

The Effect of Solution Pressure to the Release in a Supercooled Aqueous Solution

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Abstract

Supercooled type ice storage system with aqueous solution (or water) may have trouble with non-uniform release of supercooling even though it contributes to the simplicity of system and ecological improvement. The non-uniform release increases the instability of the system because it may cause an ice blockage in pipe or cooling part. In order to suppress the release of the supercooling, a cooling experiment was tried to an ethylene glycol(EG) 3 mass% solution corresponding with pressurization. Also, the frequency ratio of the release of the supercooling was measured to the pressurization from 101 to 505 kPa. At results, the frequency ratio of supercooling release tends to decrease as the pressure of the aqueous solution increased in each cooling rate. Moreover, it tends to decrease as the cooling rate of the solution decreased in each pressure.

Key words: Aqueous solution, Pressurization, Supercooling, Cooling rate, Freezing

Nomenclature

P Solution pressure [kPa]
 ΔT Supercooling degree [K]
 U Cooling rate [K/min]

1. Introduction

Supercooling is a natural characteristic in the freezing of the water or aqueous solution. Its control has an issue of refrigerating, which affects the conservation and storage of foodstuff in market and medical fluid in medicine. Especially, it has utilized in some ice thermal storage system(1,2). There are some merits of simplicity, sustainability, safety in storage media, high energy density, and transportability in the system. However, it is inevitable that the storage media should go through unstable supercooled state to make ice during cooling. And some disturbances, like as ice blockage or ice plugging, may occur to the system when the supercooling is released in the cooling part. On the release of supercooled water or aqueous solu-

tion, several studies were performed(3-8). Thijssen et al. showed that tap water has smaller supercooling degree than distilled water(3). Michelmores and Franks observed that on the supercooled aqueous solution the nucleation was inhibited by the polymer, polyethylene glycol(4). Saito and his group carried out supercooling of pure water with several parameters such as metal surface state(5). They reported that the supercooling degree increased as the roughness of cooling surface decreased. Saito's group, in addition, reported the independency of the size and amount of solid particle in supercooled water to freezing temperature(6), and the freezing of supercooled water under stronger ultrasonic wave(7).

Moreover, the air often escapes from and traps in the ice when water freezes in nature. Zhang et al. showed that the frequency of the release of the supercooling increases as the number of the air per unit volume in solution increases by using ultrasonic wave(8). And Hozumi et al. reported the dependency of the air to freezing of supercooled water in a static state(9). They showed that the air dissolved in water releases the supercooling when it separates from the

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water because of the air acting as a nucleus. The behavior, especially, may be taken out partially from water when a decrease of local pressure occurs with non-uniform flow. Regarding on the influence of the air in supercooled water to the freezing, the dissolution rate of air to water depends on temperature and pressure by Henry's law(1803) (10). Aiming at the relation that dissolution of air in water is proportional to the pressure, authors had obtained that a flowing ethylene glycol solution was supercooled stably in a pressurized cooling heat exchanger and ice slurry could be produced continuously to a remote ice storage tank *not in the heat exchanger*(11). Observing how the pressure affects to the static characteristic of supercooled solution can supply fundamental understanding to the system accompanying with solution cooling to below the freezing point. In this study, therefore, the effect of pressurization and cooling rate to the release of supercooling was observed to a static aqueous solution with a low-concentration during cooling.

2. Experiments

2.1 Experimental device

Fig. 1 shows the schematic of the experimental apparatus with measuring device. They consisted of cooling pressure vessel, low constant temperature bath, high pressure nitrogen gas vessel and circulating line. The cooling vessel with 250 mm×300 mm×5 mm ($\varphi \times H \times t$) stainless steel cylinder has 12 solution pouches on acrylic stand and a copper tube coil. Ethylene glycol(EG) aqueous solution has been used as a brine or a thermal storage material. Especially, the low concentration solution below 10 mass% has been well used in the ice thermal storage material. 12 enclosed pouches were installed in the cooling vessel. A pouch (70W×100H) was used to a half-divided one of a commercial retort pouch, which consisted of two compressed films of CPP(Casted Polypropylene, 80 μm) and PET(Polyester, 16 μm). The solution in each pouch consisted of a tap water mixing with a 3 mass% EG of 15 mL. After the solution was enclosed to each pouch, the margin of the pouch was sealed mechanically by a sealing machine. Also, the solution enclosed pouch was endured to the pressure of 1 MPa without leakage from pre-test. However, in the solution enclosed pouch, a little air pocket was found with the aqueous solution in spite of the effort of excluding it, which would dissolve to the solution till the satura-

