

# Adhesive Strength of Contaminated Ice

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Temperature dependence of adhesive strength of ice containing KCl was measured using centrifugal force in examination of an area occupied by a solution at an substrate/ice interface. The AgNO<sub>3</sub> replica technique developed by Prodi and Nagamoto was applied to examine the solution-occupied area on the surface of ice broken off from a substrate and the counterpart surface remaining on the substrate. Decrease of adhesive strength of KCl-ice at temperatures higher than the eutectic point could be interpreted by the reduction of the real contact area between ice and the substrate due to examination of a liquid solution at the interface.

Adhesion of ice on a solid surface is of practical importance. But, as has been pointed out by Jellinek(1) in 1970, precise measurement of an adhesive strength between ice and a substrate presents a real difficulty in that a number of factors influence this strength. Important among them are how broad a contact area is between ice and the substrate and whether or not liquid-phase solution layers exist at an interface between them.

Measuring the adhesive strength of a polycrystalline ice frozen from a dilute electrolyte solution by applying a shear stress on such an interface, Jellinek(2) suggested that the strength of shear adhesive force of a contaminated ice is due to the shearing of an interfacial liquid solution layer which has been formed during freezing, whereby be assumed that the thickness of a liquid solution is equivalent to that of a solution segregated at grain boundaries.

When a polycrystalline ice is formed from a dilute solution, a large part of solute molecules are segregated at grain boundaries. They can exist as a liquid solution at temperatures higher than the eutectic point of the solute and ice, when an ice containing a water-soluble impurity adheres on a substrate. Then, the adhesive strength of this ice must be greatly weakened under the influence due to the existence of a liquid solution at the substrate/ice interface, because the real contact area of ice at the interface is reduced by the presence of such a solution film. Therefore, it is important in the measurement of adhesive strength of ice to examine directly the area occupied by the liquid solution at

the interface.

The present paper aims to study temperature dependence of relative strength of adhesion of ice containing potassium chloride relating it with a change of the area occupied by a liquid solution at the interface, using a replica technique which allows to visualize the existence of a solution film. Sea ice is a contaminated ice found in abundance in nature, but both the contaminants, NaCl and MgCl<sub>2</sub>, have relatively low eutectic points. As KCl has a relatively high eutectic point of -10.7°C, it was used as a contaminant.

## Experimental Procedure

### Measurement of Adhesive Strength

Measurements in this experiments of adhesive strength of ice containing KCl were made by applying a tension force, because the surface of an ice specimen broken off vertically from a substrate by the tension allows an accurate examinations of the area occupied by solution film at a substrate/ice interface without any disturbance. If an ice specimen is sheared off from the substrate, the area which has been occupied by a solution film at the interface must be disturbed by friction, making it impossible to accurately examine the initial distribution of the area occupied by the solution and the otherwise area, i.e. the real contact area of ice.

A centrifugal device was used, as shown in Figure 1, to have a tension force applied in a simple manner to an ice specimen adhering on a brass substrate. Two ice specimens prepared in the same size are individually frozen on the surface of two brass substrates (0.03m in diameter) and they are mounted at both ends of a revolutionary arm driven by an electric motor. Figure 2 illustrated a detailed structure near the end of the revolutionary arm where an ice specimen is mounted. When a centrifugal force acting on the ice specimen exceeds an adhesive force, the specimen is broken off from the brass substrate. As seen in Figure 2, the ice specimen is protected by a cylindrical lucite cover in such a way that the specimen broken off from the substrate does not scatter by the action of centrifugal force. This lucite cover also keeps the specimen free from a wind pressure created by the revolution. The angular velocity at a moment in which the ice specimen is

Figure 1. Experimental device for measuring adhesive strength of ice by centrifugal force.

