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Suppressing Method of Supercooling State in Cool Box Using Membrane

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1. Introduction

1.1 Usage of cool box

In the area of food transportation, demand for cool boxes is increasing. There are many types of cool box which differ mainly by changing the melting temperature of refrigerant. Fixing of the melting temperature can be designed by arranging the composition of water and refrigerant and its concentration. In general, inorganic salt solutions such as sodium chloride, ammonium chloride or magnesium chloride are selected as the base and alcoholic solution such as methanol or ethanol and gelatinizing agent are added. To simplify the phenomena, sodium chloride solution is used in this research. Refrigerant in the cool box is necessary to be frozen before the use in order to store the latent heat. The stored energy is much bigger than the sensible heat. Growing demand for low freezing temperature use is rising. However, it is difficult to meet the need because of the existence of supercooling phenomenon.

1.2 Natural freezing with supercooling

When the solution is cooled down below the freezing temperature, liquid state remains which is called the supercooling state. The difference between the temperature when freezing occurred and the melting temperature is called the degree of supercooling at freezing. It is a statistical phenomenon and so it varies even the conditions are identical. It also depends on the volume and the cooling rate.

Fig. 1 shows one of the examples of natural freezing using sodium chloride solutions. Volume of solution is 0.1 ml and the cooling rate is 0.25 K/min. 20 experiments were carried out for each concentration and the average values were plotted.

Table 1 shows the melting temperature for each concentration of the solution (JSME, 1983). For example, for 10 wt% solution, the solution needs to be cooled down to -23.3 ^{o}C to obtain solidification. In a case of the cool box, since the volume and the cooling rate are different from the experimental conditions above, it needs to be installed in refrigerator having around 10 K below its melting temperature. The majority of domestic refrigerators only cool down to -18 ^{o}C. So consequently, one having melting temperature of around -10 ^{o}C has been a majority among all. Moreover, freezing of supercooled liquid is a statistical phenomenon, and so it needs around two days to assure the solidification. On the other hand, the demand for cool box with lower melting temperature is increasing and it leads to the necessity of installing another refrigerator with higher capacity.

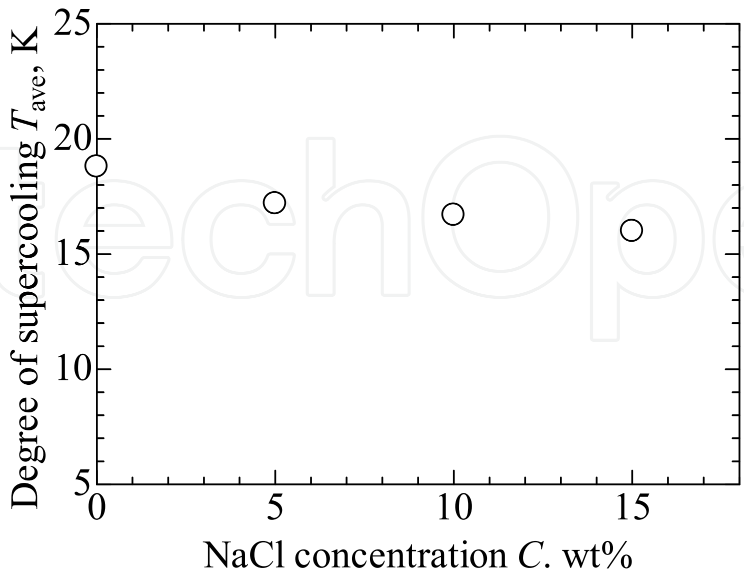


Fig. 1. Average degree of supercooling at freezing versus concentration of NaCl solution

Concentration of NaCl	melting temperature	average degree of supercooling at freezing	average temperature for freezing
0 wt%	0.0 °C	18.8 K	-18.8 °C
5 wt%	-3.046 °C	17.2 K	-20.3 °C
10 wt%	-6.564 °C	16.7 K	-23.3 °C
15 wt%	-10.888 °C	16.0 K	-26.9 °C

Table 1. Melting temperature of NaCl concentrations and its average temperature for freezing (JSME, 1983)

In usual thermal cycle, such as a power plant, high efficiency can be obtained when there is a big temperature difference between the high temperature reservoir and the low temperature reservoir. So a lot of kinetic power can be obtained. In a case of refrigerant cycle, the situation is opposite. In order to obtain a big temperature difference, a high energy is required. Therefore, to obtain the low temperature, COP (coefficient of performance) becomes low. A lot of work needs to be done by a compressor to obtain the low temperature. It increases not only the cost of installation but also the electrical load consumption. Therefore, it is necessary to find a method to induce solidification of supercooled refrigerant.

1.3 Various methods to induce solidification of supercooled solutions

There are many researchers performed experiments to induce solidification. Collision or rubbing of solids or liquid in supercooled liquid induce solidification (Saito et al., 1992). Electrical charge on solidification of supercooled liquid is effective (Shichiri & Araki, 1986; Okawa et al, 1997, 1999; Hozumi et al, 2005). Applying ultrasonic wave to induce freezing of supercooled liquid is effective (Hozumi et al., 1999, 2002a, 2002b; Inada et al., 2001). A method to predict the degree of supercooling when Silver Iodide particle is used as nuclei was introduced (Okawa et al., 2001).

1.4 Purpose

A capsule having a wall made of ion exchange membrane and containing water inside was invented (Okawa et al., 2010a, 2010b), so only water can go through it. By installing the capsule in cool box, water in a capsule freeze first because of higher melting temperature and the membrane becomes a trigger for refrigerant to freeze with very low degree of supercooling. Refrigerant package as cool box consists of a thermal storage material which has low melting temperature. By installing similar liquid material which has higher melting temperature into the refrigerant package, the liquid material with higher melting temperature freezes first and it becomes a trigger for refrigerant to freeze. Liquid material with higher melting temperature in a capsule is isolated from refrigerant by using a membrane to separate with. Hence only water can go through between the liquid material and refrigerant. The purpose of this research is to clarify the ice propagation phenomena using 3 different kinds of membranes, experimentally.

2. Type of membrane

2.1 Ion exchange membrane

There are many types of membranes used for liquids. Microfiltration membrane is for eliminating microorganisms or particles having the size around 0.1 μm to 1 μm. Uultrafiltration membrane is for eliminating particles or polymers having the size around 2 nm to 0.1 μm. Nanofiltration membrane is for eliminating particles or polymers having the size smaller than 2 nm. Reverse osmosis membrane is for desalination of sea water and waste water treatment. Dialysis membrane is for hemodiafiltration. Ion exchange membrane is for Polymer Electrolyte Fuel Cell (PEFC), Biological Fuel Cells, ultrapure water, desalination, demineralization and so on.

