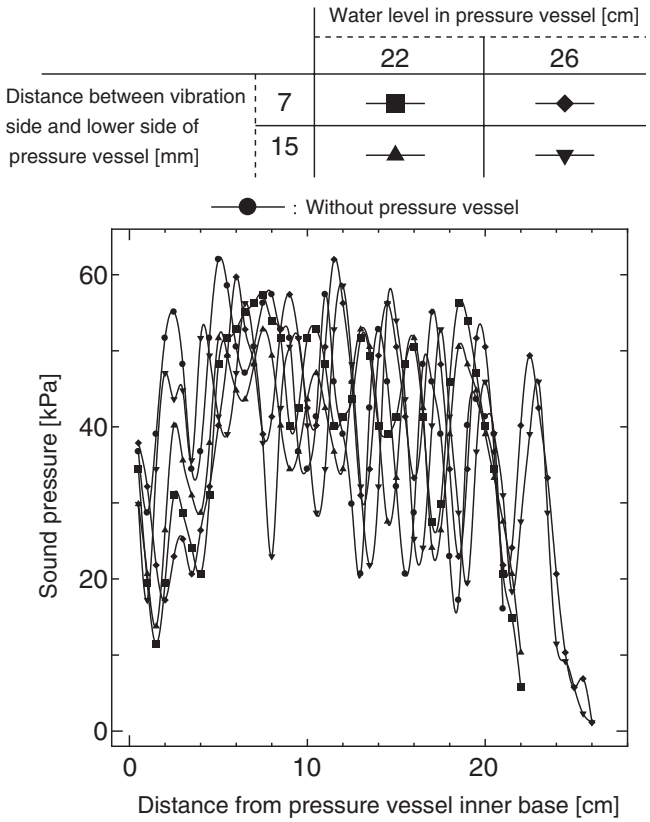

Fig. 2. Sound pressure in the pressure vessel.

temperature was room temperature (about 20 °C). An ultrasonic meter (UTK-30) was used to measure of the sound pressure. Measurements were taken at the center of the pressure vessel at intervals of 5 mm using a probe.

Figure 2 shows the results. The horizontal axis indicates the height in the pressure vessel for measurements at atmospheric pressure and the ordinate indicates the sound pressure. It is understood that the sound waves propagate in the pressure vessel, and a standing sound wave is formed in all cases, as shown in Fig. 2. Even when the water level in the pressure vessel and the distance between the vibration side of the transducer and the lower side of the pressure vessel are changed, the sound pressure obtained is almost the same as that without a pressure vessel, although the distribution is different, as shown in Fig. 2. However, the sound pressure at the position of the sample is not easily specified, so it is represented in this paper by the input electric power to the transducer.

4. Effect on Sublimation of Dry Ice

The dry ice sample was 4 cm long, 3 cm wide, 3 cm high, hexagonal in shape, and about 15 g in mass at the time of examining its of sublimation. This quality of dry ice generates about 6 L of carbon dioxide. The dry ice was placed about 13 cm from the bottom, inside the pressure vessel, which was a position that could be observed through the window.

4.1 Appearance of dry ice sublimation

First, we observed the appearance of dry ice sublimation from the window of the pressure vessel. Figure 3(a) shows the case without ultrasonic waves, and Fig. 3(b) shows the case with ultrasonic waves at a frequency of 28 kHz, an input electric power of 100 W, a pressure of 0.25 MPa, and water temperature of 25 °C. In the photograph, although unclear, it is understood that there is a more intense sublimation with ultrasonic waves than without ultrasonic waves.

4.2 Examination of dry ice sublimation

We examined dry ice sublimation. The amount of gas generated was measured by a gas flowmeter. Measured data on the quantity of flow and the cumulative quantity of gas were entered into the computer every 2 s. The elapsed time was 0 s when the pressure in the pressure vessel was that at the backpressure valve; the ultrasonic wave irradiation was begun at this same time. Figure 4 shows the elapsed time on the abscissa, and the normalized cumulative quantity of flowing gas on the ordinate for a water temperature of 5 °C, a pressure of 1.0 MPa, and an input electric power of 150 W. It is understood that the sublimation ended faster with the ultrasonic wave than without it. Next, similar examinations were carried out for the cases with water temperatures of 5, 10, 15, and 20 °C, pressures of 0.25, 0.5, and 1 MPa, input electric power of 0, 50, 100, and 150 W, and a constant frequency of 28 kHz. Five measurements were taken under each set of conditions, and the time when the normalized

