Adhesive Shear Stress between Mushy Ice and a Copper Surface

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When an ethanol-water solution of low concentration is cooled at between its equilibrium fusion temperature and its eutectic temperature, a mushy ice is formed. Ice slurry is easily made from the mushy ice because it contains a lot of small dendritic ice crystals and unsolidified liquid. Because of its large heat capacity, ice slurry is expected as useful heat-exchanging fluid in an ice storage system. The adhesive stress of mushy ice on a solid cold surface is much smaller than that of pure ice. It is another reason to apply aqueous solution to an ice storage system. However, the adhesive stress is not well known so far. It is important to know the relations among conditions of aqueous solutions, cold surfaces, solidification processes, adhesive works and adhesive shear stresses. In the present experiments, copper is used as a material of an examined cold surface. Ethanol-water aqueous solution of 2wt%-15wt% is used as a provided solution. A stainless steel cylinder is vertically located on a horizontal cold surface and is filled with provided aqueous solution. When a mushy ice is formed and comes to steady state after more than four hours under each condition, the cylinder is pulled horizontally by an actuator. The maximum value of the applied force just before the cylinder detaches is defined as an adhesive shear force. In this paper, the effects of concentration of aqueous solution, temperature and diameter of a cold surface on adhesive shear stress are discussed. Furthermore, it seems to be useful to relate adhesive shear stress to adhesive work. Adhesive work between liquid droplets and a solid surface is used in the present theoretical discussion instead of the adhesive work between mushy ice and a solid surface.

1. Introduction

In dynamic-type ice storage systems, ice slurry is one of the most possible materials for energy storage. One of the methods to obtain ice slurry is to use aqueous solution. The aqueous is cooled on a solid cold surface, forms mushy structure that contains a lot of small dendritic ice crystals, and then is removed periodically from the surface. In this method additional energy is required to remove mushy structure except for making ice itself [1,3].

There are some studies on adhesion phenomena between pure ice and solid surfaces [2,4,5], in which relations between adhesive stress and adhesive work are shown. However, no reports on adhesion between mushy structure and solid surfaces are found.

In the present study, the final target is to know the details of adhesion phenomena between mushy structure and solid cold surfaces. Here we examine effects of cold surface temperature and concentration on adhesive stress are examined. An ethanol-water system is used as an aqueous solution. Relations between adhesive work and stress are discussed.

2. Experimental Methods

2.1. Experimental Apparatus The overview of the present experimental apparatus is shown in Fig.1. Figure 2 shows the details of the test section. The test section is located in a constant low-temperature room whose temperature is near the equilibrium freezing point of the provided aqueous solution. The test section has a solid cold surface on the top that is cooled from below with coolant. A stainless-steel cylinder is located on each cold surface and is filled with provided aqueous solution.

The provided aqueous solution is cooled from the bottom and forms mushy structure in the cylinder. After a certain elapsed time is passed, an actuator pulls a string horizontally that is attached on the cylinder. The mushy structure is detached with the cylinder from the solid cold surface. A strain gauge

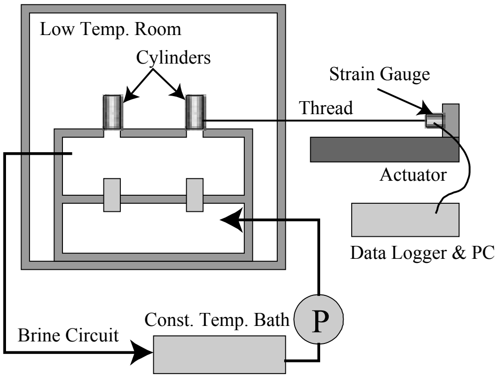

Fig.1.Experimental apparatus.

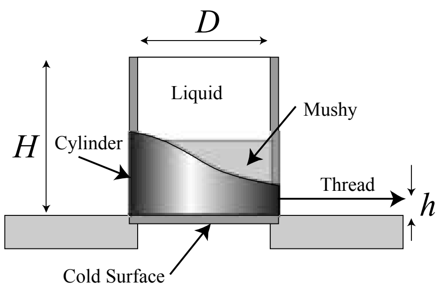

Fig.2.Details of test section.

detects the maximum value of the tension of the string.