There are two types exist for ion exchange membrane. One is cation exchange membrane and the other is anion exchange membrane.

Using Laplace equation $p_1 - p_2 = \frac{2\gamma_{iw}\cos\theta}{r}$ and Gibbs-Duhem equation $d\mu = -SdT + vdp$, the following equation can be obtained (Ishikiriyama, 1995).

$$\Delta T = \frac{2\gamma_{iw} v_w T_0 \cos\theta}{r L}$$

where ΔT is the depression of the melting temperature, γ_{iw} is the surface energy between liquid water and solid ice, v_m is the molar volume of water, T_0 is the melting temperature, θ is a contact angle, r is pore radius, L is the latent heat of fusion per mole, μ is the chemical potential, S is the entropy, p is the pressure. As shown in Fig. 2, the equation gives the results that ΔT=45.4 K for pore size 1 nm and ΔT=4.5 K for 10 nm.

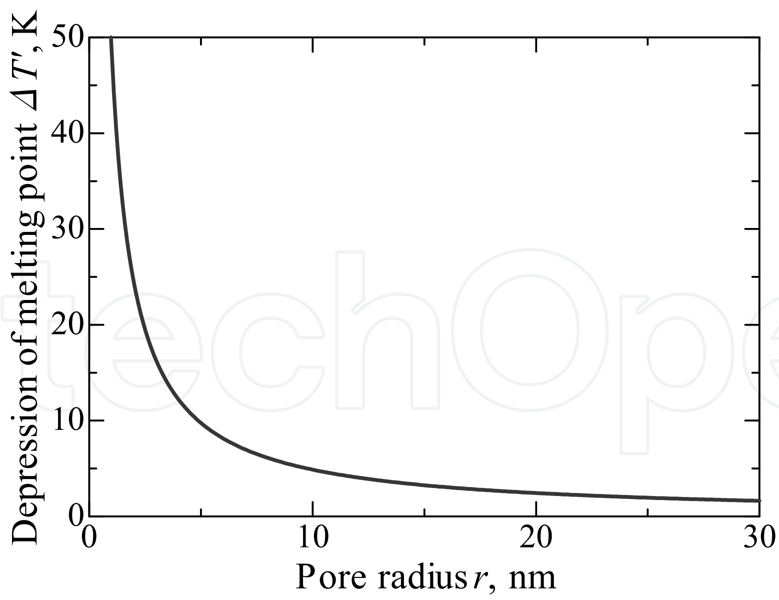


Fig. 2. Depression of the melting temperature due to a narrow space

Cation exchange membranes and anion exchange membranes with various thicknesses were used.

2.2 Porous elastic polymer membrane

The second membrane was made of porous elastic polymer material made by foaming. It is elastic and each pore is ideally independent to each other with cracks between them as shown in Fig. 3. So it is only semi-permeable when the membrane is expanded.

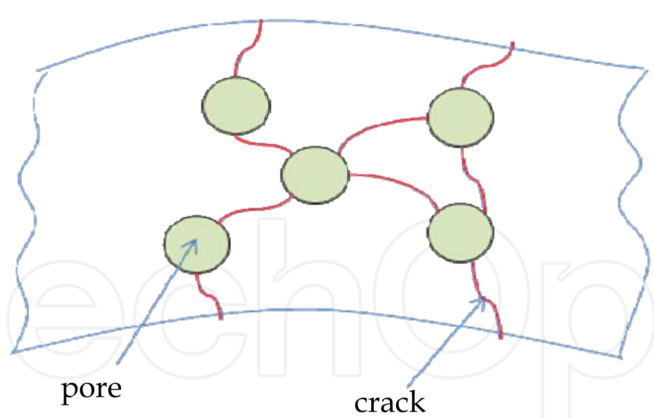


Fig. 3. Image of the cross section of porous polymer membrane

2.3 Styrene elastomer membrane

The third membrane was made of elastic polymer (thermoplastic elastomer) with a small hole in it. The material is chemical resistance to alcohol since a small amount of alcohol is in the contents of refrigerant. It has a high elongation and adequate tensile strength to keep water inside the capsule, especially at a low temperature. It is adhesive so the hole is closed when there is no volumetric expansion.

3. Propagation through ion exchange membrane

3.1 Experimental apparatus and experimental method

The type of ion exchange membrane tested in the research is shown in Table 2. Two types of cation exchange membranes and three types of anion exchange membranes were used. The purpose of the experiment was to check whether ice propagates through ion exchange membrane. The apparatus is shown in Fig. 4. The membrane was placed between two cells, namely the upper cell and the lower cell. Several kinds of concentration of NaCl solutions were prepared for both cells. The apparatus was kept under a constant temperature and artificially the nucleation was started in the upper cell under the supercooling state by installing the ice particle from the top of the needle as shown in Fig. 4. The ice gradually grew inside the needle and a single crystal ice appeared at the tip of the needle. Temperature of the solution in the upper cell was measured directly by inserting the thermocouple, and the temperature of the solution in the lower cell was measured indirectly from the outer surface of the cell to avoid natural nucleation due to the existence of the thermocouple. It was confirmed that there is almost no change in concentration during a series of experiments.

Type	Cation exchange membrane		Anion exchange membrane		
name	CMT	CMV	AMT	AMV	DSV
thickness(μm)	220	130	220	130	100
Water content ratio	0.28	0.27	0.21	0.22	0.29

Table 2. Type of ion exchange membrane

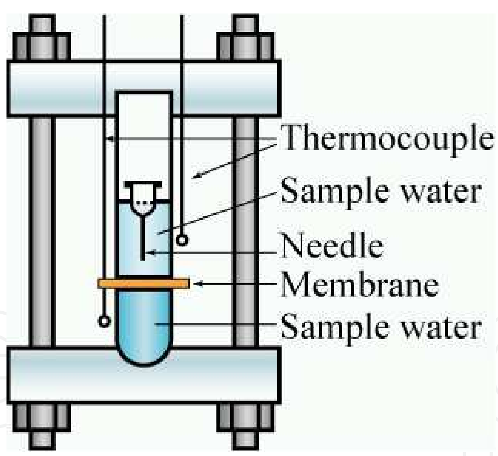


Fig. 4. Experimental apparatus

3.2 Results and discussions

Fig. 5 shows the results obtained. The abscissa shows the time after the ice touching the upper surface of the membrane. The ordinate shows the probability of propagation of ice to the lower cell. There were three degrees of supercooling tested, namely, ΔT=3 K, 5 K and 7 K. As it can be observed from the figure, the only CMV membrane propagated ice. This is a cation exchange membrane with thin thickness. So, it can be said that a thin cation exchange membrane is better.