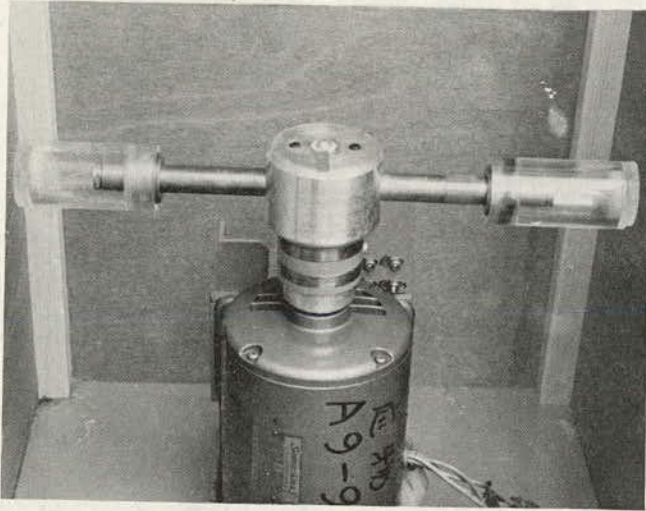
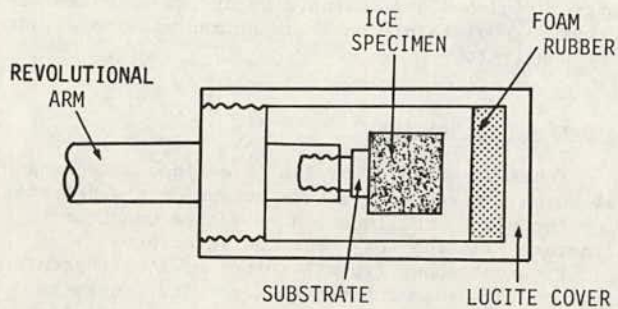


Figure 2. Schematic diagram of a brass substrate and an ice specimen mounted at the end of a revolutionary arm



broken off from the substrate is measured by the aid of a stroboscope. The strength of adhesive force is obtained by dividing the value of centrifugal force by the apparent contact area of ice.

#### Examination of Solution-occupied Area at an Interface

For the examination of a distribution of areas occupied by a KCl solution segregated at a substrate/ice interface, a replica technique developed by Prodi and Nagamoto(3) was used in this experiment. Their technique was designed to examine chlorides, e.g. sea salts, contained in a natural hailstone. Namely, onto a sectioned surface of a hailstone, they applied a piece of millipore filter paper (0.8  $\mu\text{m}$  in pore size), which was previously soaked in a concentrated  $\text{AgNO}_3$  solution and dried up. Since sea salts segregated at grain boundaries in the hailstone are in a liquid state, i.e. a brine, at temperatures higher than the eutectic point, brine solutions transferred to the millipore filter paper exhibited brown patterns of  $\text{AgCl}$  as a result of chemical reaction, allowing the examination of distribution of sea salts in the crystalline structure of the hailstone.

#### Preparation of KCl-Ice and Substrate Surface

Polycrystalline ice containing KCl, which is

Figure 3. Crystalline structure of ice containing KCl.