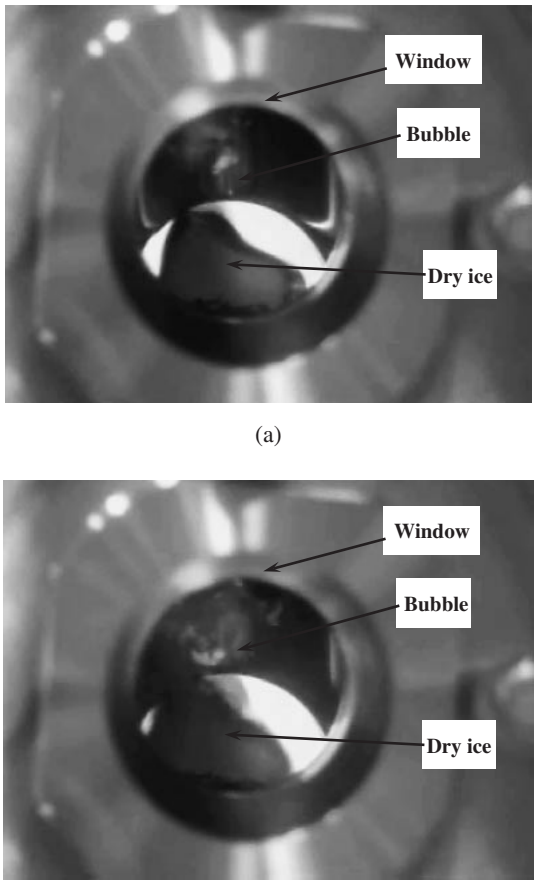

Fig. 3. Appearance of dry ice sublimation for a pressure of 0.25 MPa and a water temperature of 25 °C; (a) without ultrasonic wave and (b) with ultrasonic wave for a frequency of 28 kHz and an input electric power of 100 W.

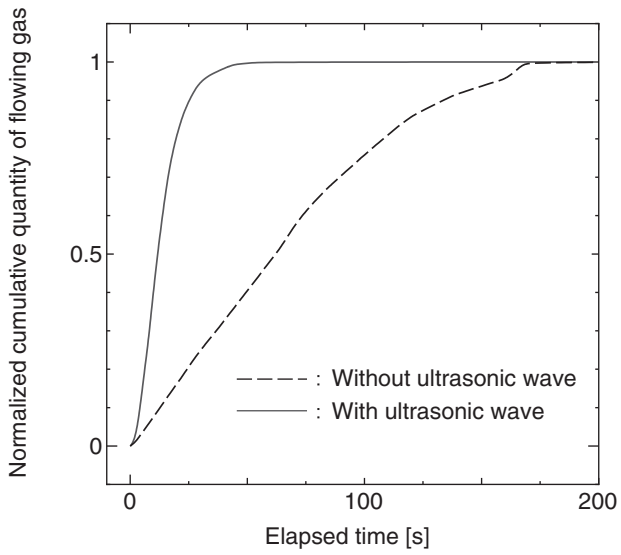

Fig. 4. Process of dry ice sublimation for a water temperature of 5 °C, a pressure of 1.0 MPa, and an input electric power of 150 W.

cumulative quantity flowing was from 0.05 to 0.95 was the sublimation time. These results were averaged, and are shown in Figs. 5–7.

Figure 5 shows the water temperature on the horizontal axis and the sublimation time on the vertical axis for variable pressure and a constant input electric power of 150 W. Figure 6 shows the pressure on the horizontal axis and the sublimation time on the vertical axis for variable water temperature and a constant input electric power of 150 W. Figure 7 shows the pressure on the horizontal axis and the sublimation time on the vertical axis for variable input electric power and a constant water temperature of 5 °C. It is understood that the sublimation time is shorter with ultrasonic waves than without, and shorter as the water temperature, the pressure, and the input electric power increase over the range measured, as shown in Figs. 5–7. These results are thought to arise because dry ice easily becomes a gas as the water temperature rises over the range

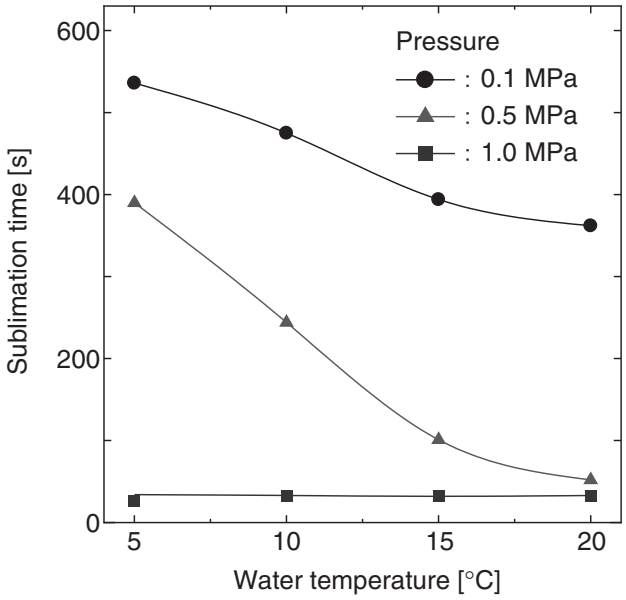

Fig. 5. Relationship between water temperature and sublimation time for a frequency of 28 kHz, and an input electric power of 150 W.

