Characteristic of the Formation and Adhesion of Ice on a Cooling Surface by a Stirring Aqueous Solution

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ABSTRACT: Ice adhesion or cohesion leads to the decrease of the performance of ice making system, especially to dynamic type ice thermal storage system (DISS) which mainly forms ice from the flow of an aqueous solution. The ice adhesion is influenced by various parameters associated with operating or geometric condition. In this study, the influence on an adhesion of ice to the characteristic of cooling surface and to composition of an aqueous solution was fundamentally observed by using batch type cooling device, a beaker. Three patterns of solution in each beaker were cooled with brine. Moreover, the characteristic of cooling surface on each beaker was distinguished to coating materials. Stirring power as a degree of the ice adhesion was measured. The stirring power to cooling heat transfer rate in each beaker was compared. As a result, the lowest stirring power of 8.9 W with non-adhesion of ice, was shown in the case of the aqueous solution of EG(4)+PG(1.5)+1,6HD(1.5) in PE coating beaker.

──── Nomenclature ────

$\overline{C}$: mean specific heat [kJ/kg·K]
L : latent heat of solidification [kJ/kg]
m : mass [g, kg]
q : cooling heat transfer rate [W]
T : temperature [℃]
x : concentration [mass%]

Greek symbols

Δ : difference
τ : time on freezing [s]
ω : angular velocity of stirring [rpm]

Subscripts

a : additive
fp : freezing point
i : i-th time step
ice : ice
N : number at final time step
s : aqueous solution
$total$: total of
w : water

1. Introduction

In a dynamic type ice thermal storage system (DISS) which forms ice continuously on cooling wall, a fluid-like ice mixture, so called ice slurry, is mainly formed. The ice slurry consisting of small ice particle and a solution, has a large heat transfer area and is possible to reject heat to a rapid variation of cooling load.

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Moreover, the fluidity of the ice slurry shows higher transportability of cold thermal energy than that of cold water per unit hour.[1] However, the occurrence of ice adhesion on cooling surface and ice blockage in flow acts negatively to the stability and initial cost of the DISS.

Ethylene glycol (EG) and Propylene glycol (PG) as glycol type brines, have a structure of two hydroxyl radicals (EG: $HO-CH_2-CH_2-OH$, PG: $CH_3-CH-OH-CH_2-OH$). An additive, the silane coupling agent (SCA: $C_9H_{23}N_2O_3Si$) is well-known as the substance to suppress the ice adhesion, intervening between inorganic and organic compound or water.[2-5] Up to the present, most freezing experiment of aqueous solution has been carried out with additives like of the EG, the PG and the SCA, which was reported effective to ice formation, heat transfer in batch cooling and ice fraction in slurry flow.[4-7] Especially, it was clarified that the concentration of solution and cooling temperature have relations with the ice adhesion on cooling wall and the ice cohesion between ice particles.[6]

1,6-Hexanediol (1,6-HD; 1,6Dihydroxy-hexane; Hexamethylenediol) is an environment friendly substance rather than the SCA, which has poly-alcoholic property. The 1,6-HD has similar structure of the EG, i.e. hydroxyl ion (-OH) is bonded to both sides of hydrocarbon group in element structure ($HO-CH_2-(CH_2)_4-CH_2-OH$).[8] Therefore, the 1,6-HD is expected

to suppress hydrogen bonding in water, because it has relatively large size of C_mH_n radical. Actually, the 1,6-HD, the nonmetal material such as a fluorine resin is a hydrophobic one with low friction.[9]

In this study, an experiment has been performed to investigate the effect of the composition of an aqueous solution and of the characteristic of cooling surface on the ice adhesion on cooling wall, which has a metal surface and nonmetal coatings on metal one.