tion point as the temperature decreases or the pressure increases. And it might affect to release the supercooling of aqueous solution as the nuclei when the air separates from the solution. Each pouch was put to an acrylic stand with 6 stems in radial direction. Every two pouches were fixed vertically to each stem of the stand. Fig. 2 shows the pouch and the acrylic pouch stand. As shown in Fig. 1, the pressure vessel was arranged in the brine of low temperature bath. On the other hand, some of the low temperature brine is circulated by brine pump(BP1) to the copper coil in the vessel. It helps to restrain heat intrusion from the side and bottom of the vessel. The top of the vessel was insulated with 5-*r* polystyrene foam.

The temperature of the brine and solution in each pouch were measured with every 2 seconds by T-type thermocouple and were acquired to a data logger(Agilent 34970A) and stored to PC as data. The measuring point of the temperature to the solution in each pouch was approximated to the surface layer of the pouch because thermocouple inserted pouch is too

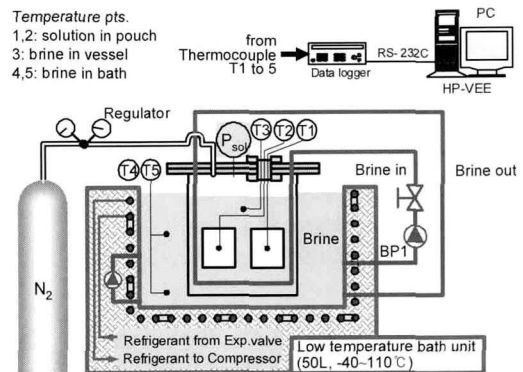


Fig. 1. Experimental apparatus.

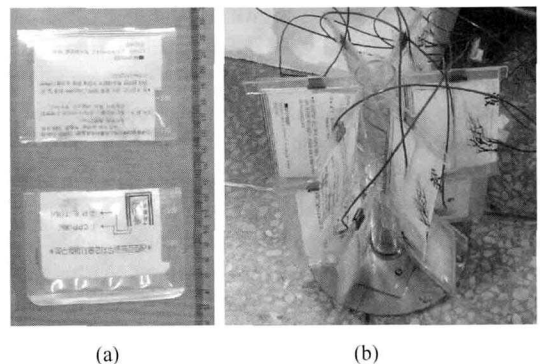


Fig. 2. (a) solution pouches (b) pouches fixing with acrylic stand.

weak to be broken up with pressurization. Then, each thermocouple was fixed closely on the outer surface of the pouch with epoxy resin and was covered with silicon sealant layer. The pressure in the vessel was measured with the eye from bourdon gauge on the top.

2.2 Experimental method

The bottom and outer side wall of the pressure vessel was cooled by the brine of the low temperature bath during solution cooling. At the same time, the 12 solution pouches were cooled by the brine in the cooling pressure vessel which was cooled by the circulating line from the bath. Cooling heat flux for the solution pouches was controlled by the brine pump(BP1) and the valve which was installed before the brine pump. It depends on brine temperature at a time. Thus mean cooling rate was introduced, which was defined as the temperature drop of the solution until to the release of supercooling divided by its cooling time.

When the pressure vessel is required to be pressurized, a high pressure is formed from the nitrogen gas vessel with regulator. The pressure of the vessel was set with five levels of 101, 202, 303, 404 and 505 kPa. The freezing point of 3 mass% EG solution used in the experiment was measured to -1.05°C which was coincident to the reference one of -1.1°C within 5 % errors (12). The solution cooling was stopped when the phase change from water to ice in the pouch occurred. On each pressure, the experiment was repeated 5 times or more. Table 1 shows the cooling condition.

Table 1. Cooling rate and solution pressure on experiment.