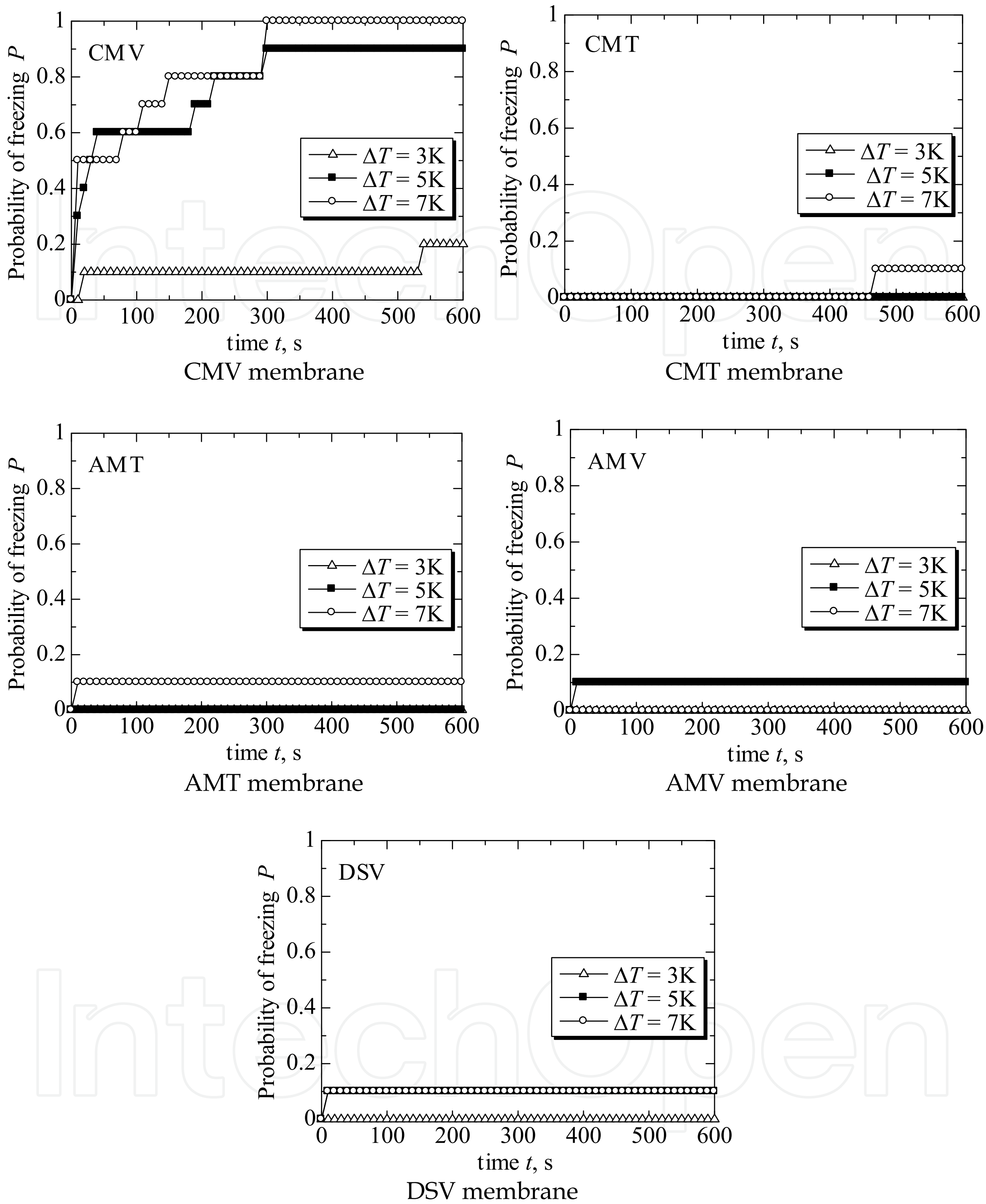


Fig. 5. Time wise variation of probability of propagation using various ion exchanger membranes

It may have a problem of durability.Since there is a volumetric expansion due to solidification, the capsule needs to have a function to absorb the volumetric change. Fig. 6 shows some of the example of having rubber material on the other side of the capsule. It has a demerit since the device becomes a little bit complicated.

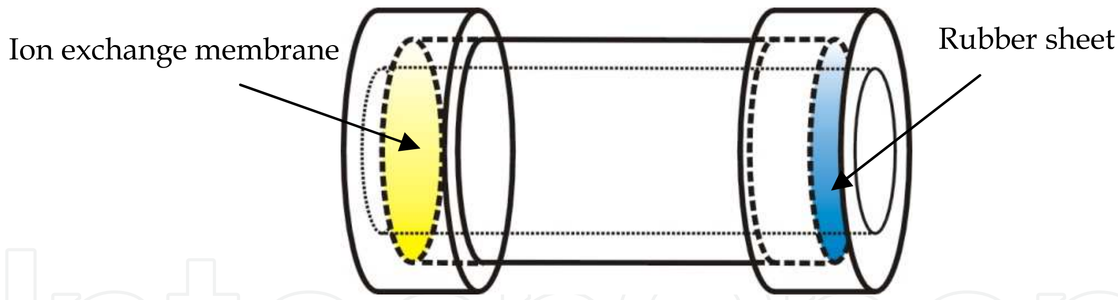


Fig. 6. Example of capsule having an ion exchange membrane on one side and a rubber sheet on the other side

4. Porous polymer material made by foaming

In order to solve the problem of complexity, an elastic porous membrane was selected. It is a porous polymer material made by foaming. Similar experiments to the one using the ion exchange membrane were carried out using the membrane. The results are shown in Figs. 7 & 8. Fig. 7 is for 10 wt% NaCl solution having the melting temperature of -6.56 ^{o}C and Fig. 8 is for 15 wt% NaCl solution having the melting temperature of -10.89 ^{o}C. It can be seen that in the case of 10 wt%, when water in the upper cell solidified, the temperature in the upper cell jumped to the melting temperature. However, since the solution in the lower cell was already in the supercooling state, ice propagated immediately with low degree of supercooling. In the case of 15 wt%, when water in the upper cell solidified, the temperature in the lower cell was above the melting temperature, so no propagation occurred at this stage. After the temperature reached down below the melting temperature for the solution, the ice propagated immediately with a low degree of supercooling.

