PERGAMON

International Journal of Heat and Mass Transfer 44 (2001) 4533–4539

International Journal of HEAT and MASS TRANSFER

www.elsevier.com/locate/ijhmt

Active control of phase change from supercooled water to ice by ultrasonic vibration 2. Generation of ice slurries and effect of bubble nuclei

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Received 4 August 2000; received in revised form 23 January 2001

Abstract

An effective and reliable method to generate ice slurry is necessary for cold-energy storage and transport systems. First we found that ice slurries were generated in supercooled water by ultrasonic vibration. Then we experimentally studied the effect of bubble nuclei on the phase change from supercooled water to ice induced by ultrasonic vibration. Our results show that the phase change is closely related to acoustic cavitation, and the probability of the phase change increases as the total number of bubble nuclei increases. Finally, simulation results based on the cavitation-induced nucleation of solid qualitatively agree with the experimental results.

1. Introduction

Ice slurry that is a mixture of fine ice particles and liquid is a promising working fluid for cold-energy storage and transport devices due to its flowability and large latent heat. For practical use, a simple, effective method must be developed that generates ice slurry while actively controlling the temperature of the phase change from supercooled water to ice.

Cavitation in a supercooled liquid can result in nucleation of solid [1]. Ohsaka and Trinh reported dynamic nucleation of ice induced by an isolated stable cavitation bubble in an ultrasonic sound field [2]. Although several mechanisms of the phase change from supercooled water to ice induced by ultrasonic vibration have been reported [2–4], these mechanisms were considered unsatisfactory because they did not appear to be compatible with experimental results. We experimentally investigated the effect of ultrasonic vibration on the phase change from supercooled water to ice [5], and found that ultrasonic vibration strongly promoted the phase change for both pure water and tap water, and was a reliable method to actively control the freezing temperature of supercooled water by adjusting the cavitation intensity. However, that study did not clarify the effectiveness of ultrasonic method in generating ice slurry and the mechanism of the phase change from supercooled water to ice induced by ultrasonic vibration.

In this study, to develop an effective method to generate ice slurry, we experimentally observed the phase change from supercooled water to ice. Then, to clarify the relationship between the phase change from supercooled water to ice and acoustic cavitation, we investigated the effect of bubble nuclei in water on the phase change. Finally, we simulated the phase change assuming that ultrasonic-induced cavitation influences ice nucleation, and then compared simulation results of this phase change with our experimental results.

2. Generation of ice slurries

Based on cavitation-induced nucleation, ultrasonic vibration might generate a high number density of ice

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Nomenclature

N number of bubble nuclei and solid particles per unit volume in a radius interval specified by the optical particle counter, cm^{-3}
N_b number of bubble nuclei per unit volume in a radius interval specified by the optical particle counter, cm^{-3}
N_{bt} total number of bubble nuclei per unit volume, cm^{-3}
N_s number of solid particles per unit volume in a radius interval specified by the optical particle counter, cm^{-3}
N_{st} total number of solid particles per unit volume, cm^{-3}
N'_{st} total number of solid particles per unit volume measured by laser microscopy, cm^{-3}
N_{tot} total number of bubble nuclei and solid particles per unit volume, cm^{-3}
$p_{A\,max}$ maximum acoustic pressure amplitude, MPa
r_{max} maximum measurable size of the optical particle counter, m
r_{min} minimum measurable size of the optical particle counter, m

Greek symbols
ΔT degree of supercooling, K
λ ultrasonic wavelength, mm

crystals in supercooled water. Therefore, the ultrasonic method could be effective for generating ice slurry. Here, we describe our experiments that achieve it.

2.1. Experimental apparatus and procedure

For successful observation of the ice formation in supercooled water, premature nucleation of ice originating from other nucleation sites such as the container wall must be eliminated. In this study, we therefore used a double-walled acrylic vessel to observe the generation and growth of ice crystals as shown in Fig. 1. The outer vessel was filled with air at room temperature to maintain the temperature of the inner-vessel wall higher than 0°C and to prevent dew formation on the outer-vessel wall. A stainless-steel ultrasonic generator was located beneath the square inner vessel (150 mm × 150 mm square, and 160 mm high), and its frequency was 39 kHz and its output power was 4.4 kW m^{-2}. The frequency and power was chosen so that cavitation could occur in water.