2.2. Experimental Conditions Diameters of the provided solid surface are 11, 14, and 17 mm. Concentration of the aqueous solution is set as C=2, 5, 10, and 15 %. Temperatures of the cold surface are set so that the difference from the equilibrium freezing temperature of the aqueous solution is about ΔT=4, 6, and 8 K.

3. Results and Discussion

3.1. Effect of Diameter Figure 3 shows the relation between adhesive stresses and diameters of the cold surfaces. The concentration is fixed at 5% in this figure. 4, 6, and 8 K refers to 3.9-4.2 K, 5.8-6.2 K and 7.3-8.2 K in the actual experiment, respectively.

If adhesive force is characterized with adhesive stress, the measured adhesive stresses do not depend on diameters of the surfaces. However, adhesive stresses are small when diameters are large according to Fig.3. Because mushy structure is a soft material, it deforms largely before detaching when diameter is large. Mushy structure collapses under some conditions. When collapse occurs, the force at the collapse is detected as an adhesive force, which is smaller than the true adhesive force.

Detected forces vary in wide range when diameter is small. There are two reasons; one is that effects of subcool degree are not considered in Fig.3. Adhesive stresses are measured at more than four hours after subcool is dissolved. However, the temperature of the solution just before subcool is dissolved affects the microscopic structure and adhesive stresses as well. Another reason is that mushy structure is not regarded as uniform substance any more when the diameter is small. Mushy structure contains a lot of small dendritic ice crystals and can be regarded as uniform substance because it is regarded as random structure. Effects of directions of each dendritic ice crystal cannot be ignored when the diameter is small.

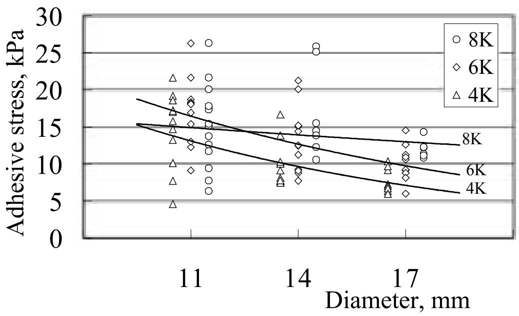

Fig.3.Effect of diameter: C=5 %.

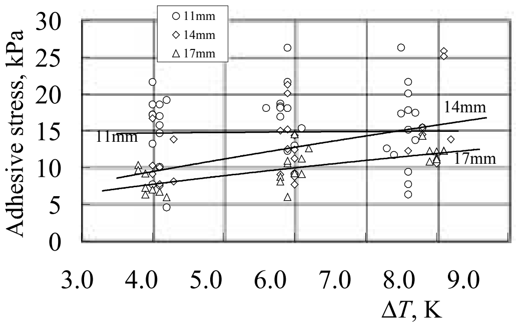

Fig.4.Effect of surface temperature: C=5 %.

3.2. Effect of Temperature Figure 4 shows the relation between adhesive stresses and temperatures of cold surfaces. Adhesive stresses are large when temperatures of cold surfaces are low. The present results do not differ from the previous study on pure ice [5].

3.3. Effect of Concentration Figure 5 shows the effect of concentration. Adhesive stress is small when concentration is high. The reason is described later in section 3.6.

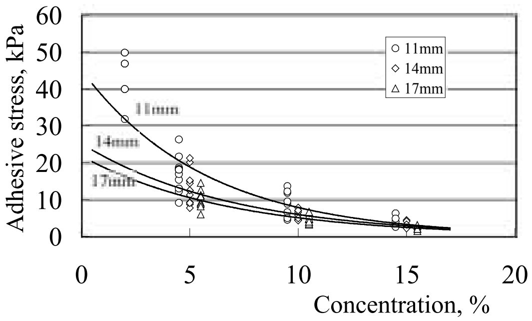

Fig.5.Effect of concentration: ΔT=6 K.

3.4. Value of Adhesive Stress In Fig.5, the extrapolated values at C=0 % are expected as the values of pure ice. According to the previous study [5], however, the adhesive stress of pure ice on a copper plate is about 600 kPa, which is smaller than the present values of aqueous solution by more than one digit.