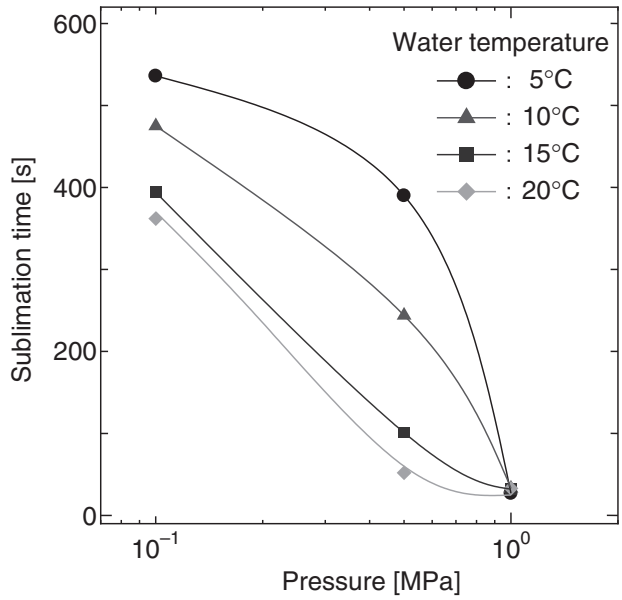

Fig. 6. Relationship between pressure and sublimation time for a frequency of 28 kHz, and an input electric power of 150 W.

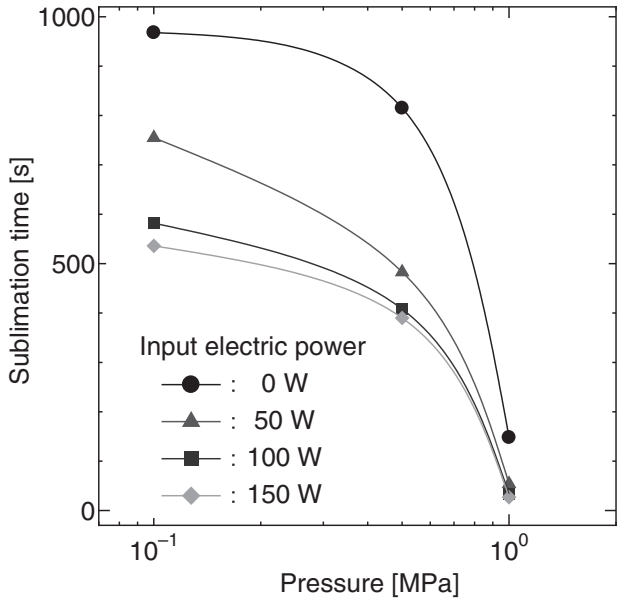

Fig. 7. Relationship between pressure and sublimation time for frequency of 28 kHz, and a water temperature of 5 °C.

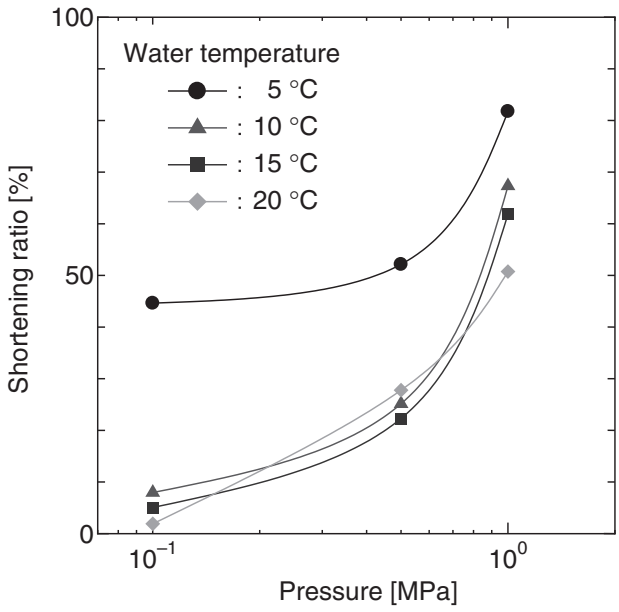

Fig. 9. Relationship between pressure and shortening ratio for a frequency of 28 kHz, and an input electric power of 150 W.