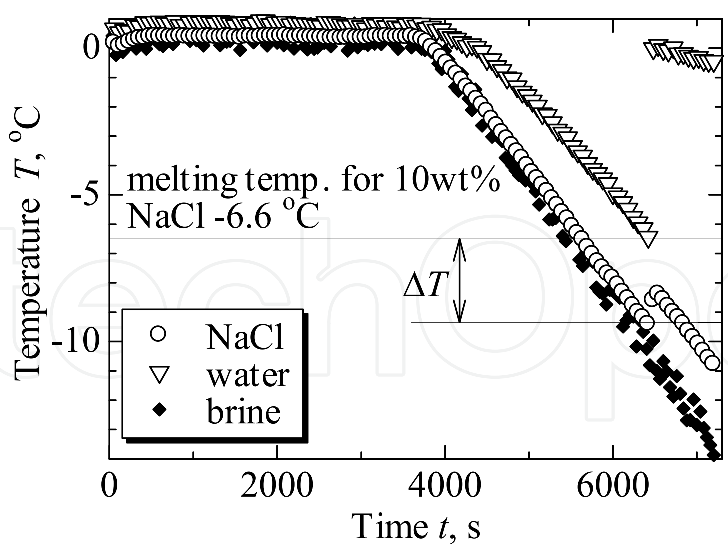


Fig. 7. Experimental result of propagation using porous polymer membrane with 10 wt% NaCl solution

Influence of the cooling rate on propagation of the ice was examined. Under two kinds of cooling conditions, temperature of the solution in the lower cell may differ to each other at the time of propagation. It is due to the existence of thermal resistance of the capsule. So the phenomenon was confirmed by the following method. The water in the upper cell was completely frozen and the whole apparatus was kept at the melting temperature of the solution in the lower cell. Then, experiments were started with constant cooling rates. The results are shown in Fig. 9. In both cases, there were ice propagations in 80 % of the experiments and the natural freezing in the lower cell occurred in 20 %. Fig. 9 shows that there is no difference in the degree of supercooling at propagation by changing the cooling rate. Hence it was found that the temperature of the membrane is the important factor for propagation of ice.

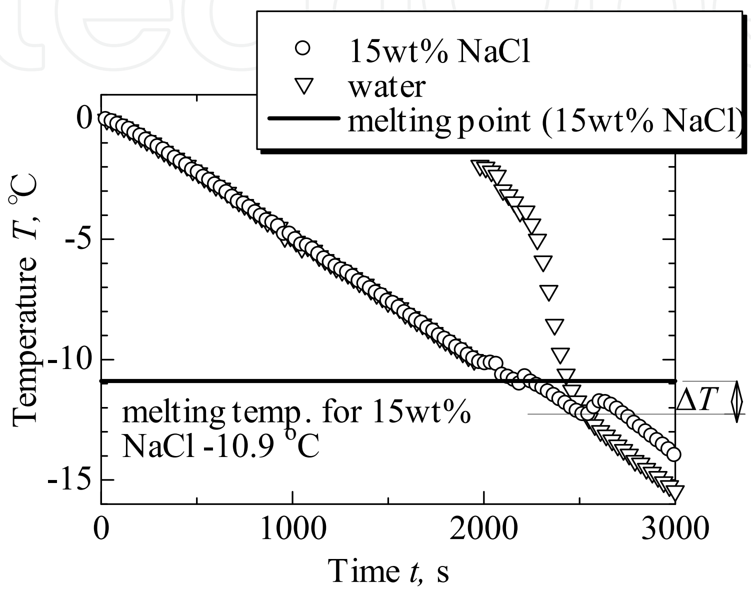


Fig. 8. Experimental result of propagation using porous polymer membrane with 15 wt% NaCl solution

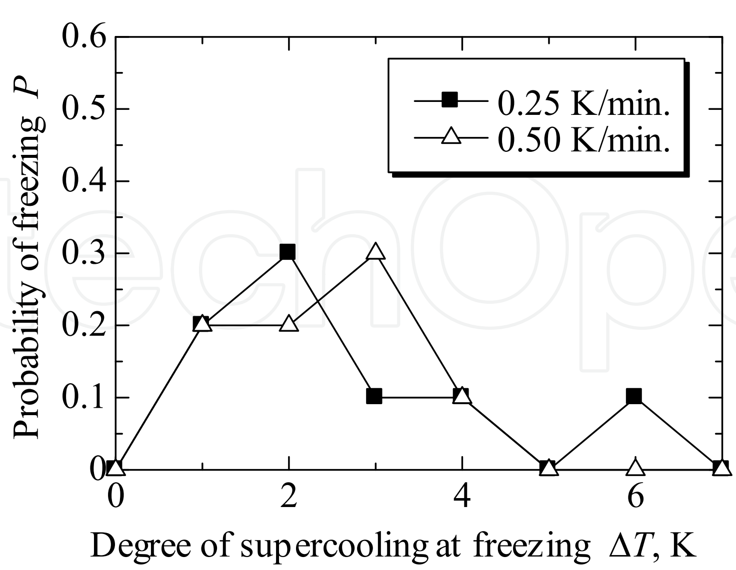


Fig. 9. Probability of propagation under two different cooling rates

By varying the location of ice appearance in the upper cell, it was found that the time taken for propagation of the ice and the probability of propagation are strongly influenced by the location of the ice appearance in the capsule. Especially when liquid in the upper cell was a solution, the probability of propagation became low when the ice appeared at the location far away from the membrane. The reason seems to be that the temperature in the upper cell rises above the melting temperature for the lower cell and also concentration in the upper cell near the membrane becomes higher due to the elimination of solute from the ice during the solidification. Hence the melting temperature in the upper cell becomes lower which leads to a decrease of the degree of supercooling in the upper cell.

Capsules were made using porous polymer membrane. The material can easily be melted by heating, so as shown in Fig. 10, one sheet of membrane was put on top of the other having a spacing material between them. The reason for the spacing material to put between them was to avoid water in the capsule to be vanished away from the capsule due to the osmotic pressure. The circumference was sealed by heating. Air in the capsule was removed from the pipe and water was installed instead. The thermocouple was inserted from the pipe as well. The diameter of the membrane was 25 mm.