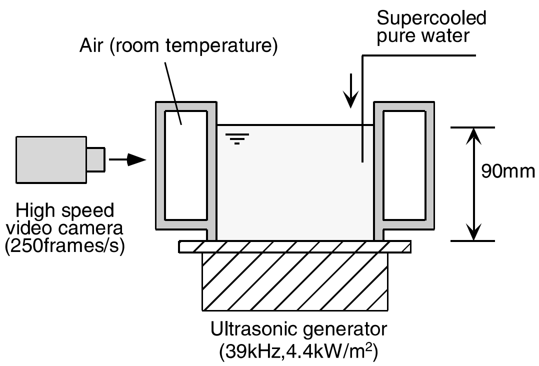

Fig. 1. Experimental apparatus used to generate and observe the phase change from supercooled water to ice.

To generate supercooled water, first, filtered ion-exchanged water (efficiency of the filter was 0.2 μm) was poured into a polyethylene vessel and then left in a cold-room (−6°C) for over 6 h. Next, the supercooled water was poured into the inner-vessel gently and slowly so that no ice was formed. The resonance condition of the ultrasonic generator is met easily when the water level is an integer multiple of half of the wavelength. To generate a standing acoustic wave in the water, we set the height of water in the inner vessel to be 90 mm, which is five times $1/2\lambda$, where λ is the ultrasonic wavelength. The temperature of the water at the center of the inner vessel was approximately −4°C, measured by using a thermocouple. Because the temperature near the inner-vessel wall exceeded 0°C just after the supercooled water was poured into the inner vessel, ice formation on the inner-vessel wall was prevented. Finally, ultrasonic vibration was applied to the supercooled water, and the resulting ice formation was observed by using a high-speed video camera (250 fps).

2.2. Results

The observed ice formation is shown in Fig. 2. A high number density of fine ice crystals appeared within a short time (1 s) after ultrasonic vibration was applied, and grew in dendritic form in the water. No ice formation on the inner-vessel wall was observed. This high number density of fine ice crystals generated within a short time is significant for practical use of ice slurries.

Photograph (a) in Fig. 2 corresponds to the time just before ice crystals appeared. Photograph (b) shows that a high number density of fine ice crystals appeared in layers where antinodes of acoustic pressure were along the vertical direction.

The dendrite grew at approximately 0.4 cm s^{-1}, which is comparable to the growth rates reported in the literature, 0.68 cm s^{-1} [6] and 0.24 cm s^{-1} [7]. The structure of ice crystals is shown in Fig. 3. A thin den-

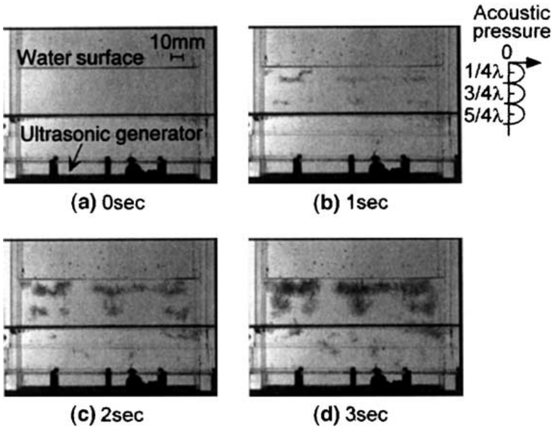

Fig. 2. Ice crystal growth in supercooled water induced by ultrasonic vibration: (a) 0 s; (b) 1 s; (c) 2 s; (d) 3 s.

drite grew from a single point of nucleation, and the ensuing growth segments were symmetrically located about the plane of dendrite. This growth pattern is similar to the growth of normal structures initiated with a seed crystal [8]. These results show that ultrasonic vibration did not significantly affect either the growth or structure of ice crystals.

3. Effect of bubble nuclei

Although ice slurries can be generated in supercooled water by ultrasonic vibration, the mechanism of the phase change from supercooled water to ice induced by ultrasonic vibration was unclear. Cavitation is an important factor in the phase change from supercooled water to ice according to the existing theories [2–4], and the number of bubble nuclei is an important parameter for cavitation. Therefore, in this section, we discuss the relationship between the phase change from supercooled water to ice and acoustic cavitation by focusing on the number of bubble nuclei in the water. Then, we compare simulation results and experimental results.

3.1. Preparation of test water

To obtain different test waters that respectively, contained significantly different numbers of bubble nuclei for our experiments, we needed to understand the dependence of the total number of bubble nuclei on the duration of the quiescent interval of the test water.