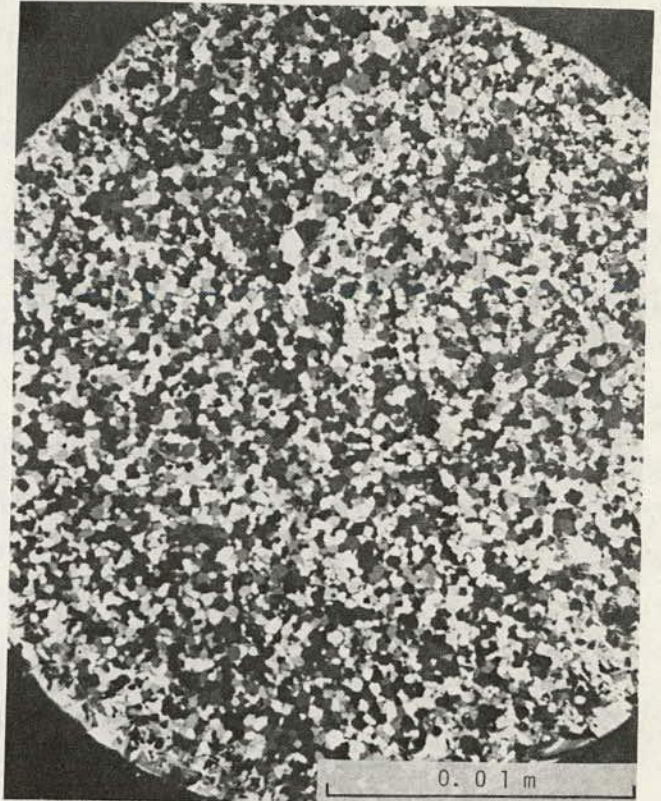
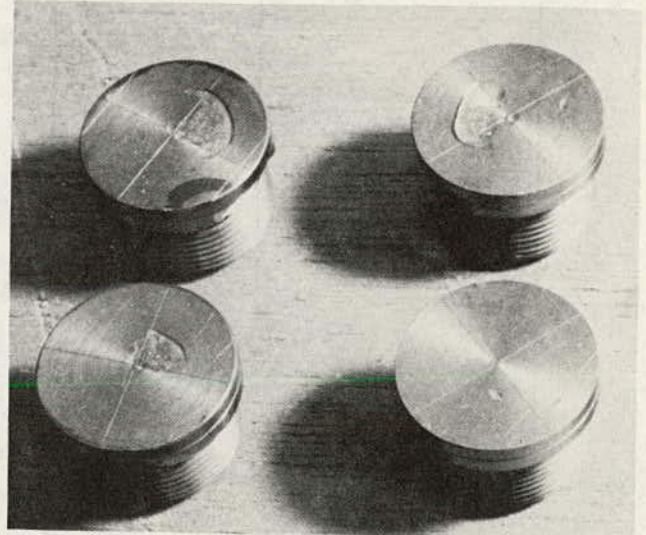


Figure 4. Ice fragment left on a brass substrate surface.



called KCl-ice hereafter, was formed by freezing of a KCl solution ranging in 0.05%~1% in concentration. For Preparation of a fine grained polycrystalline ice, a cylindrical container packed with fine disintegrated snow grains was soaked in a KCl solution cooled near  $0^\circ\text{C}$ , air having been expelled from the solution. Then the container was placed in a cold room to freeze a mixture of snow grains and the KCl solution. Figure 3 shows a typical crystalline structure of fine grained ice thus formed. The ice

Figure 5. Temperature dependence of adhesive strength of pure ice.

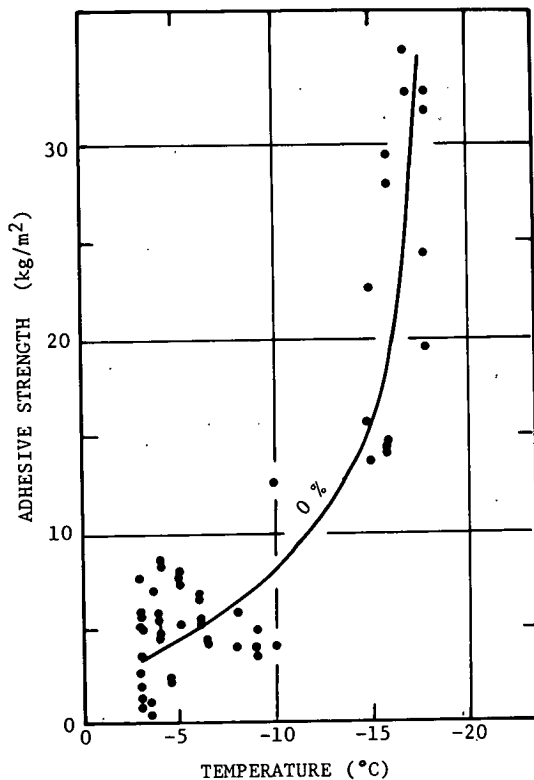
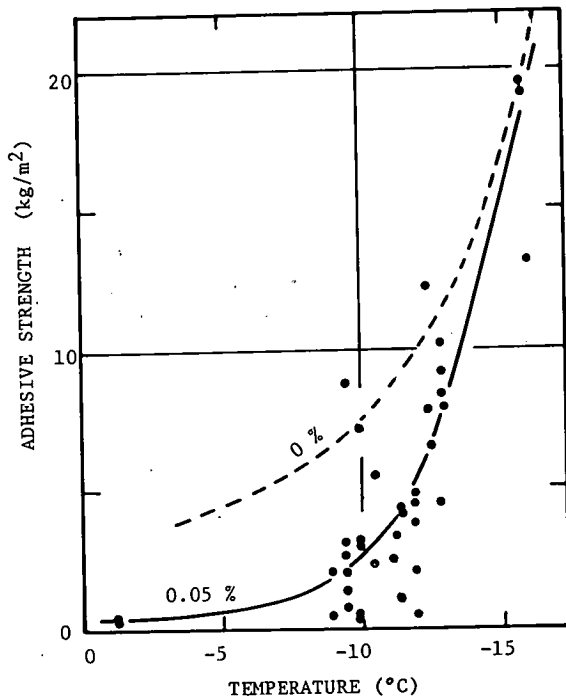