Figure 6 shows the schematic model of adhesion near a solid surface. Solid part (pure ice crystals) and liquid part (unsolidified aqueous solution) are on the cold surface. Adhesive force is dominated by the solid part. Under present conditions, however, the fraction of the area of solid part is about 80 % [6]. The present values of aqueous solution are still small compared with 80 % of the value of pure ice. This means that the reason why the values of aqueous solution are much smaller than those of pure ice is not explained only with solid area fraction as shown in Fig.6.

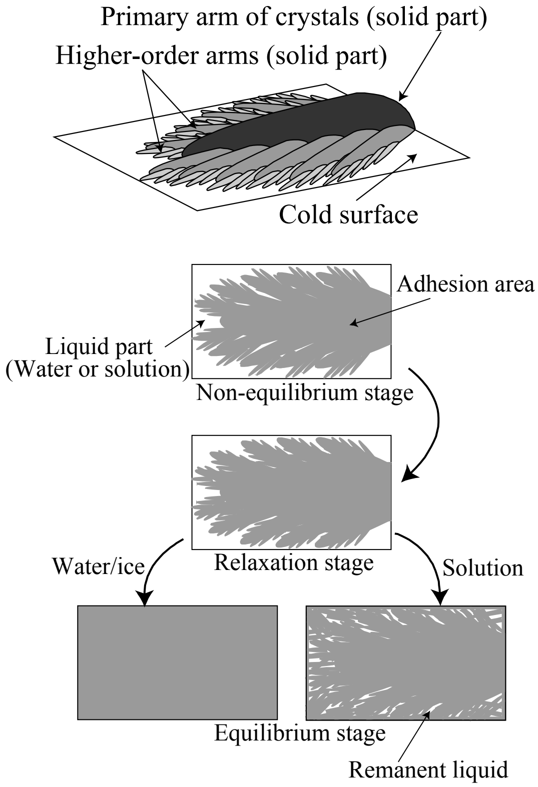

Fig.6.Microscopic structure.

3.5 Microscopic Structure and Adhesive work Relation among macroscopic adhesive work W_{SM} [mJ/m^2] as shown in Fig.6, A as area fraction of solid part and W_{SI} as adhesive work between solid part and cold surface is

$$W_{SM} = W_{SI} \times A. \tag{1}$$

W_{SM} is equal to the strain energy of mushy structure just before detaching.

$$W_{SM} \times \frac{\pi}{4} D^2 = \frac{1}{2} \sigma^2 / E \times \frac{\pi}{4} D^2 H$$

$$W_{SM} = \frac{1}{2} \sigma^2 / E \times H \tag{2}$$

The modulus of elasticity of mushy structure E is expressed as a production of E_0 (pure ice) and volume fraction α of solid part in mushy structure that is defined by lever law of equilibrium diagram.

$$E = E_0 \alpha \tag{3}$$

where $\alpha = \dfrac{C(T_W) - C_i}{C(T_W)}$.

W_{SM} is expressed as

$$W_{SM} = \frac{1}{2}\sigma^2 \times \frac{C(T_W)}{C(T_W) - C_i} \times \frac{H}{E_0}$$

$$W_{SI} \times A = \frac{1}{2}\sigma^2 \times \frac{C(T_W)}{C(T_W) - C_i} \times \frac{H}{E_0}. \tag{4}$$

Figure 7 shows another schematic model of adhesion near a solid surface. In the case of aqueous solution, small dendritic ice crystals are on a cold surface. Applying Young-Duple relation to the adhesion phenomena,

$$\begin{aligned} W_{SI} &= \gamma_{SL} + \gamma_{LI} - \gamma_{SI} \\ &= \gamma_{LI}(1 + \cos\theta) \end{aligned} \tag{5}$$

There is the same kind of relation in the case of pure ice. However, if the transition state exists during the solidification process of pure ice as shown in Fig.7 left-bottom, the liquid under ice crystals solidifies at steady state as shown in Fig.7 right-bottom. Thus the contact angle between pure ice and a cold surface θ does not exceed 90 degrees. In the case of aqueous solution, however, the unsolidified liquid part under ice crystals contain solute that is extracted as solidification proceeds. Because the concentration of the local liquid is high, the liquid does not solidify at steady state as shown in Fig.7 top. In such cases, θ is obtuse angle. W_{SI} in Eq(5) is then smaller than that of pure ice. At $\theta = 5\pi/6$, for instance, $W_{SI} \cong \gamma_{LI} \times 0.1$, which means that the adhesive work of mushy structure is smaller than that of pure ice by about one digit. Because adhesive work has positive relation to adhesive stress as described before, the difference of adhesive stress values of between mushy structure and pure ice as shown in section 3.4 is explained not with area fraction but with adhesive work.