2. Experiments

2.1 Experimental apparatus

Figure 1 shows the experimental apparatus for ice formation with measurement system. It consists of a low temperature bath with brine, a stainless steel beaker with a stirrer and measuring equipment for temperature, stirring power.[4] An aqueous solution in the beaker was stirred to 120 rpm by the stirrer (impeller type: vertical plate of $3 \times 2 \, cm^2$, 3 airfoils). Simultaneously, the solution was cooled with stirring in the low temperature bath which was maintained to $-7.5°C$. The upper part of the beaker was plugged with an insulator of polystyrene foam block (thick. 30 mm). When the solution reached a supercooled state of the supercooling degree of 1 K, it was dissolved by
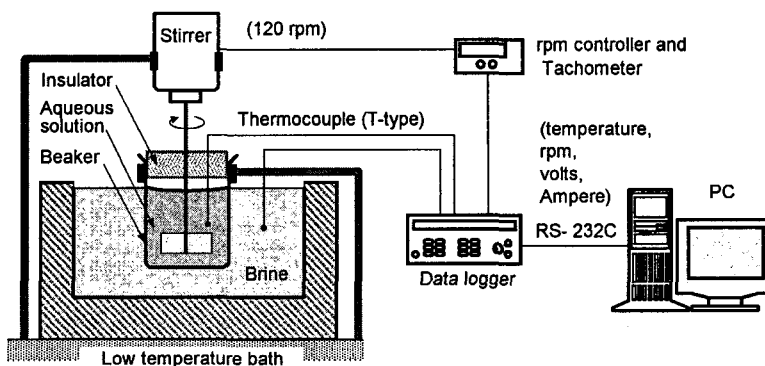

Fig. 1 Schematic of the experimental apparatus.

ice particles insertion less than one gram. After that time, a few of fine ice particles occurred, which corresponds to the sensible heat of the solution due to the supercooling degree. After then, a mixture of fine ice particles and residual solution, so called ice slurry, was formed. And the cooling of the mixture with the stirring lasted up to an hour or more. The temperature of the mixture and the brine were measured with T-type thermocouple in the beaker and the low temperature bath, respectively. Moreover, stirring power as a degree of ice adhesion was measured. Therefore, the stirrer plays a role of stirring the mixture and of sensing the stirring resistance.

Allowing for the suitability of aqueous solution of 6 to 7 mass% on slurry making, component ratios to the aqueous solution were used to three patterns, like as EG 7 mass% (solution1), EG 4 + SCA 3 mass% (solution2) and

EG 4 + 1,6-HD 1.5 + PG 1.5 mass% (solution3).[2,4] Total mass fraction of the additive for each solution of 300 grams was fixed to 7 mass%. Table 1 shows each component ratio of solution.

Table 2 shows a part of the thermophysical property of the beaker and coating materials. The material of bare beaker was the stainless steel (304SS) with the size of $75 \times 120 \times 1 (D_o \times H \times t)$ mm^3. And nonmetal materials for coating were fluorine resin of polytetrafluoroethylene (PTFE), perfluoroalkoxy (PFA) and a plastic of polyethylene (PE). It was remarkable that the dynamic coefficient of friction and the critical surface tension of the fluorine resin are smaller than those of the PE and SS. Beakers in the experiment are shown in Fig. 2. Each of the PTFE, PFA and PE was coated respectively on inside the bare beaker (304SS), which was treated to below 100 μm thickness by electric resistance and conversion coating method.

On freezing, the concentration of the solution in the mixture was expressed to Eq. (1). Also, it was predicted indirectly from a measured freezing point of the solution, which had an approximately linear relationship with the freezing point as shown in Eq. (2). Thus the amount of ice at a time was obtained indirectly from Eq. (3) because it was too difficult to measure

Table 1 Aqueous solutions for experiment [mass%]

	EG	SCA	PG_HD	Water
Solution 1	7	–	–	93
Solution 2	4	3	–	93
Solution 3	4	–	3	93

$T_{brine} = -7.5\,℃$, Supercooling degree = 1 K

Table 2 Thermophysical property of coating material

	PTFE	PFA	PE	SS
Thermal conductivity[*] [W/m·K]	0.25	0.25	0.33	16.3
Dynamic coefficient of friction[*]	0.04	0.08	0.08~0.18	0.19
Critical surface tension[*] [dyne/cm]	18	18	31	47

[*]Ref(9,10)

(a) SS (bare)   (b) PTFE coating   (c) PFA coating   (d) PE coating
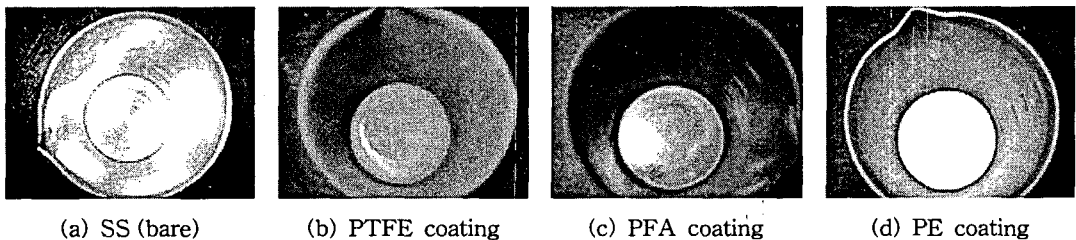
Fig. 2 Picture of the inside of coating vessel.