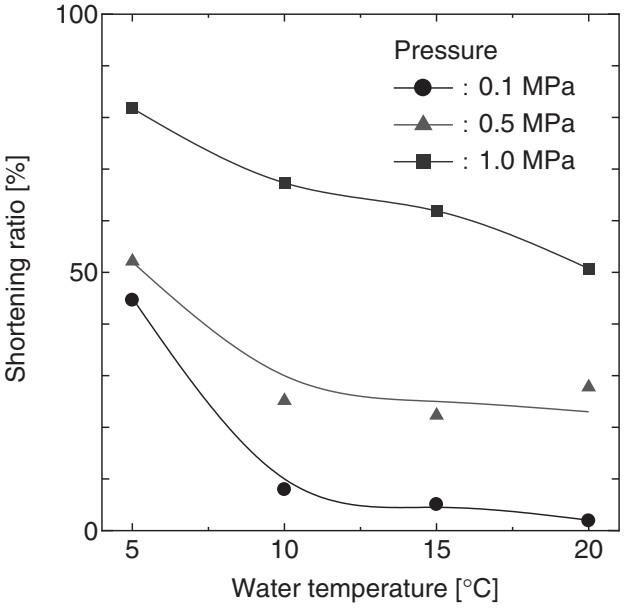

Fig. 8. Relationship between water temperature and shortening ratio for a frequency of 28 kHz, and an input electric power of 150 W.

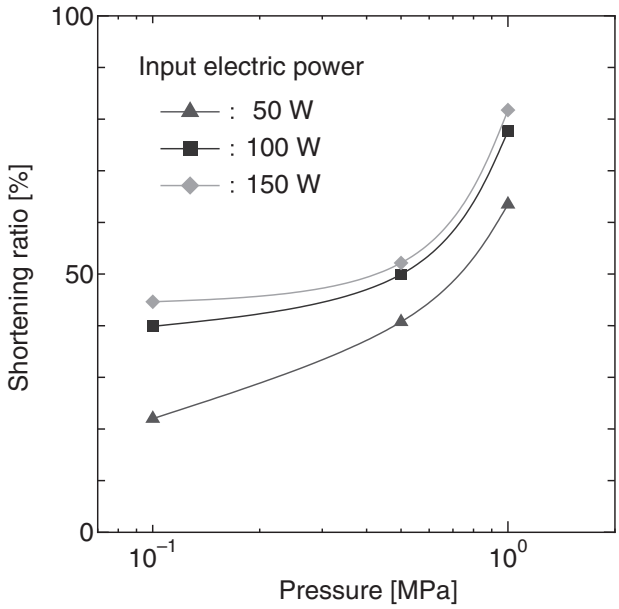

Fig. 10. Relationship between pressure and shortening ratio for a frequency 28 kHz, and a water temperature of 5 °C.

measured, as seen from the phase diagram of dry ice. Dry ice is also easily converted into a liquid at high pressure.

Next, the shortening ratio at the sublimation time was calculated, using these results, as the ratio of the difference in the sublimation time due to the presence of an ultrasonic wave to T_a, the sublimation time without the ultrasonic wave, $(T_a - T_b)/T_a \times 100\%$. Here, T_b is the time with the ultrasonic wave. T_a and T_b were read from the graphs of normalized cumulative quantity of flowing. These results are shown in Figs. 8–10.

Figure 8 is obtained from Fig. 5, and it shows the water temperature on the horizontal axis plotted against the shortening ratio on the vertical axis for variable pressure. Figure 9 is obtained from Fig. 6, and it shows the pressure on the horizontal axis plotted against the shortening ratio on the vertical axis for variable is the water temperature. Figure 10 is obtained from Fig. 7, and it shows the pressure on the horizontal axis plotted against the shortening ratio on the vertical axis for variable the input electric power. The shortening ratio improves as the water temperature decreases, and the pressure and the input electric power increase, as shown in Figs. 8–10. For example, when the shortening ratio of the sublimation time is 82%, sublimation requires 1/5 of the time needed without the ultrasonic wave at a water temperature of 5 °C, a pressure of 1.0 MPa, and an input electric power of 150 W, as shown in Figs. 8–10.

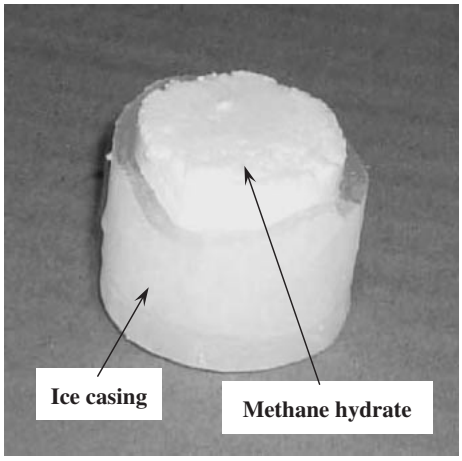

Fig. 11. Methane hydrate used as a sample (upper part of the ice casing has been removed).

