Ice Adhesion Studies:
Properties of Defects in the Interfacial Region

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Considerable work has been done on the surface chemical aspects of ice adhesion. Another point of view, however, is that ice adhesion may be primarily a function of the strength of ice in the interfacial region; i.e., ice sheared from a surface breaks away cohesively in the ice rather than adhesively at the substrate. The properties of ice in the interfacial region, especially those factors that influence the strength of ice (point and line defects), have been investigated this past year. Investigations, including Berg-Barrett and Lang X-ray topography, have revealed line defects in ice to be charged. The presence of this charge is considered in the devising of methods to weaken ice in this region. Other studies include surface self-diffusion, effects of ice-weakening impurities such as hydrofluoric acid, and microhardness investigations to determine the effects on ice dislocation mobility after the use of ice-release agents.

Ice, the most common form of water in the cold regions, has the peculiar property of adhering to almost any substance and, consequently, causing a large variety of problems. Examples include icing on airplane wings causing loss of lift, icing on telephone and power lines causing interruption of services (Fig. 1), and frozen sea spray on the upper structure of a small boat causing it to capsize. Icing on windshields, freezedown of vehicles, engine ice formation, and many other ice formations are all problems of great practical and tactical importance.

There are many secondary factors, such as impurities or irregularities of the surface, that greatly affect the practical problem of ice adhesion and sometimes completely conceal the fundamental mechanism of adhesion. Our approach to the ice adhesion problem is twofold: (a) to obtain fundamental information on those adhesion mechanisms and processes understandable by using solid-state physics, and (b) to find practical and long-lasting methods of ice adhesion control.

In this treatment of the ice adhesion problem, our attention has been not on the actual interfacial bonding process but rather on the forces and mechanical actions that seem to have the preponderant influence in practical situations when the attempt is made to remove ice from a substrate.

The first consideration to be applied is, in essence, a practical one. By looking at the structure of certain materials and water, we can draw conclusions concerning their attraction for one another. Depending on the chemical structure of this substrate material, various interactions with water molecules can be postulated such as hydrogen bonding, dipole-dipole, electrostatic, electrical double layer effects, induced dipole-induced dipole, London dispersion, and van der Waal's forces. The degree of interaction can be characterized by the relative ability of water to spread on a surface; i.e., water will completely wet those surfaces with high interactions and will bead on surfaces with lower interactions. However, certain things became evident in this forest of views. The first point is that even though some substances, such as Teflon, are extremely hydrophobic, that is, they completely repel water, they still require a definite and, in some cases, considerable force to remove ice formed on their surfaces (1). So water repellency does not imply ice phobicity. Therefore, problems in ice adhesion require a somewhat complex and multidisciplinary approach.

As shown by Anderson, (2) Hoekstra (3), and Murrmann (4), the properties of surface adsorbed water are considerably different from that of either bulk water or bulk ice. We also know that on the molecular scale it is extremely difficult to keep things clean so that at the interface there are definite impurity actions that further complicate the attractive interactions of the bonding process. Therefore, with regard to the ice adhesion problem, the interaction of the surface adsorbed layers with the bulk ice and bulk substrate will be very important. There are other views, however, and certain points about this interaction that need clarification.

Figure 1. Downed power and telephone lines near Bradford, Vt., caused by ice loading.

The first question is that of the process that occurs when ice is removed. In most cases the position of the break is such that the surface adsorbed water remains on the substrate. This situation arises because of the tightly bound nature of this water, which requires very high temperatures along with a quite high vacuum to remove it (5). This nature of surface water is also shown by its attraction for surfaces. For example, to use low energy electron diffraction (LEED), which is a method of looking at the structure of metal surfaces, requires a quite clean surface. Generally, a surface cleaned under a vacuum of 10^{-10} torr is necessary. Even under these conditions, water vapor leached from the vacuum system will absorb on the metal surface and make measurements impossible after only about one hour of operation (6). Evidence by Zisman and Bernett (7) on contact angle measurements on metals and metal oxides indicated that complete monolayers of adsorbed water formed on these surfaces in conditions down to 0.6 percent relative humidity. Therefore, to look at ice adhesion requires that the zone of interest be clearly defined. More confusion will probably be added by the definitions given in Table 1, but they summarize the view taken here and are compatible with those posed by Murrmann. Our contention is that these types of break occur and that they occur predominantly in either Zone 3 or Zone 1 (28). There is no evidence to indicate that the separation of ice from an interface can remove these last few layers of adsorbed water. The structure of this interface will influence and control the defect structure of the ice in Zone 3, but in the study of ice adhesion our prime area of consideration has been the structure of this highly defective ice where we believe most breaks occur. To define the influence that the interfacial layers have on this break zone of highly defective ice, we must know the characteristic defect structures in this zone.