Cooling rate [K/min]	Pressure of solution [kPa]
0.10	101
0.13	202
0.14	303
0.16	404
	505

3. Experimental results

3.1 Cooling rate

Fig. 3 shows the temperature of solution measured at the pouch surface when the solution was cooled with cooling rate of 0.16 K/min under the solution pressure of 505 kPa. The temperature of the pouch increased abruptly about 40 minutes later from the start of cooling. It shows supercooled solution was

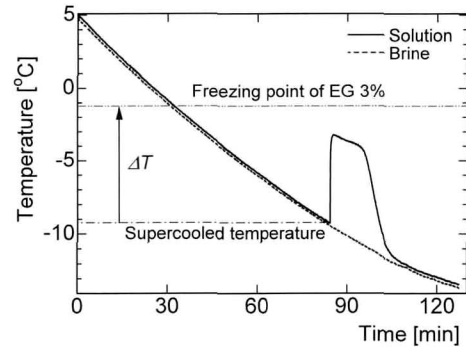


Fig. 3. Supercooling degree and release of supercooled solution ($U = 0.1$ K/min, $P = 505$ kPa).

released and the ice was formed. At that time, there exists a difference between the maximum temperature after releasing and the freezing point. It is predicted to two reasons as following; First, the ice product(the amount of latent heat) is not enough to increase the temperature of other supercooled solution to the freezing point so that the temperature of all the supercooled solution can not reach to the freezing point. Second, the heat transfer from the thermocouple to low temperature brine is greater than that from the formed ice to the thermocouple. Let us define the supercooling degree(ΔT) to the difference between the freezing point and the temperature right before releasing of supercooled solution. Also, Frequency ratio is defined as the ratio of the number of the pouches which were released in each supercooling degree section during cooling, to the total number of pouches(all the pouches were released) under a constant cooling rate and solution pressure. And it was obtained from the number of released pouch to each section which divided the range of supercooling degree from 5 to 12 K into 14 equal parts. Fig. 4 shows the variation of averaged supercooling degree of the solution to cooling rate in each solution pressure, which was obtained from averaging those supercooling degrees in each cooling rate. The arithmetic mean of data in each cooling rate was shown to circle. The absolute deviations of all readings were distributed from 0.26 to 1.06 K. Although the deviations were shown in all the data and larger deviations were shown in low cooling rate of 0.1 K/min, the averaged supercooling degree increased as the cooling rate decreased to each solution pressure. Furthermore, the overall increase of mean supercooling degree during the cooling degree from 0.1 to 0.16 K/min became large as the solution pressure increased from 101 to

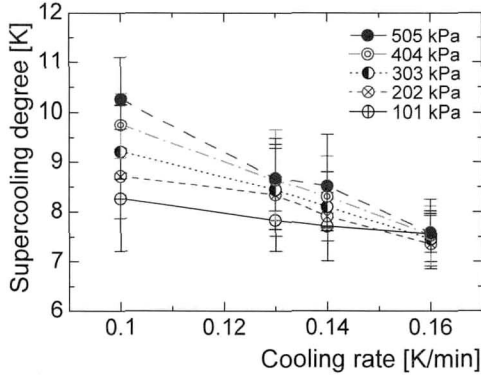


Fig. 4. The relation between the cooling rate and the supercooling degree.

505 kPa. In detail, frequency ratio of supercooling release in each section of supercooling degree range was compared to the variation of cooling rate. Local frequency ratio was defined to the number of released solution in each supercooling degree section to the total number(30 samples) in each cooling rate. Fig. 5 shows the frequency ratio plotted cumulatively with each section of supercooling degree to each cooling rate under a pressure. Also, they are displayed in order with pressure. From the figure, in the supercooling degree section comparatively lower than that from 8 to 9 K the local frequency ratio increased as the cooling rate increased. On the other hand, in the supercooling degree section higher than that from 8 to 9 K the local frequency ratio decreased. And the trend of the increase of supercooling degree to the decrease of the cooling rate agreed with the result of Fig. 4, qualitatively. This supports that the frequency of the number of the nuclei(air) generation which connects to supercooling release, tended to increase faster as the cooling rate increased relatively(8, 9). The trend that the release of supercooled water was more suppressed as cooling rate was smaller, is also consistent with the release of supercooling of water to cooling rate(5).