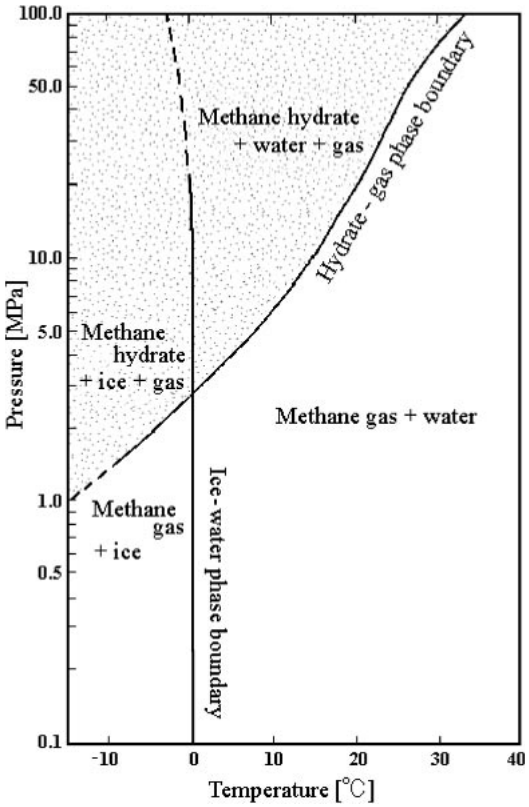

Fig. 12. Phase diagram of methane hydrate.

5. Effect on Dissociation of Methane Hydrate

For the examination of dissociation, we used methane hydrate 3 cm in diameter and 2.5 cm high, which was encased in ice about 3 mm thick, as shown in Fig. 11. Figure 11 shows a sample of methane hydrate with the ice casing removed from the upper part. The ice casing was used so that the methane hydrate did not dissociate until the desired conditions were attained. Figure 12 shows the phase diagram of methane hydrate,[9] where the horizontal axis is the temperature and the vertical axis is the pressure. The upper left of Fig. 12 indicates a stable domain, and the lower right of Fig. 12 indicates a dissociation domain. The amount of gas generated from this methane hydrate was about 0.3 to 0.6 L. The location of the methane hydrate was about 13 cm from the bottom inside the pressure vessel, which was a position that could be observed from the window.

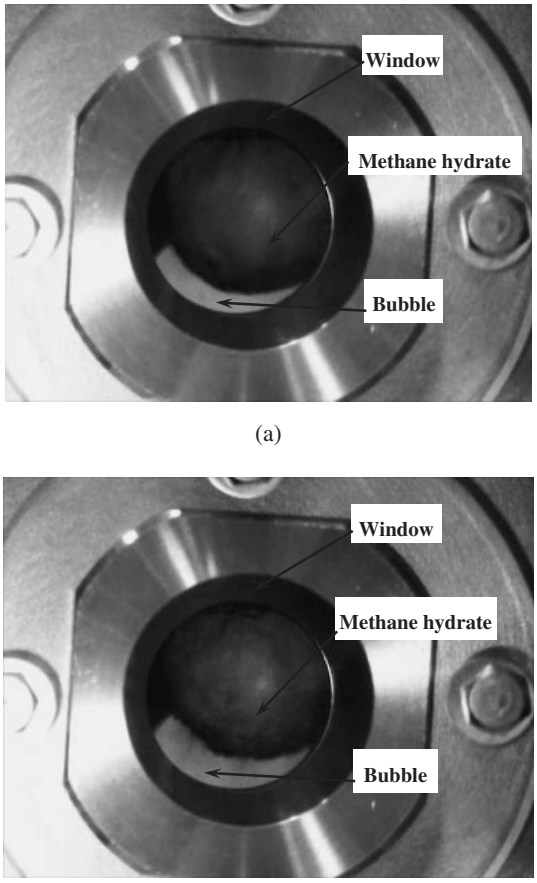

Fig. 13. Appearance of methane hydrate dissociation for a pressure of 0.25 MPa and a water temperature of 15 °C; (a) without ultrasonic waves and (b) with ultrasonic waves for a frequency of 28 kHz, and an input electric power of 100 W.

5.1 Appearance of methane hydrate dissociation

First, we observed the appearance of the methane hydrate viewed through the window of the pressure vessel. Figure 13(a) shows the appearance of methane hydrate without ultrasonic waves, and Fig. 13(b) shows it with ultrasonic waves at a frequency of 28 kHz, an input electric power of 100 W, a pressure of 0.25 MPa, and water temperature of 15 °C. From the photographs, it is understood that dissociation from the surface with ultrasonic waves is more intense than that without ultrasonic waves.