MECHANICAL INTERACTIONS INFLUENCING ICE ADHESIVE STRENGTH

Several theories have developed regarding the strength of adhesive bonds, but the object here will be to speak of only those ideas that pose causes for ice adhesion or a way of reducing it by purely mechanical means, either at the interface or in the bulk of

TABLE 1
ZONES AND TYPES OF BREAKS

Zone	Definition	Type of Break
1	Bulk substrate material	Failure of Zone 1, i.e., the bulk substrate, whether an oil or low shear strength solid
2	Interfacial adsorbed water	Interfacial breaks leaving a clean substrate with no adsorbed water
3	Highly defective ice	Breaks within the highly defective ice

ice. Others have outlined these purely mechanical interactions that influence ice adhesive strength, and they will be briefly reviewed.

Expansion Effects

It has been shown by Bascom et al. (1) that roughing the surface of a substrate can increase the ability of ice to adhere to that surface. Presumably small valleys in the surface trap droplets of water that, upon freezing, expand their volume and push apart the sides of the depression that in turn grip the frozen droplet (8).

There is also a surface roughness effect in the shear-type testing that has been used to measure ice adhesion in the past (8, 9). Mass transfer is required for a deformation to follow the surface profile along the direction of stress. The adhesive strength measured by this shear stress would depend on whether the loading rate allowed plastic deformation to follow the surface profile or whether the shear proceeded by a series of microfractures. Therefore, the surface roughness may cause a high sensitivity of the adhesive strength to the loading rate.

Orientational Effects

Ice deforms plastically much more easily if sheared parallel to the basal plane than in any other direction. Plastic materials have sometimes shown a propensity toward orienting ice crystals preferentially so that the majority of the grains can slip easily in shear (1). Therefore, a careful check of orientation should be made in ice release experiments because orientation effects arise not only from the nature of the substrate but also from the growth habit of the samples. That is, the cooling rate or the way that heat is carried away from the interface can strongly influence the growth habit and the preferred orientation of the grains, which in turn will influence the mechanical strength of the bond, especially if the break obviously occurs cohesionally within the ice.

Mechanical Deformation of the Substrate

Fracture occurs in the substrate material that is either a grease or an oil or a low shear strength crystalline solid such as graphite (9).

Air Entrapment at the Interface

A consequence of the freezing process and of the influence of the substrate material may be that air present when water freezes on the substrate is not driven out as the freezing front moves from the interface but instead is entrapped at or near the interfacial region. This type of ice is considerably weaker at the interface than bubble-free ice and, as a consequence, fracture is initiated more easily in this area and the ice is more easily removed (1).

Impurity Concentrations

Pounder (10) has described this procedure whereby impurities pass preferentially into crystal grain boundaries within the ice, widen them, and thereby weaken the ice structure. Very small amounts (ppm range) of the impurity hydrofluoric acid also have the ability to have the strength of ice as shown recently by Jones and Glen (11). Apparently the cause is quite different from the effect of relatively higher concentration of impurities described earlier and is more intimately related to the dislocation factors described later.

Impurity Effects on Fracture Properties

Impurities can affect not only the strength of ice but also the fracture and plastic properties, areas that have not been studied until quite recently. Nakamura (29) has taken ice bars dipped in HF and drawn them into points similar to molten glass or tied them in bows just with hand pressure. Itagaki and Sabourin (12) in charpy testing (impact hammer) on doped ice crystals found that certain impurities changed the mode of fracture so that the sample shattered into 5 or 6 small pieces unlike the 2- or 3- piece

fractures normally seen. Fracture behavior has generally not been closely studied but is an area of great importance for ice adhesion studies because it is more intimately related to the way ice is removed in practical situations.

Defect Processes in the "Thick" Transition Zone

This area has previously been described as a liquid-like layer by Jellinek (13) and others (8). However, our philosophy is to think of this region as a solid with a high concentration of certain types of defects with definite properties associated with defects in a solid as opposed to a liquid. At the temperature considered the solid processes are certainly highly mobile, but it is still verified by our X-ray topography and diffusion studies that the properties of the thick zone are better described by the order more typical of solids than of liquids.

Our particular interest has been in a certain type of defect known as a dislocation. A dislocation is a line defect within a crystal and, simply described, is the absence of a row of atoms over quite a long distance compared with the spacing between individual atoms. Dislocations reduce the shear strength of ice by a factor of about 10^5 compared with ice that contains no dislocations. These defects can also increase the strength of certain materials if tremendous numbers or networks are introduced into the material and they become locked or immobile by interactions between the defects themselves. This network introduction has been used for thousands of years to strengthen metals and is the well-known cold-working or work-hardening procedure. However, the reasons that this process worked have only been understood since the advent of dislocation theory a few years ago. Dislocation structure can also influence fracture properties by concentrating stress at certain points or causing stress relief in preferred directions when a fracture is initiated (14).

The actual measured adhesive strength appears as the weakest link of many mechanisms and cannot consistently be attributed to one mechanism.