Fig. 6a shows the distribution of local frequency ratio to the supercooling degree in each cooling rate. The frequency ratio was plotted cumulatively with pressure to each supercooling degree section under a cooling rate. The cumulative frequency ratio was nearly formed to a shape of distribution function and had maximum cumulative frequency ratio in each cooling rate. As the cooling rate increased, it was shifted gradually from right to left on the supercooling degree axis. Besides, the width of the occurrence

in supercooling degree was getting narrow with the increase of the cooling rate.

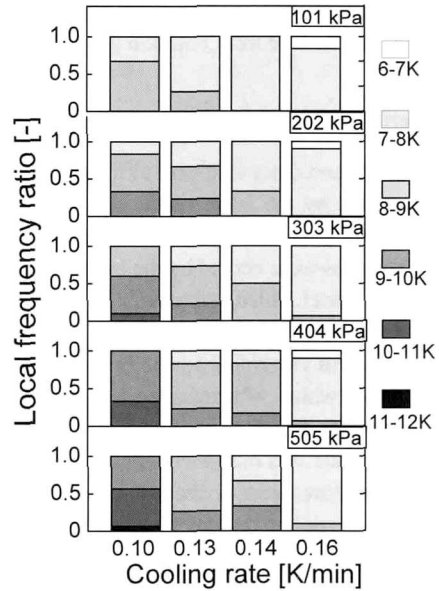


Fig. 5. Distribution of frequency ratio to cooling rate including supercooling degree.

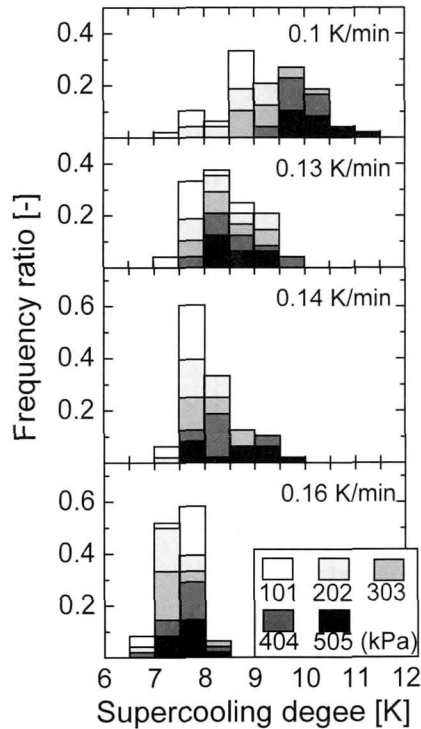


Fig. 6. The distribution of the frequency of supercooling release to the supercooling degree in each cooling rate.

3.2 Pressure of solution

Fig. 7 shows a trend dispersed but increased supercooling degree as shown in Fig. 4 when the cooling rate was 0.1 K/min. There were dispersions with 10 to 12 data for each pressure. Even though it shows a characteristic of supercooling as stochastic data, the supercooling degree was found to be dependant to solution pressure, i.e. the supercooling degree increased as the solution pressure increased. In order to find clearly the effect of the solution pressure to the distribution of supercooling degree, all the obtained supercooling degree to the cooling rate was averaged in each solution pressure and cooling rate. Fig. 8 shows the arithmetic mean of supercooling degree of the solution with dispersion to the solution pressure by using the data of Fig. 4. The mean in each solution pressure was shown to square, circle, triangle and inverse triangle to the cooling rate of 0.1, 0.13, 0.14 and 0.16 K/min. Even though the data is equal to Fig. 4, the mean increased as the solution pressure increased in each cooling rate. Especially, the trend of the increase in the supercooling degree was different from that in the cooling rate of 0.16 K/min which was nearly equal to all the solution pressure in the experiment. It shows that the effect of the solution pressure to the suppression of the supercooling is weaker as the cooling rate increases. Fig. 9 shows the effect of the solution pressure to the frequency ratio of release in each supercooling degree. When the cooling rate was 0.1 K/min of Fig. (a), the distribution of local frequency was nearly normal with five supercooling sections. However, it became to concentrate on a supercooling degree section as the cooling rate increased. It is interesting that the supercooling degree region from 7 to 8 K in Fig. (d) was dominant at the cooling rate of 0.16 K/min. And it agreed to the