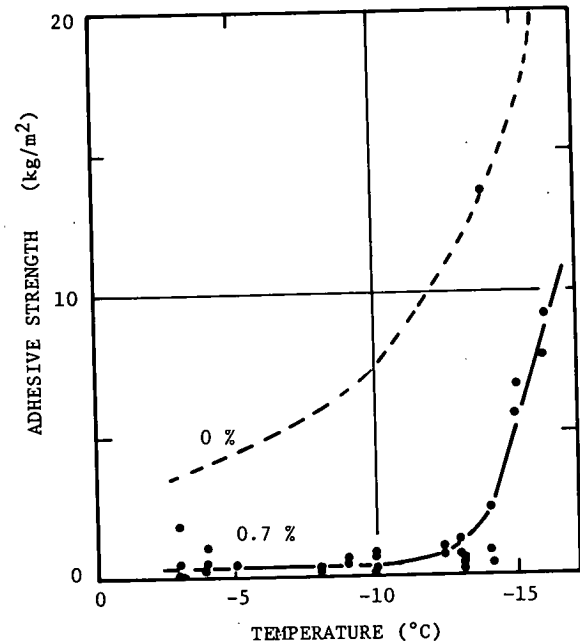
Figure 6. Temperature dependence of adhesive strength of KCl-ice frozen from a 0.05% solution.



specimen prepared for the measurement of adhesive strength had the weight of  $8 \sim 15 \times 10^{-3}$  Kg and the apparent contact area of  $0.7 \sim 3.5 \times 10^{-4}$  m<sup>2</sup>, which depended on the ambient air temperatures adjusted.

The surface of the brass substrate used was not

Figure 7. Temperature dependence of adhesive strength of KCl ice frozen from a 0.7% solution



mirror finished, but cleaned by absorbent gauze with ethyl alcohol before an ice specimen was frozen onto the substrate.

#### Experimental Results

Adhesive strength of ice is defined as strength at which a break or fracture occurs at a substrate/ice interface, the location of such a break or fracture existing very near the interface.

Figure 4 shows typical shapes of ice fragments left on the brass substrates after ice specimens were broken off by the action of centrifugal force at  $-15^{\circ}\text{C}$ . As seen in this figure, breaks or fractures of pure ice occurred partly within an ice mass very near the interface (cohesive breaks), in which term "pure ice" means the ice frozen from a water distilled twice. However, most of breaks of KCl-ice occurred at the interface at temperatures higher than the eutectic point (adhesive breaks). Figure 5 shows adhesive strength of pure ice measured as a function of ambient air temperature. As seen in this figure, measured values were widely scattered, suggesting that the scattering of data may be caused by non-uniform breaks at the substrate/ice interface as shown in figure 4. In spite of the fact that breaks at the interface were not uniform, the adhesive strength of pure ice showed a tendency of increase with the lowering of temperature as shown by a solid curve in Figure 5.