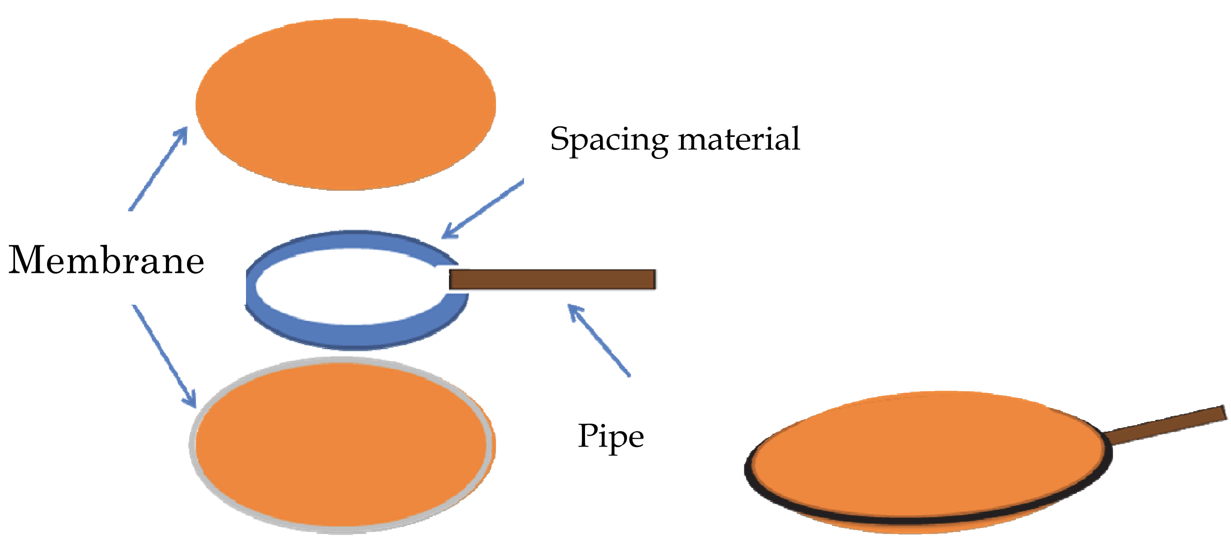
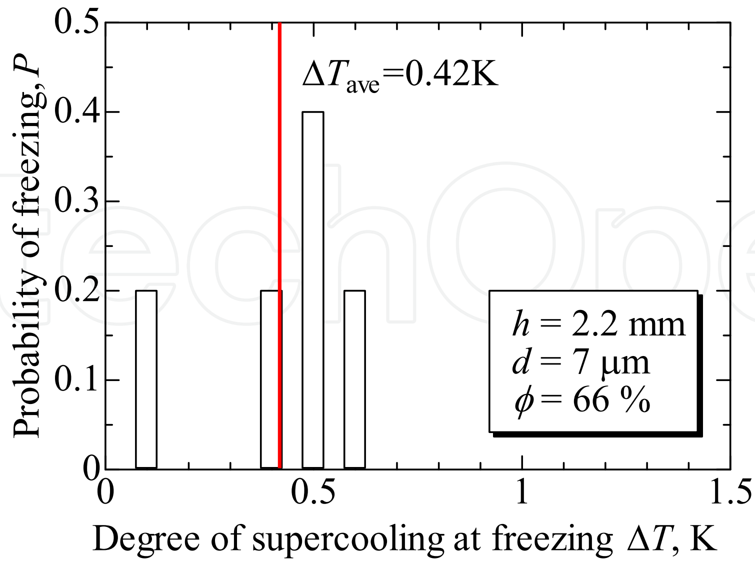


Fig. 10. Capsule made of porous polymer membrane

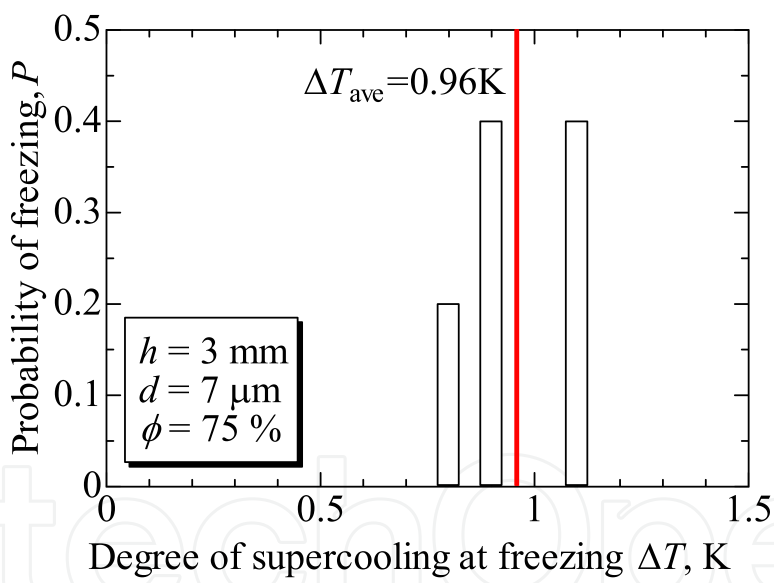
100 ml of 15 wt% of NaCl solution was put inside the beaker and the capsule was installed in the solution. The beaker was cooled down with a constant cooling rate and the temperature at ice propagation was measured. Two types of membranes were selected. One membrane had a thickness of 2.2 mm, the average pore size of 7 μm and the porosity of 66 %. The other membrane had a thickness of 3 mm, the average pore size of 7 μm and porosity of 75 %.

The results are shown in Fig. 11. The figure shows the frequency distribution against the degree of supercooling at propagation. It can be seen that in both cases, propagation occurred at around 1 K of the degree of supercooling. So it can be said that the capsule is effective.

The instant of propagation was observed. The typical example of the propagation was shown in Fig. 12. The camera was set at the side of the capsule in order to observe the ice appearance on the membrane. It can be seen that ice grew slowly from the membrane.