the amount of formed ice during cooling. Moreover, cooling heat transfer rate was calculated with time average as Eq. (4).

$$x_i = \frac{m_a}{m_{w,i} + m_a} \times 100 \tag{1}$$

$$T_{fp,i} = A x_i + B \tag{2}$$

Here, $A = -0.35$, $B = 0.068$ for EG, EG + SCA and $A = -0.35$, $B = 0.36$ for EG + PG + HD solution.[11] The coefficients were calculated from an experiment in reference (11).

$$m_{ice} = m_{ice,N} = m_{total} - \frac{100 A m_a}{T_{fp,N} - B} \tag{3}$$

$$q_i = \frac{1}{\Delta \tau}\left[-\Delta m L_{ice} + m_s \overline{C_s} \Delta T\right] \tag{4}$$

Here, $m_{total} = m_{w,i} + m_a + m_{ice,i}$, $\Delta m = m_{ice,i} - m_{ice,i-1}$ and $\Delta T = T_{fp,i} - T_{fp,i-1}$.

$\overline{C_s}$ is the approximate specific heat of solution, which was dominated to the concentration of EG. The variation of the specific heat was neglected because the specific heat decreased within 1% when the concentration increased from 4 to 10 mass%. Also, the latent heat of melting on ice (L_{ice}) was used to 334 kJ/kg with the assumption of the change from water only to the ice.
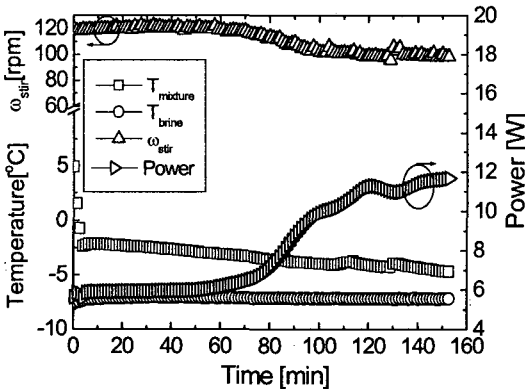
3. Results and discussion

3.1 Freezing of solution

Figure 3 shows time histories of temperature and stirring power for the solution 1 (EG 7 mass% aqueous solution) cooling in the bare (304SS) beaker. The solution was forcedly dissolved when it reached to supercooling degree of 1 K. After one hour from the dissolution, the stirring power increased. And after 2 hours 30 minutes from the dissolution, the stirring power was settled to about 12 W. It means that the ice formation and growth might be suppressed. This reason would probably be the increase of the concentration and the decrease of the temperature difference between an aqueous solution and brine. After the end of the cooling, the ice slurry was discharged from the beaker by inclining the beaker. Therefore, it was estimated that the ice did not adhere on the beaker wall (non-adhesion of ice). However, the ice adhered hard on the cooling wall (ice adhesion) when the stirring power increased 15 W above the previous study.[12] Figure 4 shows the time variation of the cooling heat transfer rate in Fig. 3. The gradient of the heat transfer rate decreased as the thermal resistance increased with the ice amount in the mixture.
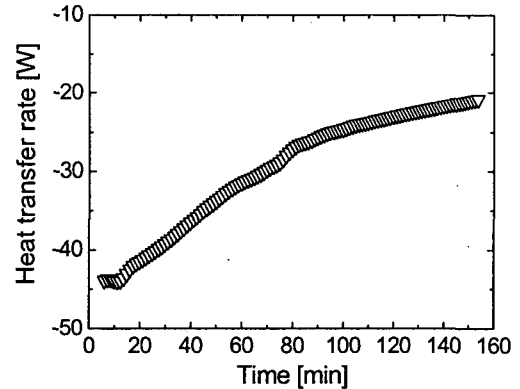

Fig. 3 Time history of solution temperature and stirring power (EG 7 mass%, SS beaker).

Fig. 4 Time history of heat transfer rate in beaker (EG 7 mass%, SS beaker).