Figure 6 and 7 show temperature dependence of adhesive strength of KCl-ice. Values of percentage labeled to an individual curve in the figures indicate the concentration of KCl in the initial solution in which ice was frozen. As shown in these figures, the adhesive strength of KCl-ice decreased with an increasing concentration of KCl in the initial solution. It is interesting to note here that the value of adhesive strength of KCl-ice frozen from a 0.05% solution decreased at temperatures higher than around  $-11^{\circ}\text{C}$ , and that it increased sharply with lowering of temperature below  $-11^{\circ}\text{C}$  as shown in Figure 6. In the case of KCl-ice frozen from a 0.7% solution, the critical temperature



Figure 8.  $\text{AgNO}_3$  replica of a KCl-ice surface broken off vertically from a substrate. Replication temperature:  $-8^\circ\text{C}$ ; KCl concentration of initial solution: 0.7%.

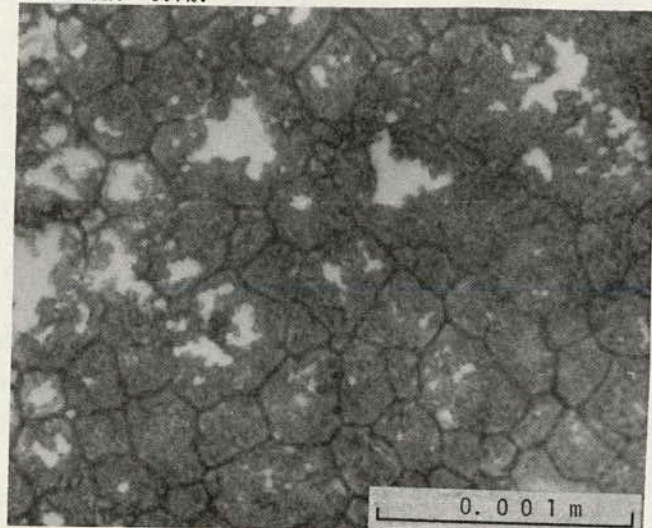
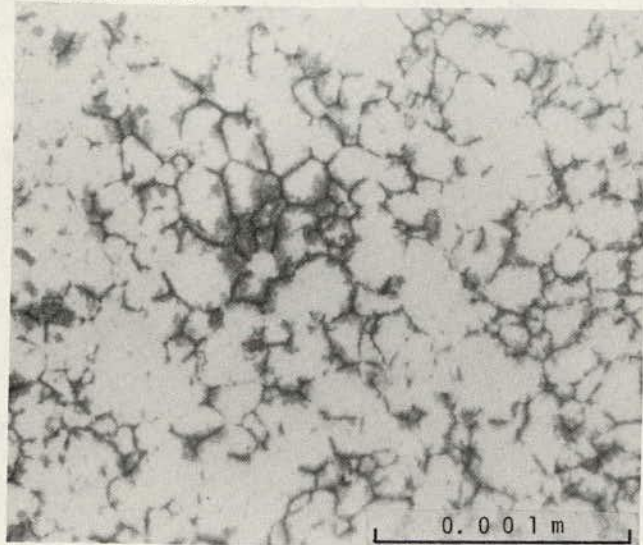


Figure 9.  $\text{AgNO}_3$  replica of a KCl-ice surface broken off vertically from a substrate. Replication temperature:  $-14^\circ\text{C}$ ; KCl concentration of initial solution: 0.7%.



shifted slightly to a lower temperature than  $-11^\circ\text{C}$  as shown in Figure 7.

According to the International Critical Table, the eutectic point of the KCl-ice system is referred to be  $-10.7^\circ\text{C}$ . Hence, a drastic reduction of adhesive strength observed at temperatures higher than  $-11$  to  $-13^\circ\text{C}$  can be explained by an interpretation that a thin solution film existing at the substrate/ice interface may contribute to the reduction of the real contact area of ice.

This interpretation was tested by placing a piece of millipore filter paper containing  $\text{AgNO}_3$  on the surface of an ice specimen broken off from the substrate and applying a slight pressure onto the surface of the millipore filter paper to make its contact with the ice surface closer. The distribution of a solution film segregated at the substrate/ice interface was successfully replicated through chemical reaction between  $\text{AgNO}_3$  and a KCl

Figure 10.  $\text{AgNO}_3$  replica of a brass substrate surface taken immediately after the removal of a KCl-ice specimen (0.7% in initial solution).



solution.