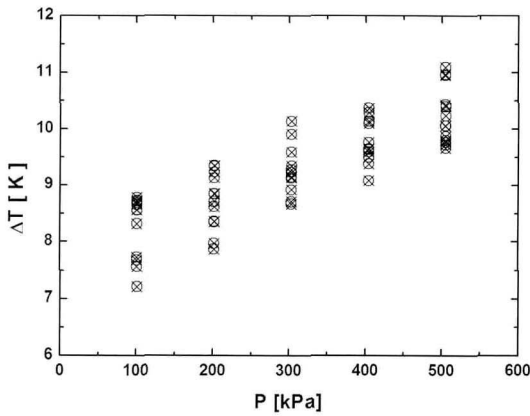


Fig. 7. The data of supercooling degree to the solution pressure ($U=0.1$ K/min).

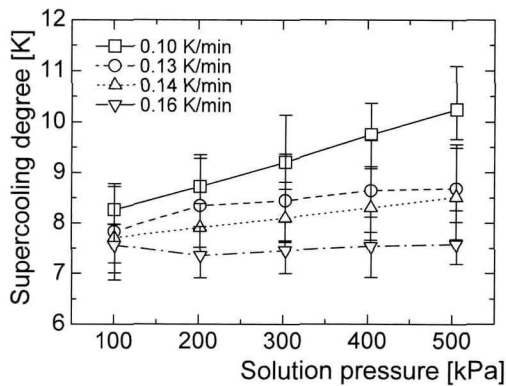


Fig. 8. The averaged supercooling degree having dispersion to solution pressure in each cooling rate.

and 0.16 K/min. Even though the data is equal to Fig. 4, the mean increased as the solution pressure increased in each cooling rate. Especially, the trend of the increase in the supercooling degree was different from that in the cooling rate of 0.16 K/min which was nearly equal to all the solution pressure in the experiment. It shows that the effect of the solution pressure to the suppression of the supercooling is weaker as the cooling rate increases. Fig. 9 shows the effect of the solution pressure to the frequency ratio of release in each supercooling degree. When the cooling rate was 0.1 K/min of Fig. (a), the distribution of local frequency was nearly normal with five supercooling sections. However, it became to concentrate on a supercooling degree section as the cooling rate increased. It is interesting that the supercooling degree region from 7 to 8 K in Fig. (d) was dominant at the cooling rate of 0.16 K/min. And it agreed to the

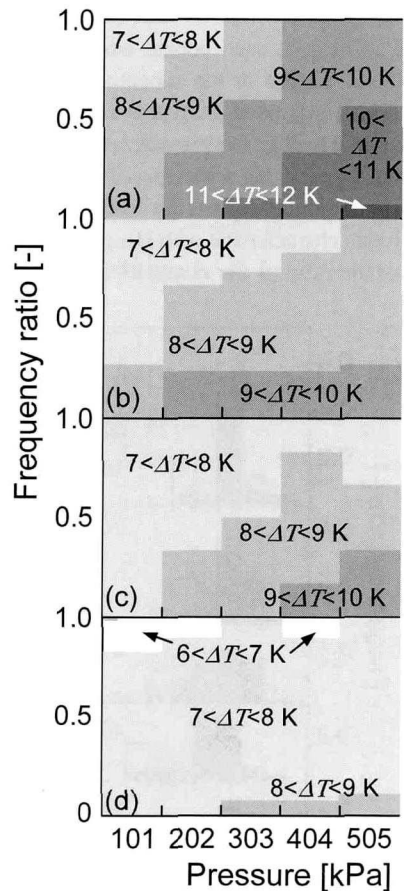


Fig. 9. The frequency ratio to the solution pressure with the supercooling degree (a) 0.1 K/min (b) 0.13 K/min (c) 0.14 K/min (d) 0.16 K/min.