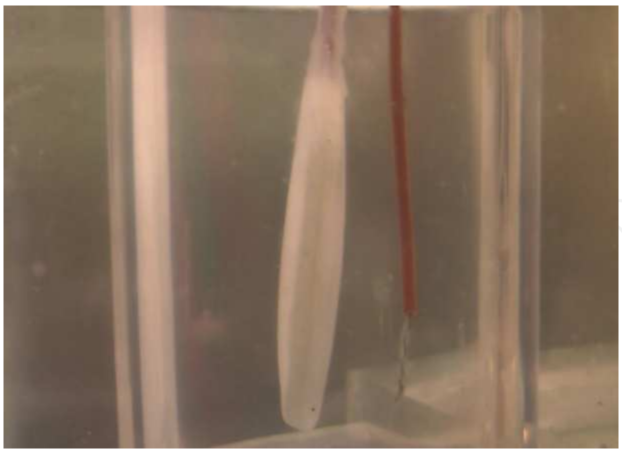
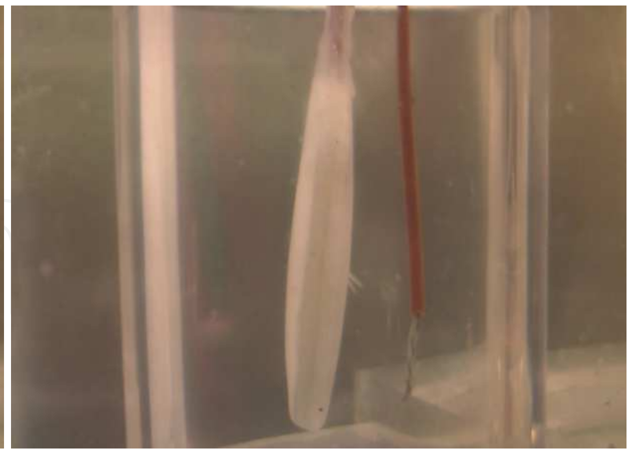
(a)



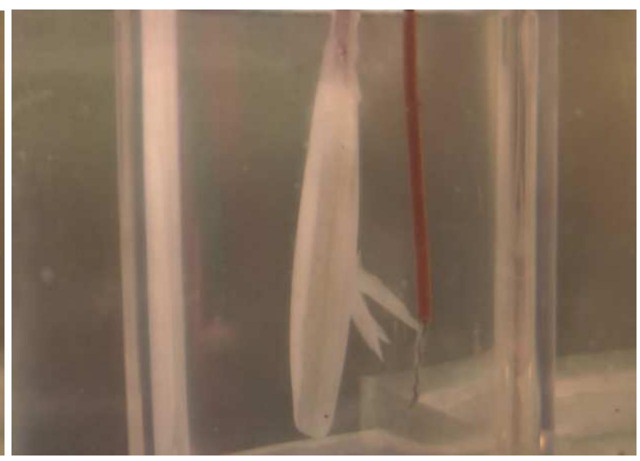
(b)

Fig. 11. Frequency distribution of ice propagation through porous polymer membrane

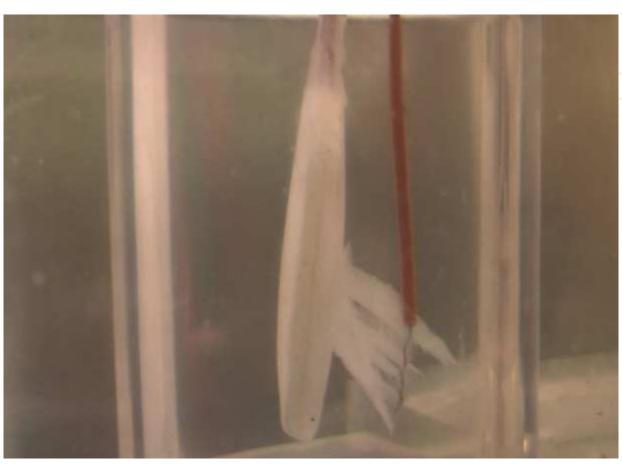
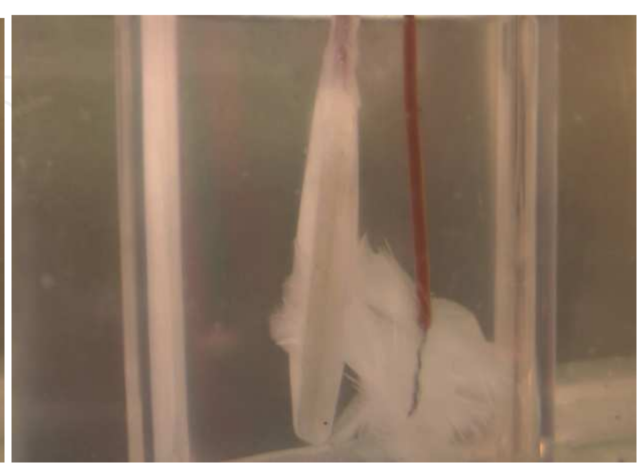
Fig. 13 shows a typical example of the difference with and without using the capsule. It can be seen that the installation of the capsule was effective for propagation of ice. Fig. 14 shows a typical example of the performance under the repeated use of the capsule. It can be seen that the capsule is effective for a repeated use. However, by repeating the experiment and measuring the concentration inside the capsule, it was found that there was an individuality in the quality of the membrane, such as pore size and the distribution of the pore in the membrane. So, it was rather difficult to produce a membrane with a constant quality.

(a) 0min (b) 1min

(c) 2min (d) 3min

(e) 4min (e) 5min

Fig. 12. Typical example of photos during propagation

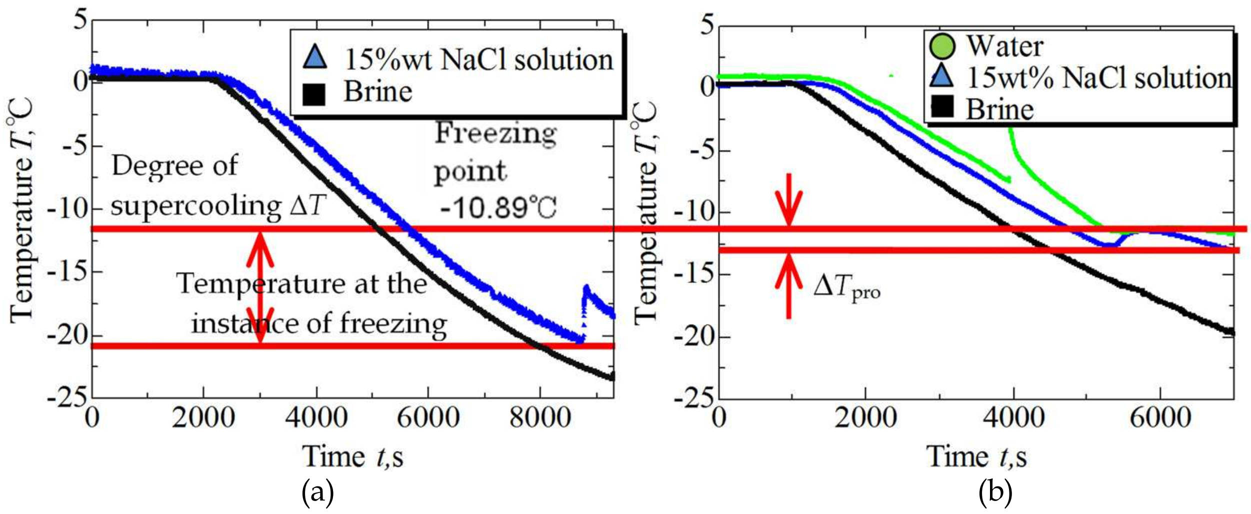


Fig. 13. Typical example of freezing of solution with and without capsule (a) without capsule, (b) with capsule