Figures 8 and 9 show photomicrographs of replica of an ice surface taken at  $-8^\circ\text{C}$  and  $-14^\circ\text{C}$  respectively. The specimen was KCl-ice frozen from a 0.7% solution. From these two photomicrographs, it is clear that the solution-occupied area at  $-8^\circ\text{C}$  is much broader than that at  $-14^\circ\text{C}$ . It is interesting to note that KCl molecules segregated at grain boundaries were still in a liquid state even at  $-14^\circ\text{C}$ , which is lower than the eutectic point as seen in Figure 9.

Figure 10 shows an  $\text{AgNO}_3$  replica of the surface of the brass substrate matched with Figure 8, where the ice specimen which adhered was broken off vertically by the action of centrifugal force. Immediately after the breaking off of ice, a piece of millipore filter paper was applied on the substrate surface to examine a distribution of a solution film which was left on the surface. Unlike the replicated pattern of a solution film on the ice surface shown in Figure 8, a liquid solution was dispersed in the form of patches or microscopic droplets on the substrate.

#### Discussion and Conclusion

As has been pointed out by many authors, the adhesive strength of ice is greatly influenced by a number of factors including ambient air temperature, rate of stress applied, physical properties of a substrate surface and purity of ice. This study focused on how the adhesive strength of ice is influenced by the existence of a liquid solution at the substrate/ice interface. When an ice containing a water-soluble impurity adheres onto a substrate surface, a solution film exists usually at an interface between ice and the substrate, reducing the real contact area of ice. It was found useful to select KCl as a convenient contaminant of ice and adopt the  $\text{AgNO}_3$  replica technique developed by Prodi and Nagamoto(3) in the examination of the area occupied by a liquid solution film and the otherwise area, i.e. the real contact area of ice at the interface.

Adhesive strengths of KCl-ice were measured by the application of a tension using a simple centrifugal device. As was expected, the relative strength of an adhesive force of KCl-ice decreased with the increasing concentration of KCl in the initial solution from which ice was formed.

When ambient air temperature shifted from a higher range than the eutectic point to a lower range, the adhesive strength of KCl-ice changed sharply as seen in Figures 6 and 7. This temperature dependence of adhesive strength of KCl-ice could be explained by the existence of a liquid solution film at the substrate/ice interface, as was proved by the  $\text{AgNO}_3$  replica technique. The estimation of Chloride reaction areas seen in Figures 8 and 9 was made by the aid of a photo pattern analyzer. The following results were obtained: the solution-occupied area was approximately 87.8% and 27% for the replica taken at  $-8^\circ\text{C}$  and  $-14^\circ\text{C}$  respectively.

As the first approximation, it is allowed to say that a darkness of brown color exhibited by  $\text{AgCl}$  as a result of a chemical reaction with chlorides is proportional to the concentration of chlorides in a segregated solution. Therefore,  $\text{AgNO}_3$  replicas shown in Figures 8 and 9 indicate that a fairly thick concentrated liquid solution is segregated at grain boundaries, wherefrom it extends to the substrate/ice interface in the form of a thin solution film, resulting in the reduction at the real contact area of ice. Consequently, the thickness of an extended solution film at the interface is not equivalent to that of a solution segregated at grain boundaries as has been assumed by Jellinek(2). Since the contact between grain boundaries and the substrate is almost completely broken by the existence of a thick concentrated liquid solution, grain boundaries do not contribute to the adhesive strength of ice, but a thin solution film which extends from grain boundaries to the substrate/ice interface reduces the adhesive strength of ice, depending on its thickness. Though an ionic diffusion can occur at the substrate/ice interface as shown by Murrman et al.(4) the authors believe that the filmy extension of a liquid solution at the interface observed in this experiment is accelerated by a pressure applied on an ice specimen in the freezing of it on the substrate surface.

#### Acknowledgement

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