We therefore prepared air-supersaturated test water as follows. First, filtered ion-exchanged water (efficiency of the filter was 0.2 μm) at room temperature was gently and slowly poured into a polyethylene vessel and then left undisturbed for 15 h. Then, the vessel was shaken up and down 30 times to mix the water with air.

By using an optical particle counter (Pacific Scientific, Hiac/Royco PA-720), we measured the total number of bubble nuclei and solid particles (N_{tot}) in air-supersaturated test water alone for various quiescent intervals. Fig. 4 shows that N_{tot} decreased as the quiescent interval was increased. As discussed later in detail, differences in N_{tot} among the test waters reflect differences in the total number of bubble nuclei among the test waters.

Based on the results shown in Fig. 4 for the experiments to study the effect of bubble nuclei on the phase change from supercooled water to ice, we then used the following three types of test water:

(a) *Filtered ion-exchanged water*. Filtered ion-exchanged water (efficiency of the filter was 0.2 μm) was poured into a polyethylene vessel and then left undisturbed for 15 h.

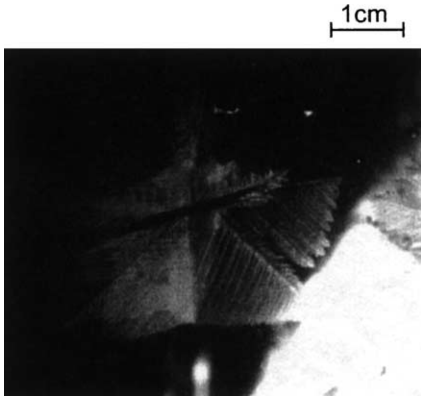

Fig. 3. Structure of ice crystals generated from supercooled water and induced by ultrasonic vibration.

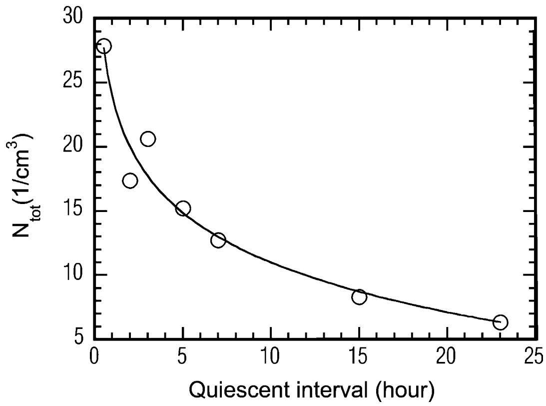

Fig. 4. Dependence of N_{tot} on the quiescent interval of air-supersaturated test water at room temperature.

(b) *Filtered ion-exchanged water mixed with air*. Filtered ion-exchanged water (efficiency of the filter was 0.2 μm was poured into a polyethylene vessel and left undisturbed for 15 h, then shaken up and down 30 times, and then left undisturbed for 1–2 h.

(c) *Degassed water*. Filtered ion-exchanged water (efficiency of the filter was 0.2 μm) was first boiled for 30 min, then left undisturbed for 15 h, and finally filtered (efficiency of the filter was 0.2 μm) again to remove the solid particles generated from the vessel wall during the boiling process.

For simplicity, we call these three types of test water, *water* (a), (b) and (c), respectively.

The optical particle counter cannot distinguish between bubble nuclei and solid particles in water, and thus measures them simultaneously. Fig. 5 shows a histogram of the normalized size of bubble nuclei and solid particles for the three types of test water measured by using the optical particle counter. The absolute size was difficult to obtain because the optical particle counter was calibrated by using standard solid particles. Therefore, we normalized the size (x-axis in Fig. 5) by the maximum measurable value (41.6 μm) of the optical particle counter. The N and N_{tot} in Fig. 5 were given by using the following equations:

$$N = N_s + N_b, \quad (1)$$

$$N_{tot} = N_{st} + N_{bt}, \quad (2)$$

$$N_{tot} = \sum_{r=r_{min}}^{r_{max}} N, \quad (3)$$

where N_b and N_s are the number of bubble nuclei and solid particles, respectively, per unit volume in a radius interval specified by the optical particle counter, and N_{bt} and N_{st} are the total number of bubble nuclei and solid particles, respectively, per unit volume in the measurement region from r_{min} to r_{max} for the optical particle counter.