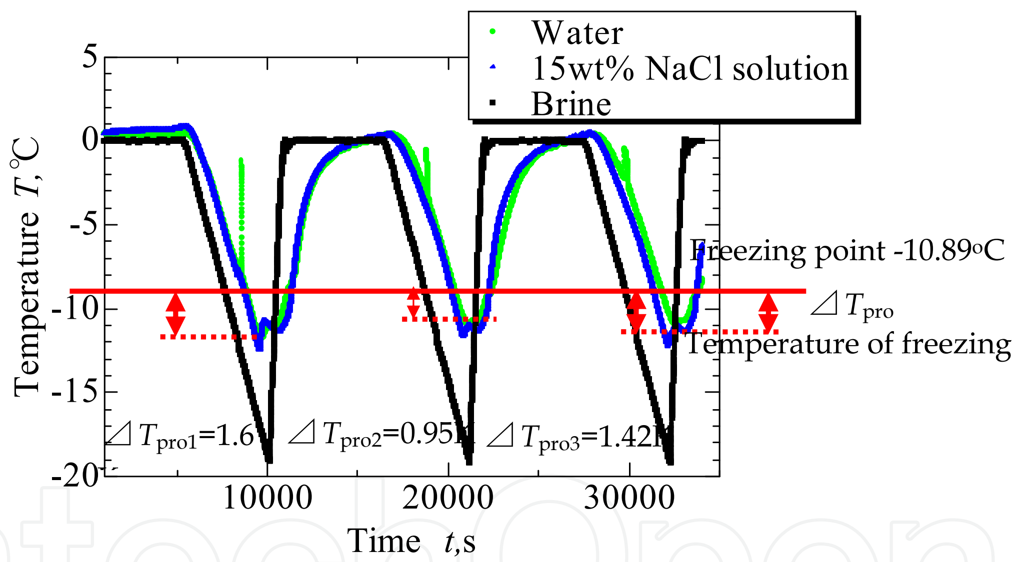


Fig. 14. Typical example of the performance under the repeated use of the capsule

5. Styrene elastomer membrane with pinhole

The details of the capsule are shown in Fig. 15. The main body of the capsule is made of polypropylene tube. The open part of the two tubes was facing to each other having 2 mm gap between them. Then styrene elastomer membrane with several pinholes was rolled to cover the gap. The membrane can easily be melted by heating, so it can be glued together. The styrene elastomer has a phenomenon that it is elastic at a low temperature. So, the membrane was enlarged in one direction up to 300 % and 6 holes having 0.4 mm diameter were created. It was confirmed that the hole was closed under the condition of no enlargement, and the elasticity was kept at the low temperature.

The logic of the propagation of freezing using the capsule is explained as follows. There is a difference in melting temperature between the refrigerant in a cool box and water in the capsule. After installing the capsule in the cool box, the cool box is cooled down. Then the water in the capsule starts to freeze first because the melting temperature is higher. When the temperature in the cool box reaches the melting temperature of refrigerant, the water in the capsule is frozen completely. The volume of the capsule is expanded due to phase change of the water contained inside. So, the membrane is expanded and ice in the capsule is uncovered to the refrigerant through pinhole. Then the pinhole becomes a trigger for the refrigerant to freeze with a low degree of supercooling.

Experiments were carried out by preparing 100 ml of 15 wt% of NaCl solution in a beaker. The capsule was also installed inside the solution. Temperature inside the capsule and the solution near the capsule were measured. The melting temperature of the solution was -10.89 ^{o}C. The solution in the beaker was cooled down with a constant cooling rate of 0.15