5.2 Examination of methane hydrate dissociation

We examined methane hydrate dissociation. The amount of gas generated was similar to that in the case of when dry ice was used. The gas generated was measured starting at 0 s, the time when the starting value of the backpressure valve was set. The ultrasonic wave irradiation was begun at the time when the cumulative quantity of flowing gas was 1.5 mL. Figure 14 shows one example of the results with ultrasonic wave irradiation, where the horizontal axis is the

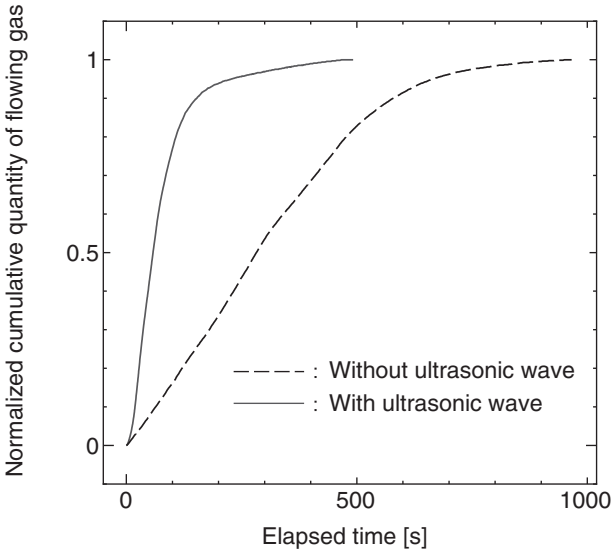

Fig. 14. Process of methane hydrate dissociation for a water temperature of 5 °C, a pressure of 2.0 MPa, and an input electric power of 100 W.

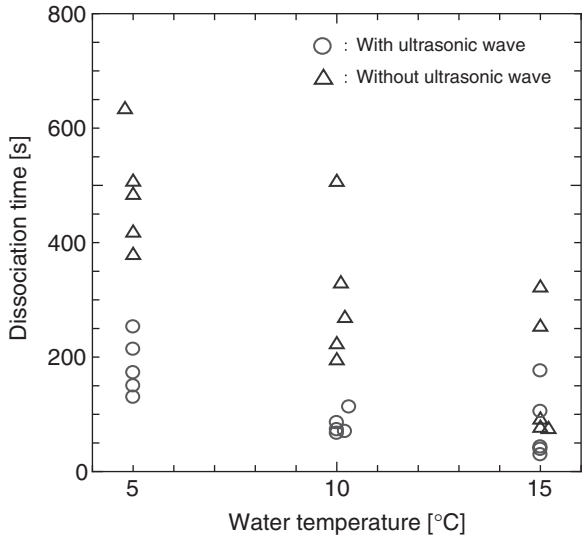

Fig. 16. Relationship between water temperature and dissociation time for a frequency of 28 kHz, a pressure of 1.0 MPa, and an input electric power of 100 W.

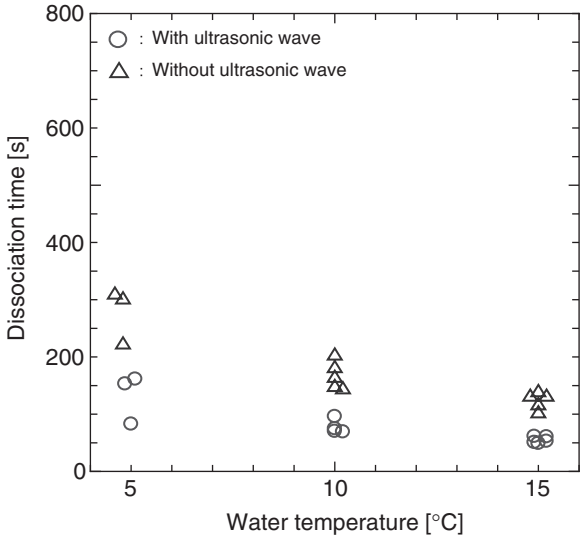

Fig. 15. Relationship between water temperature and dissociation time for a frequency of 28 kHz, a pressure of 0.5 MPa, and an input electric power of 100 W.