3.2 Ice formation to component ratio and different cooling surfaces

Figures 5 and 6 shows the relationship be-tween the cooling heat transfer rate (proportional to cooling time) and the stirring power to the solution 1 and 2, respectively. In both solutions the stirring power showed the maximum at the near end of cooling. Among maximum stirring powers, the lowest one revealed at the PTFE coating beaker. However, the largest stirring power showed at the PFA one though the thermophysical property is similar to the PTFE one. From Figs. 5 and 6, the lowest stirring power at the end of cooling (PTFE beaker) in the solution 2 was 1 W smaller than that in the solution 1. Thus the SCA was more effective to suppress the ice adhesion on the polymeric coating wall than on the metal one. Figures 5 and 6 shows that the stirring power increased and finally stabilized in PTFE, PE and SS wall. On the contrary, the stirring power near-ly diverged in PFA wall because a strong ice adhesion occurred to the cooling wall. It was considered that the increase of the concentra-tion of solution and the decrease of the cooling heat transfer rate may suppress the growth velocity of ice particle, i.e. the size of the ice particle might be small. Unfortunately, the rate of change of the size was not confirmed be-cause the time variation of the distribution of ice size was not measured with the restriction of measurement system.

In Fig. 7(solution 3), the decrease of the stir-ring power after the maximum was greater than that in Fig. 6(solution 2). The final stir-ring power was 8.9 W in PTFE wall. Therefore, it was found that more effective suppression of ice adhesion occurred at the polymeric coating wall. And at least, uniform size of ice particle might be more obtained with 1,6 HD than with the SCA. Figure 8(a) shows the picture of the ice slurry with the solution 3 (1,6-HD with PG) at the end of cooling in the PTFE coating
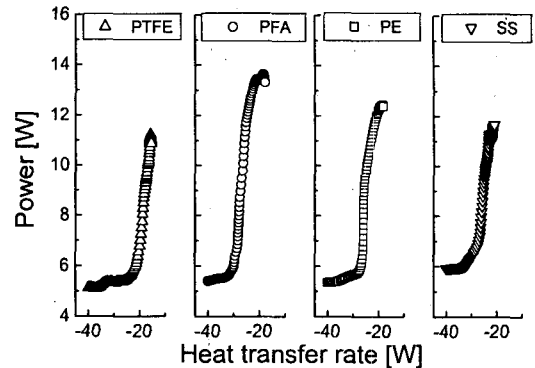

Fig. 5 Comparison of stirring power with cool-ing heat transfer rate for different cool-ing surfaces (EG 7 mass%).
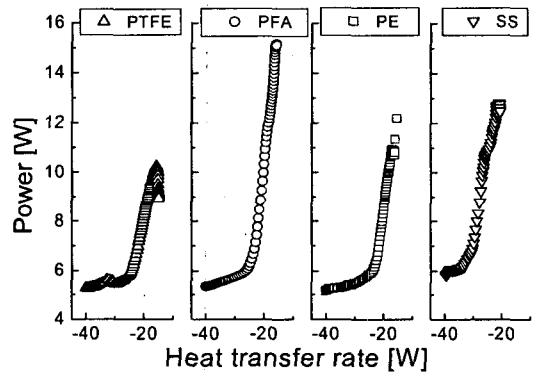

Fig. 6 Comparison of stirring power with cool-ing heat transfer rate for different cool-ing surfaces (EG 4+SCA 3 mass%).
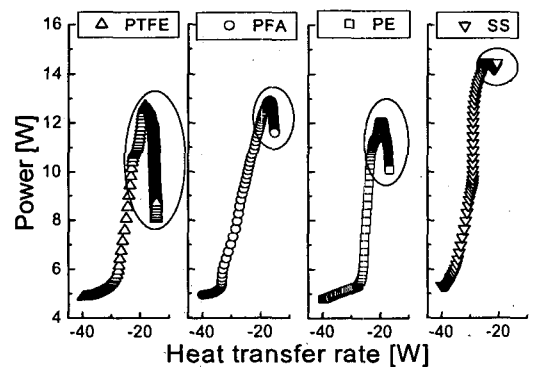

Fig. 7 Comparison of stirring power with cool-ing heat transfer rate for different cool-ing surfaces (EG 4+PG_HD 3 mass%).
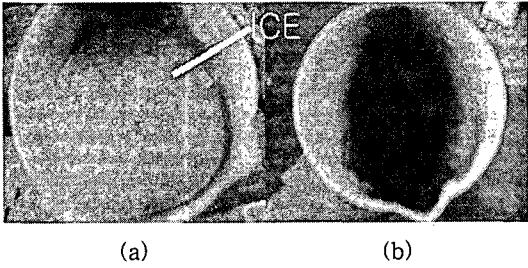
(a)   (b)

Fig. 8 Non-adhesion of ice on cooling wall
(PTFE coating at beaker inside).

beaker. Figure 8(b) shows the beaker inside when the ice slurry was poured out.