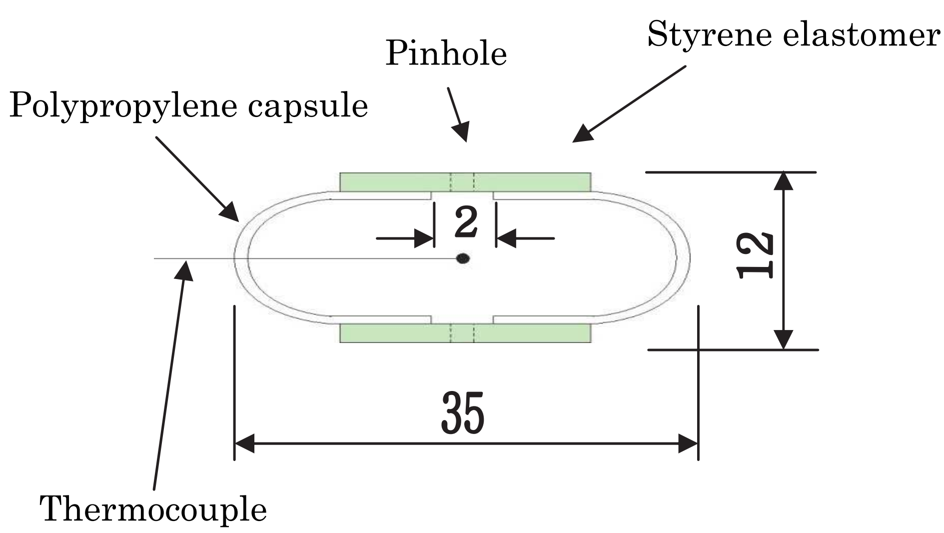


Fig. 15. Capsule using styrene elastomer

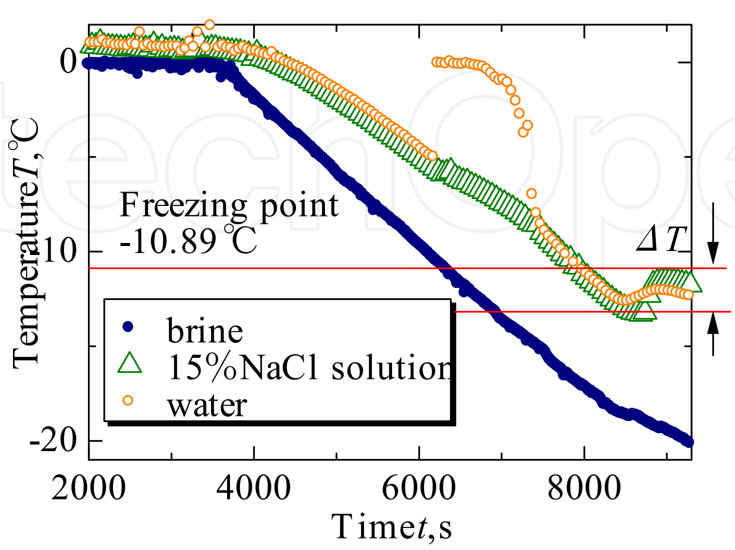
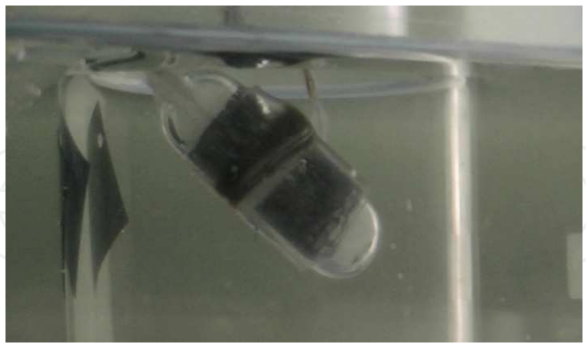
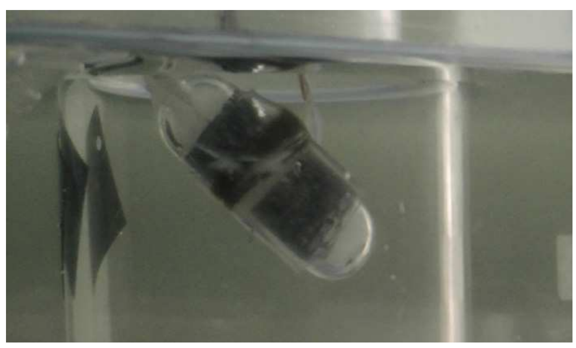


Fig. 16. Typical example of temperature record in a case of 15 wt% NaCl with a styrene elastomer capsule installed

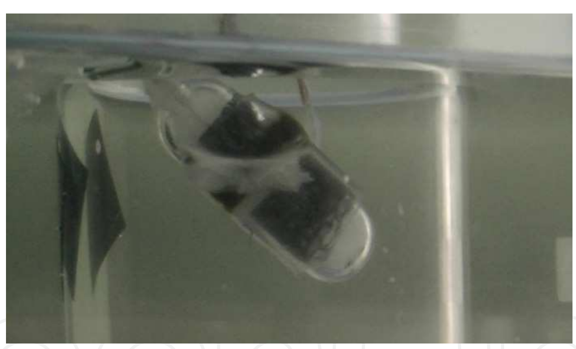
K/min. The temperatures in the capsule and outside the capsule were measured and the propagation of freezing was checked. Due to the freezing of the water inside the capsule, the middle part of the capsule expanded and the size of the pinhole became bigger.



(a) 0 s



(b) 30 s



(c) 60 s

(d) 180 s

Fig. 17. Typical example of ice propagation using styrene elastomer capsule

One of the typical examples of the time wise variation of the temperature is shown in Fig. 16. Due to the solidification of water inside the capsule, the temperature of the water jumped to 0 °C. Then, the water kept the temperature for a while and it started to drop down again until the temperature of the solution started to jump. It was the instance of propagation of freezing. The degree of supercooling at freezing was around 2 K.

One of the examples of propagation view is shown in Fig. 17. Since the water inside the capsule was frozen completely at this moment, the color inside the capsule looked white and the middle part of the capsule swelled. The original color of the membrane was transparent and it was difficult to observe the propagation on the surface. So, the inner surface of the membrane was painted in black. From the photos it can be observed that the ice propagation started at two points on the membrane and the ice grew slowly. The reason for the slow growth was because of the low degree of supercooling and the high concentration of the solution.

6. Conclusion

A method to induce solidification of supercooled refrigerant using membranes was introduced. Three kinds of membranes were selected, namely, ion exchange membrane, porous elastic polymer membrane and styrene elastomer membrane. The following conclusions were made.

1. Cation exchange membrane and anion exchange membrane with different thickness were examined. It was found that cation exchange membrane with thin thickness propagated the ice.
2. Porous elastic polymer membrane was used to establish the capsule and experiments were carried out. It was found that the membrane was effective for propagating the ice with a low degree of supercooling. Influence of various factors on propagation of ice through membrane, such as difference in the melting temperature between the refrigerant and the liquid material, difference in the cooling rate, difference in the location of the initial ice appearance, difference in the thickness of membrane, were investigated. It was confirmed that the refrigerant with a low melting temperature can be frozen with a small degree of supercooling by inserting a capsule with water or solution having a higher melting temperature in it and a sheet of membrane to separate between them. The propagation time becomes longer when the difference in the melting temperature of two solutions is big. It is because the solution with higher melting temperature solidifies before the solution with the lower melting temperature reaches its solidification temperature. The temperature rises due to solidification and it needs time to lowdown the temperature again.
3. Styrene elastomer membrane which has high elasticity at low temperature was selected and a small pinhole was put through it under the expanding condition in one direction. The shape of the capsule to suit with the characteristics of expansion was prepared and water was put in the capsule. The capsule was set in the refrigerant and the propagation of freezing with a low degree of supercooling was investigated, experimentally. As a result, due to the volume expansion by freezing, the pinhole on the membrane was expanded and it became a trigger for the refrigerant to freeze under the degree of supercooling at around 2 K. Hence, it can be proved that the idea of installing the capsule can suppress the supercooling phenomenon.

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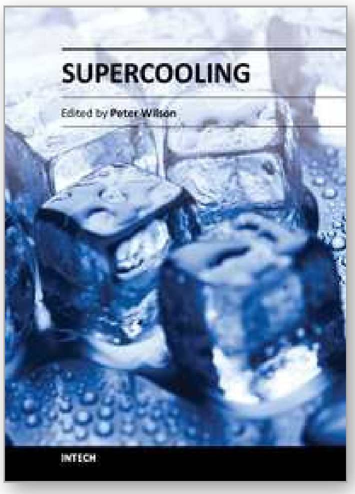

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Supercooled liquids are found in the atmosphere, in cold hardy organisms, in metallurgy, and in many industrial systems today. Stabilizing the metastable, supercooled state, or encouraging the associated process of nucleation have both been the subject of scientific interest for several hundred years. This book is an invaluable starting point for researchers interested in the supercooling of water and aqueous solutions in biology and industry. The book also deals with modeling and the formation subsequent dendritic growth of supercooled solutions, as well as glass transitions and interface stability.

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