nearly constant supercooling degree of 7.5 K in Fig. 8. At results, the supercooling degree of solution increased as the solution pressure increased under lower cooling rate. And this shows the pressurization of a supercooled aqueous solution under lower cooling rate increases the suppression of the supercooling release. Fig. 10 shows the distribution of local frequency ratio to the supercooling degree in each solution pressure. The frequency ratio was plotted cumulatively with cooling rate to each supercooling degree section under a pressure. The cumulative frequency ratio was nearly formed to a shape of distribution function with the maximum near the supercooling degree of 8 K. As the pressure increased, the maximum frequency was smaller but the release of supercooling occurred at wider range, i.e. supercooling degree increased. This shows the pressurization of aqueous solution is effective to suppress the release of supercooling. At the beginning of enclosing the solution to the pouch, a little air was included with the aqueous solution in each pouch, which would contribute to the release of the supercooling. Although the air which separated from the solution was not measured at freezing, the pressurization to the solution would suppress the separation of the air from the supercooled solution and would lead to more stabilized solution characteristic with Henry's law(10). Fig. 11 shows the ratio of the cumulative frequency that

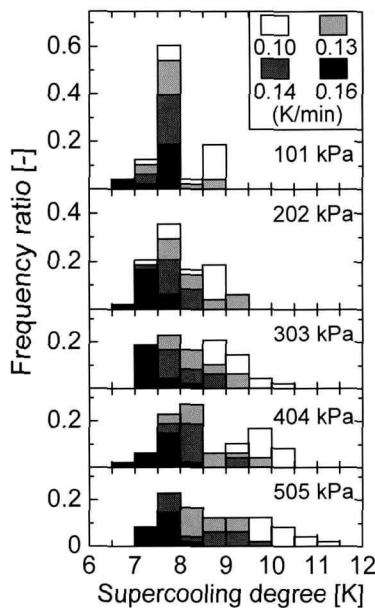


Fig. 10. The distribution of the frequency of supercooling release to the supercooling degree in each solution pressure.

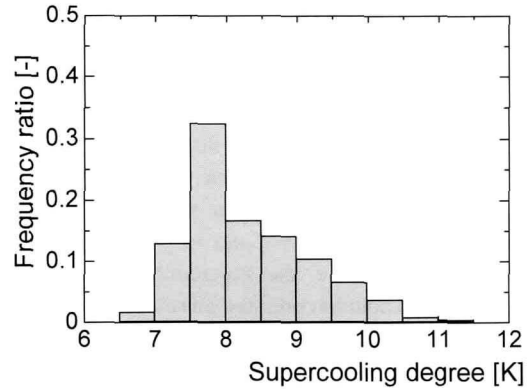


Fig. 11. The relationship between supercooling degree and cumulative frequency ratio with all cooling rate and solution pressure.

counted the cumulative number of frequencies in all of the cooling rates and pressures to the supercooling degree section from 6 to 12 K. The frequency ratio was formed to a pattern of probability distribution function with the maximum of 32.5% at the supercooling degree section from 7.5 to 8 K.

4. Conclusion

On the release of 3 mass% of EG supercooled aqueous solution, the following conclusion (1) and (2) was obtained to the effect of the cooling rate from 0.1 to 0.16 K/min and (3) to (5) to the solution pressure from 101 to 505 kPa. And the experiment was performed to a typical supercooling as shown in conclusion (6).

(1) the averaged supercooling degree increased as the cooling rate decreased to each solution pressure. And the release of supercooled water was more suppressed as cooling rate was smaller. (2) As the cooling rate increased, maximum cumulative frequency ratio was shifted gradually from right to left on the supercooling degree axis. Moreover, the width of the occurrence in supercooling degree was getting narrow with the increase of the cooling rate. (3) The supercooling degree or mean supercooling degree generally increased as the solution pressure increased in each cooling rate. And the pressurization of a supercooled aqueous solution under lower cooling rate increases the suppression of the supercooling release. (4) The cumulative frequency ratio was nearly formed to a shape of distribution function with the maximum near the supercooling degree of 8 K. (5) As the pressure increased, the maximum frequency was smaller

but the release of supercooling occurred at wider range, i.e. supercooling degree increased. (6) The cumulative frequency ratio in all of the cooling rates and pressures was formed to a pattern of probability distribution function with the maximum of 32.5% at the supercooling degree section from 7.5 to 8 K.

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