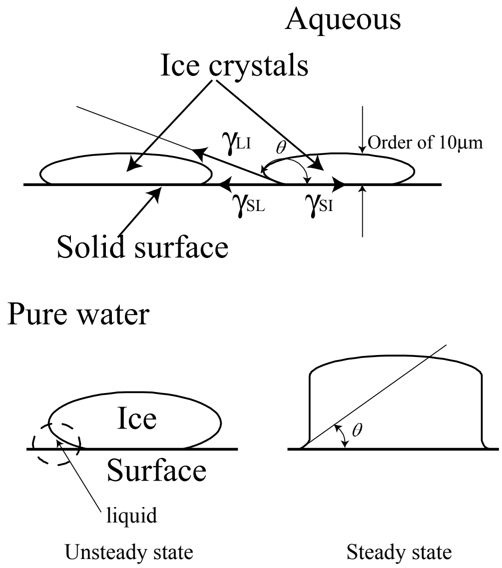

Fig.7.Structure near solid surface.

3.6 Relation between Adhesive Work and Stress The final target of this paper is to predict adhesive stress via adhesive work. The relation is expressed in Eq.(4). Substituting Eq.(5) into Eq.(4), adhesive stress is predicted when γ_{LI}, θ and A are given as a function of thermal conditions.

Although it is now difficult to express γ_{LI} and θ as a function of macroscopic conditions, the adhesive work between liquid aqueous droplets and a solid surface

$$W_a = \gamma_S + \gamma_L - \gamma_{SL} \tag{6}$$

has a certain relation to W_{SI}. For instance,

$$W_{SI} = K W_a \tag{7}$$

is applied and A is regarded as almost constant value, Eq.(4) is expressed as

$$W_a \frac{C(T_W) - C_i}{C(T_W)} = \frac{1}{2}\sigma^2 \times K_0, \tag{8}$$

where $K_0 = \dfrac{H}{E_0} \times \dfrac{1}{KA}$.

According to Eq.(8), the important parameters for describing relation between adhesive stress and adhesive work are given by

$$W_a^* = W_a \frac{C(T_W) - C_i}{C(T_W)} \text{ á } \sigma^* = \frac{1}{2}\sigma^2. \quad (9)$$

Applying Eq.(9) to the present experimental data, we obtain the results shown in Fig.8.

11 mm: $W_a^* = 11.6 \ln \sigma^* + 9.2$

14 mm: $W_a^* = 12.3 \ln \sigma^* + 11.2$

17 mm: $W_a^* = 12.1 \ln \sigma^* + 14.9$

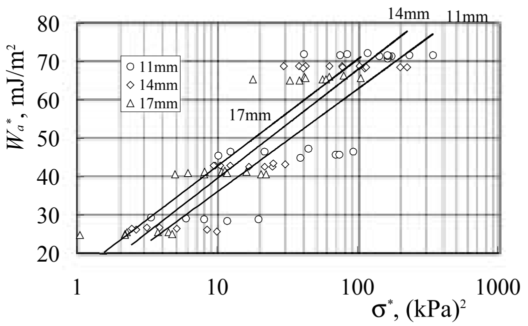

Fig.8.Adhesive work and stress.

In section 3.3, it is shown that the adhesive stress is small when concentration is high. This is because of Eq.(6). The surface free energy γ_L of pure water and pure ethanol are 75.6 mJ/m^2 and 21.1 mJ/m^2, respectively. Because γ_L is small when concentration is high, W_a in Eq.(6) is also small, which leads to small adhesive stress.

4. Conclusions

(1)Adhesive stress does not depend on temperature of a cold surface but strongly depend on concentration of aqueous solution.
(2)Adhesive stress of mushy structure is smaller than that of pure ice by more than one digit.
(3)Eq.(9) is one of the parameters to describe relation between adhesive stress and adhesive work.

References and Notes

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