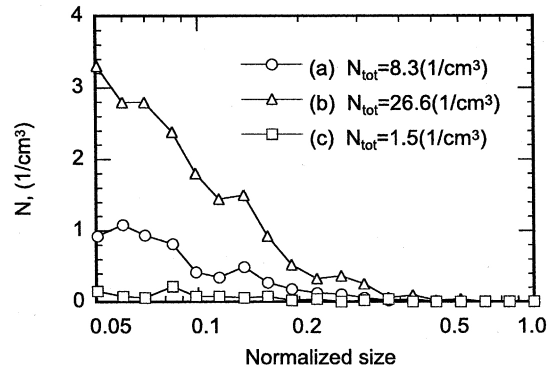

Fig. 5. Histogram of normalized size of bubble nuclei and solid particles for the three types of test water.

To analyze the effect of solid particles on the measurement of the bubble nuclei by the optical particle counter for the three types of test water, for each type, 500 cm^3 of water was filtered (efficiency of the filter was 0.8 μm), thus capturing only the solid particles on the filters. We then determined the total number of solid particles per unit volume in the test water (N'_{st}) by using a laser microscopy (×300) to count the number of particles on the filter. Fig. 6 shows the measured N'_{st} for the three types of test water. The differences in N'_{st} among the three types of water were not statistically significant.

The relationship between N_{tot} and N_{bt} is clarified by the ratio of N_{tot} determined by the optical particle counter and N'_{st} determined by laser microscopy for the three types of test water as shown in Table 1. The maximum N'_{st} ratio was 1.5 and the minimum N_{tot} ratio was 5.5, indicating that the effect of solid particles on the differences in N_{tot} among the different types of test water was small and that the differences in N_{tot} reflect the differences in N_{bt}.

Although a quantitative comparison between the optical particle counter method and laser microscopy method is difficult because the measurement principles of these methods are different, comparison of the ratio of the measurement results for the different types of test water shows that the total number of bubble nuclei in decreasing order of the test water is as follows: (b) > (a) > (c).

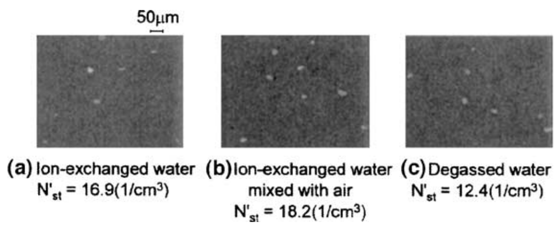

Fig. 6. Laser microphotographs of residual solid particles on filters: (a) ion-exchanged water $N'_{st} = 16.9$ cm^{-3}; (b) ion-exchanged water mixed with air $N'_{st} = 18.2$ cm^{-3}; (c) degassed water $N'_{st} = 12.4$ cm^{-3}.

Table 1
Comparison of normalized N_{tot} obtained by an optical particle counter with normalized N'_{st} obtained by laser microscopy

Optical particle counter		Laser microscopy	
$N_{tot}(a)/N_{tot}(c)$	5.5	$N'_{st}(a)/N'_{st}(c)$	1.4
$N_{tot}(b)/N_{tot}(c)$	17.7	$N'_{st}(b)/N'_{st}(c)$	1.5

3.2. Experimental apparatus and procedure

Fig. 7 shows a schematic of the experimental apparatus used to study the effect of bubble nuclei on the phase change from supercooled water to ice. A stainless-steel ultrasonic generator was located beneath an inner vessel of a double-walled acrylic vessel, and its frequency was 39 kHz and its output power was 4.4 kW m^{-2}. The temperature of the calcium chloride solution (20.9 wt%, freezing-point is −19.2°C) in the inner vessel was controlled by a circulating bath of ethanol in an outer vessel, which was connected to a constant-temperature bath. One of the two glass test tubes (21 mm outer diameter, 1.3 mm thickness) in the inner vessel contained 10 cm^3 of test water and the other contained 10 cm^3 of ethanol solution (24.0 wt%, freezing-point is −14.5°C). The height of each liquid in the test tubes was about 41 mm. The wavelength λ for 39 kHz ultrasonic vibration was about 36 mm for the test water at 0°C. Therefore, the test water in the test tube contained at least two acoustic pressure antinodes when ultrasonic vibration was applied. The calculated transmissivity of ultrasonic vibration through the glass wall of the test tube was 0.92. Therefore, sufficient energy from the ultrasonic vibration can pass through the glass wall of the test tube to reach the test water.