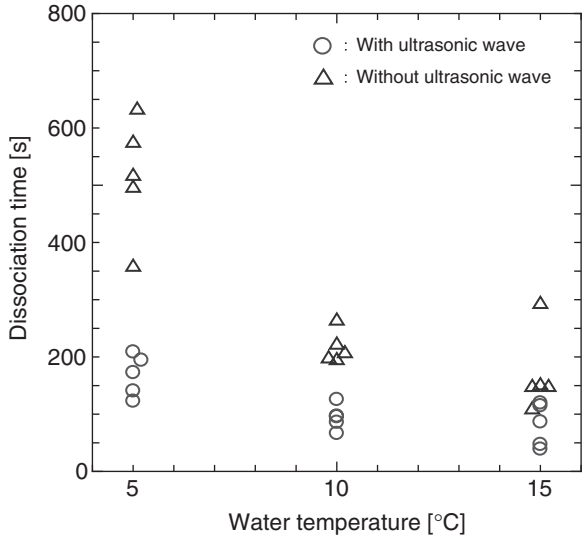

Fig. 17. Relationship between water temperature and dissociation time for a frequency of 28 kHz, a pressure of 1.5 MPa, and an input electric power of 100 W.

elapsed time and the vertical axis is the normalized cumulative quantity of flowing gas at a water temperature of 5 °C and a pressure of 2.0 MPa. Similar to the dissociation with ultrasonic waves ended faster than that without ultrasonic waves. Next, similar experiments were carried out for in cases of water temperatures of 5, 10, and 15 °C, pressures of 0.5, 1.0, 1.5, and 2.0 MPa with frequency constant at 28 kHz. Input electric power was held constant at 100 W because dissociation times at 100 and 150 W did not make a large difference in the experiments using dry ice. Measurements were performed from three to five times under each set of conditions. The time at which the normalized cumulative quantity flowing was from 0.05 to 0.95 was the dissociation time. The results are shown in Figs. 15–18.

Figure 15 shows the results for a pressure of 0.5 MPa; Fig. 16, for 1.0 MPa; Fig. 17, for 1.5 MPa; and Fig. 18, for 2.0 MPa, where the horizontal axis is the water temperature and the vertical axis is the dissociation time in each figure. In all cases, the dissociation time with the ultrasonic wave is shorter than that without the ultrasonic wave as shown in Figs. 15–18. There was no change in water temperature during the measurement. The methane hydrate was defrosted from the outside as shown Fig. 13. The reason behind this result is thought to be that in this experiment heat transfer was promoted to methane hydrate by the ultrasonic wave because over this measured range it was dissociated. It has been defrosted from the outside of the sample, and defrosting was promoted by the ultrasonic wave.[5)] At high pressures, the sound pressure did not change, because the sound pressure was half the value about 50 kPa compared with the atmospheric pressure (0.1 MPa) as shown Fig. 2. The vapor phase was not change by the rising temperature,

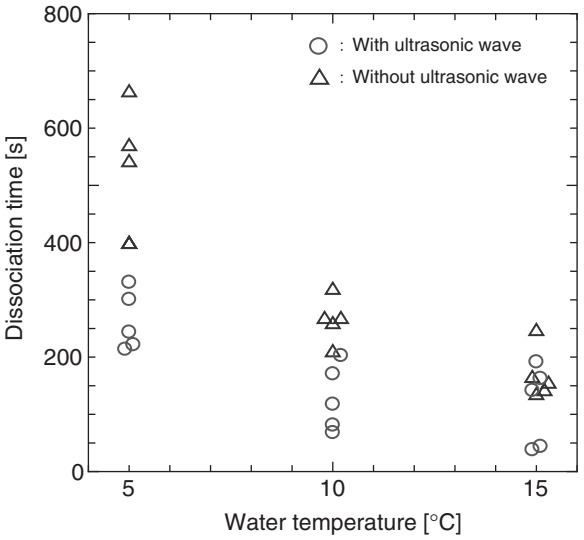

Fig. 18. Relationship between water temperature and dissociation time for a frequency of 28 kHz, a pressure of 2.0 MPa, and an input electric power of 100 W.

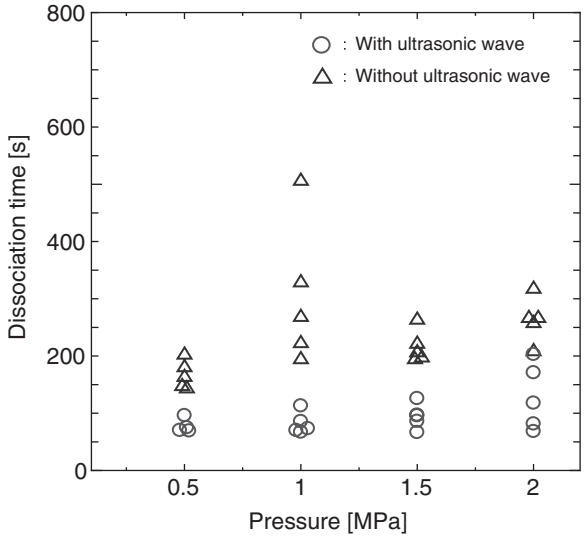

Fig. 20. Relationship between pressure and dissociation time for a frequency of 28 kHz, a water temperature of 10 °C, and an input electric power of 100 W.