Among the maximum stirring power, the lowest power of 10.3 W was shown to the solution 2 with the PTFE coating beaker at the time average heat transfer rate of 15.5 W. Moreover, a lower stirring power of the solution was shown in the PTFE coating beaker with the dynamic coefficient of friction comparatively lower than that of the PFA. On the other hand, the stirring power of the PE coating was lower than that of the PFA one, even though the thermal conductivity, the dynamic coefficient of friction and the critical surface tension in the PE are higher than those in the PFA one. The result was against the experimental expectation. The contribution of the thermal conductivity and the dynamic coefficient of friction to the ice adhesion were not

clear if the two physical properties coexisted. However, it was found that the critical surface tension contributed clearly in the interface between metal (304SS) and nonmetal (PTFE, PFA and PE) surface, i.e. the stirring power of the non-metal surface was smaller than that of the metal one.

Figure 9 shows the stirring power at the end of each cooling process with respect to the dynamic coefficient of friction of cooling wall (PTFE, PFA, PE and SS). The stirring power increased in the solution 2 and 3 as the dynamic coefficient of friction increased, except in the PFA coating beaker. In the SS beaker, the stirring power was 12.5 W at the solution 2 and 14.5 W at the solution 3, which is greater than that of the solution 1. It might be shown that the SCA and the HD on the SS wall would act as the contributor rather than the suppressor for the ice adhesion. Meanwhile, the 1,6 HD was more effective to suppress the ice adhesion on polymeric surface than the SS one. The minimum stirring power was shown in the solution 2 and 3 which involve the SCA or 1,6 HD with the PTFE coating beaker. Thus the additives might show a good affinity to polymeric surface.

In Fig. 10, the stirring power of the solution 2 and 3 increased except in the PFA coating beaker as the critical surface tension increased,
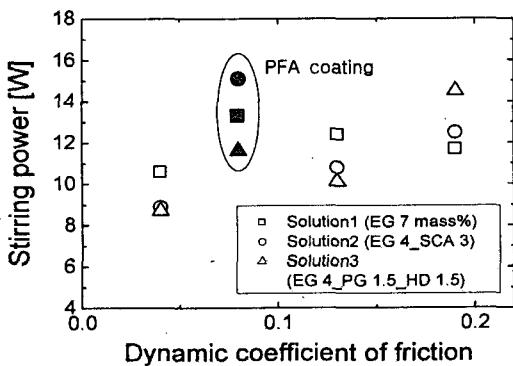

Fig. 9 Comparison of stirring power to four beakers (different frictions).
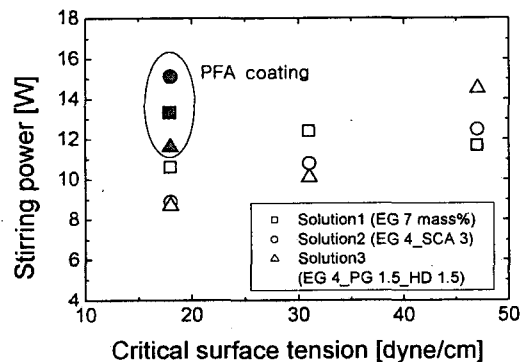

Fig. 10 Comparison of stirring power to four beakers (different surface tension).

which is similar to the result of Fig. 9.

From the result, the additive, 1,6 HD showed the suppression of ice adhesion on polymeric cooling surface, which will be adopted to a supplementary data on heat exchanger for ice making and thermal storage materials.

4. Conclusions

An experimental study of ice slurry formation was performed with an aqueous solution containing additives. The following characteristic of ice adhesion was obtained.

Stirring power increases as time average cooling heat transfer rate removed from inside of beaker decreases. In coating beaker, a comparatively lower stirring power was obtained with 1,6 HD containing solution. Moreover, using PG and 1,6 HD instead of SCA, the stirring power decreased to the amount of 2 W. The additive, SCA or 1,6 HD is more effective to suppress the ice adhesion on polymeric surface than stainless steel one. In the solution containing SCA or HD, the stirring power increased as the dynamic coefficient of friction and the critical surface tension increased, except in the PFA coating beaker. Minimum stirring power of 8.9 W was obtained by the solution containing 1,6 HD in the PTFE coating beaker.

Ice slurry sliding out from the beaker was shown at the stirring power below about 15 W, which was considered as non-adhesion of ice.

Acknowledgement

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