The temperature of the test water in the test tube was monitored by using a thermocouple placed in the test tube filled with ethanol solution. Due to the symmetry of the apparatus, in preliminary experiments we confirmed that the temperature of the test water was the same as that of the ethanol solution. After the test water was cooled to various temperatures representing different degrees of supercooling ΔT (1, 3, 5, and 7 K), ultrasonic vibration was applied to the test water for 9 s, and the phase change from supercooled water to ice was observed in the test tube by using a video camera. We made about 20 measurements for each experimental condition, and then calculated the probability of the phase change when ultrasonic vibration was applied to the supercooled test water at different ΔT.

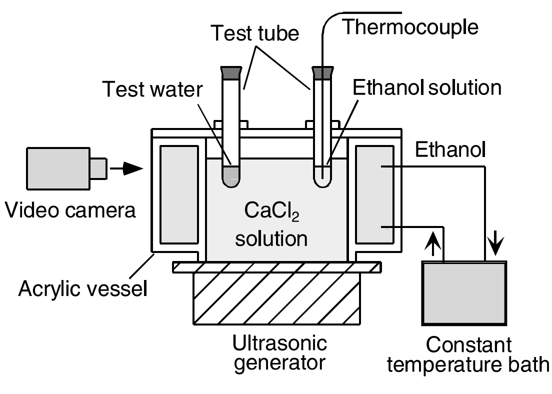

Fig. 7. Experimental apparatus used to study the effect of bubble nuclei on the phase change from supercooled water to ice.

3.3. Results

Fig. 8 shows that, independent of ΔT, the probability of the phase change from supercooled water to ice increased as the total number of bubble nuclei increased. (The error bars in Fig. 8 are based on a statistical calculation at a 90% confidence level. The x-axis was slightly shifted to clearly show the error bars.) We also observed that ice crystals were usually generated on the acoustic pressure antinodes.

When N_{tot} was large, for example, as in water (b), the probability of the phase change from supercooled water to ice was 1 (except for $\Delta T = 1$ K), independent of ΔT. When N_{tot} was small, for example, as in water (c), the probability of the phase change was less than 0.1, again independent of ΔT. However, when N_{tot} was between that in water (b) and water (c), for example, as in water (a), the probability of the phase change was between 0.14 and 0.64, for different ΔT. Considering the confidence interval of the experimental data, the probability of the phase change was independent of degree of supercooling for the experimental conditions studied here.

The experimental result showed that the probability of the phase change from supercooled water to ice increased as the total number of bubble nuclei increased and ice crystals which were usually generated on the acoustic pressure antinodes showed that the phase change induced by ultrasonic vibration was caused by acoustic cavitation.

Here, we discuss the relationship between bubble nuclei and acoustic cavitation. The acoustic pressure

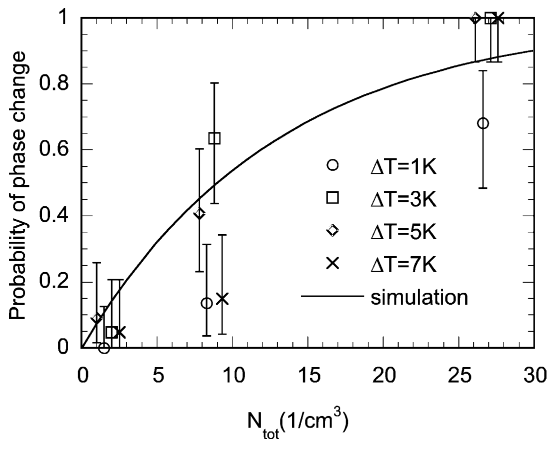

Fig. 8. Probability of the phase change from supercooled water to ice as a function of N_{tot} for different degrees of supercooling ΔT.

amplitude necessary to cause cavitation is usually called the cavitation threshold. By simply increasing the number of bubble nuclei, cavitation is easily generated [9], that is, increasing the number of bubble nuclei decreases the cavitation threshold, because the number of weak spots caused by bubble nuclei in the liquid also increases [10].

Although factors other than cavitation accompany the ultrasonic vibration, such as acoustic streaming, vibration of the vessel and solid particles, these factors are not affected by the number of bubble nuclei. Therefore, the results in Fig. 8 show that the phase change from supercooled water to ice was mainly caused by the onset of cavitation induced by ultrasonic vibration.

3.4. Simulation and discussion

To further investigate the effect of bubble nuclei on the phase change from supercooled water to ice induced by the acoustic cavitation, we used a simulation model [5] that is based on the cavitation-induced nucleation of solid. Parameters used in this simulation model were based on the present experiment on the effect of bubble nuclei on the phase change from supercooled water to ice.