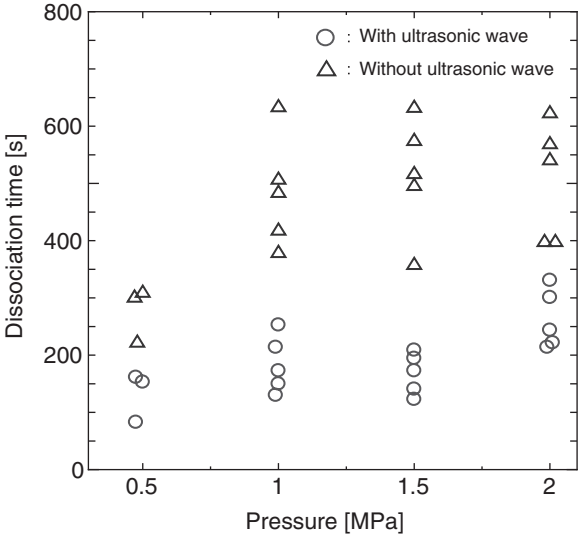

Fig. 19. Relationship between pressure and dissociation time for a frequency of 28 kHz, a water temperature of 5 °C, and an input electric power of 100 W.

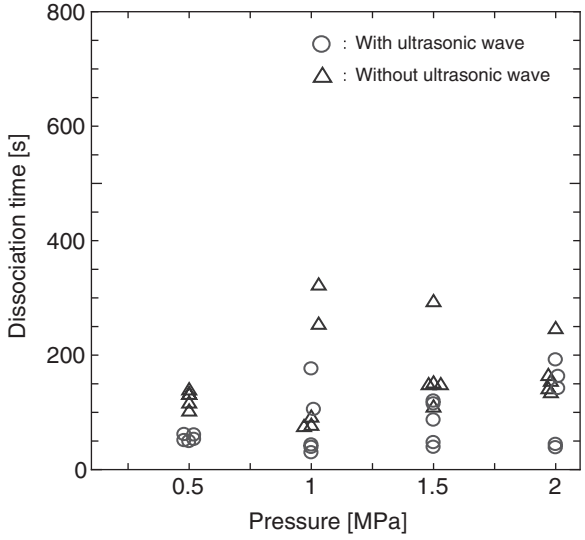

Fig. 21. Relationship between pressure and dissociation time for a frequency of 28 kHz, a water temperature of 15 °C, and an input electric power of 100 W.

because there was no change water temperature.[10] The vapor phase decreases with lower pressure and higher water temperature regardless of the presence of the ultrasonic wave over this measured range of pressure as shown in Figs. 15–18. It is thought that the methane hydrate easily exists as methane gas and water when the water temperature is high over the measured range, on the basis of the phase diagram of methane hydrate. This observation is also thought to be related to the fact that methane hydrate easily liquefies when the water pressure is high.

Next, the graphs were redrawn and are shown in Figs. 19–21. Figure 19 shows the results for a water temperature of 5 °C; Fig. 20, for 10 °C; and Fig. 21, for 15 °C, where the horizontal axis is the pressure and the vertical axis is the dissociation time in each figure. Again, in all cases, it is understood that the dissociation time becomes shorter as the pressure rises regardless of the presence of the ultrasonic wave, as shown in Figs. 19–21. The reason is that methane hydrate exists as methane gas and water when the pressure is high over the measured range based on the phase diagram of methane hydrate. For example, the dissociation time becomes half that without the ultrasonic wave at a water temperature of 5 °C and a pressure of 2.0 MPa, as shown in Figs. 19–21.

However, the results using methane hydrate indicated a different tendency from using dry ice. This behavior is thought to be related to the fact that dry ice and methane hydrate have difference of material characteristics and solubilities in water.

6. Conclusions

We performed examinations with and without ultrasonic

waves in order to study the effect of underwater ultrasonic waves on the dissociation of methane hydrate. We used dry ice in the preliminary examination, followed by an investigation using methane hydrate. The frequency was held constant, and the pressure, water temperature, and input electric power were changed when using dry ice; and the frequency and input electric power were held constant and the pressure and water temperature were changed when using methane hydrate.

As a result, the following was clarified. In the experiments using dry ice, the sublimation time with ultrasonic waves was shorter than that without as the water temperature, pressure, and input electric power rose. The shortening ratio of the sublimation time improved as water temperature decreased and as pressure and input electric power increased. In the experiments using methane hydrate, the dissociation time with ultrasonic waves was shorter than that without as pressure decreased and water temperature increased.

It is concluded that the application of underwater ultrasonic waves is effective in promoting the dissociation of methane hydrate. We expect heat is transferred to methane hydrate by ultrasonic wave. We think the technology that uses ultrasonic waves may be applied to existing dissociation technologies. In the future, we will clarify the physical dissociation of methane hydrate by ultrasonic waves.

Acknowledgements

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