Fig. 9 shows the simulation results for the probability of the phase change from supercooled water to ice for different ΔT as a function of N_{bt} in water, where $p_{A\ max}$ is the maximum acoustic pressure amplitude. The probability of the phase change increases as N_{bt} increases, which agrees with the experimental results shown in Fig. 8.

Moreover, the probability of the phase change is relatively independent of ΔT in Fig. 9. This simulation results show the same tendency as the experimental results in Fig. 8. Generally, without ultrasonic vibration, the probability of the phase change from supercooled water to ice increased as ΔT was increased. However, when $\Delta T \leqslant 7$ K in this study, the probability of the phase change without ultrasonic vibration was 0 (verified in preliminary experiments). Therefore, the probability of the phase change when ultrasonic vibration is applied is relatively independent of ΔT, because physical properties (vapor pressure, viscosity, etc.) do not change significantly as ΔT changes from 1 to 7 K.

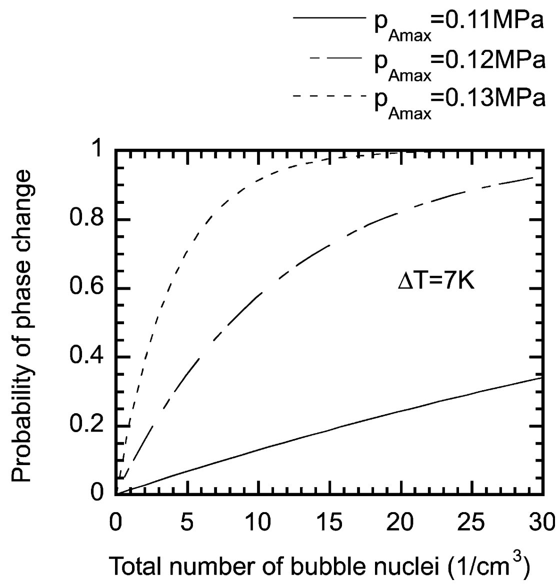

Fig. 10. Simulation of the probability of the phase change from supercooled water to ice as a function of total number of bubble nuclei N_{bt} for different maximum pressure amplitude $p_{A\ max}$.

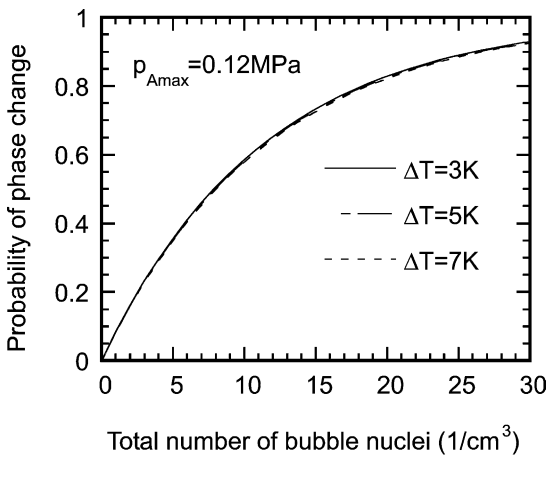

Fig. 9. Simulation of the probability of the phase change from supercooled water to ice as a function of total number of bubble nuclei N_{bt} for different degrees of supercooling ΔT.

The simulation results of the probability of the phase change from supercooled water to ice for different $p_{A\ max}$ as a function of N_{bt} in water (Fig. 10) show that the probability of the phase change is sensitive to $p_{A\ max}$. To fit the simulation results to the experimental results, we set $p_{A\ max}$ to 0.12 MPa. The simulation results (solid line in Fig. 8) agree with the experimental results qualitatively.

4. Conclusion

The conclusions of this study are as follows:

1. Ultrasonic vibration can generate a high number density of fine ice crystals from supercooled water within a short time, which is a result that is significant for practical applications of ice slurry.
2. The phase change from supercooled water to ice induced by ultrasonic vibration is mainly caused by the onset of acoustic cavitation. The probability of the phase change induced by ultrasonic vibration in-

creases as the total number of bubble nuclei increases, independent of the degree of supercooling for the experimental conditions studied here. Simulation results based on the cavitation-induced nucleation of solid agree well with the experimental results.

Acknowledgements

This study was supported by the Proposal-Based New Industry Creative Type Technology R&D Promotion Program from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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