RESULTS AND DISCUSSION

Studies on Interface Structure

X-Ray Topography Study—Two techniques are being employed to study dislocation structure in the interface layer. Figure 2 shows a Lang X-ray topograph of ice near an interface. The dislocations appear as dark lines in this topograph. A thin slab of ice was frozen onto a support. The very heavy concentration near the interface layer indicates that the ice is heavily deformed by freezing. The dislocation structure in the interface layer could not be revealed by this topograph because the density is too high, but the strain introduced by the freezing process is evident.

Dislocations were found to be electrically charged because the dislocations can be swept by an electric (ac) field between their pinning points and vibrate as shown in Figure 3 (T = -10 C). The sign is positive and the line is highly charged ($\frac{1}{3}$ elementary charge per latice spacing). Charged dislocation motion could be a major mechanism of the dielectric relaxation and constant, unlike the previous theory based on the Bjerrum point defect (15). A high density of charged dislocations in the interface layer may produce additional attractive forces due to the
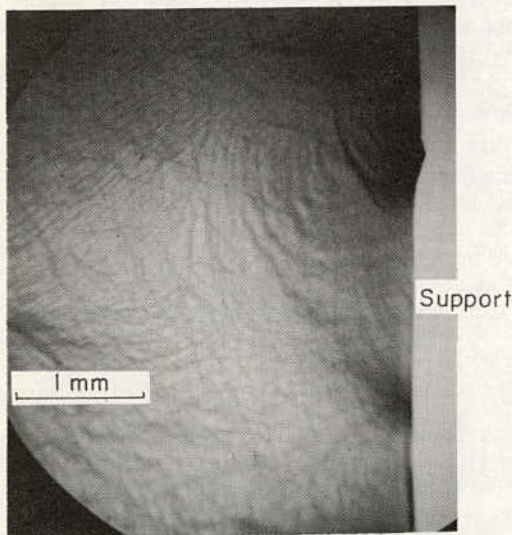

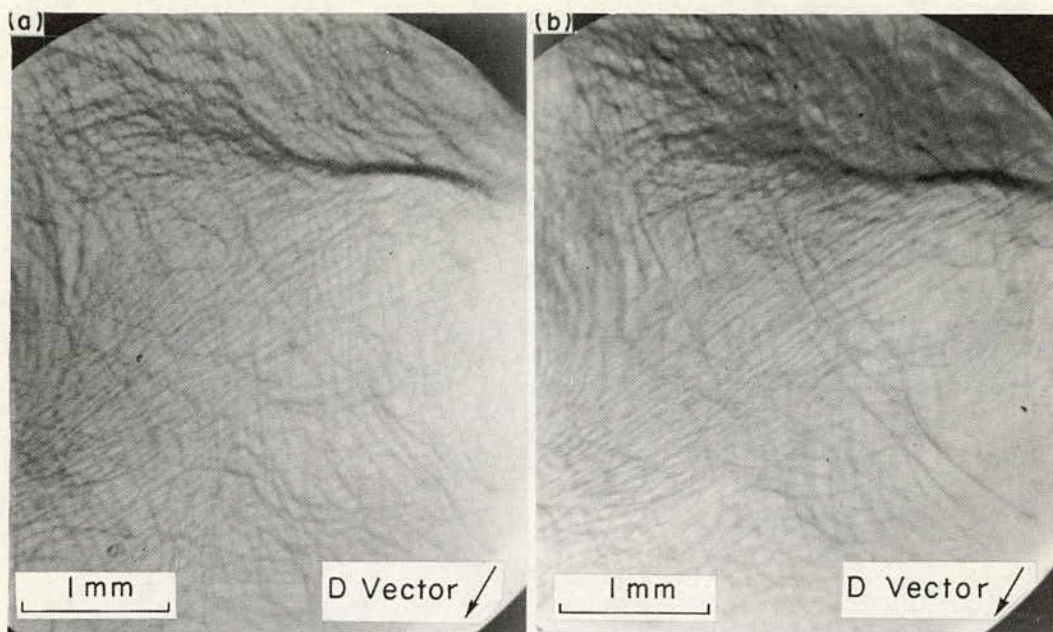Figure 2. Lang topograph showing dislocations introduced by freezing.

Figure 3. Dislocation structure in a single ice crystal: (a) without electric field and (b) with field, 320 V/cm, 1⅓ Hz.

surface charges and provide another contributory mechanism to ice adhesion.

The Berg-Barrett method is another X-ray topography technique that is more suitable to studies of the near surface layer. Studies are in progress to reveal the dislocation structure in the interface region by freezing the ice onto a substrate and then reducing the ice thickness by successive sublimation. This method should separate out the bulk and near interface ice defect structures and make comparisons possible.

Dielectric Study—Because the dislocations in ice are electrically charged, their motion can be detected by dielectric measurement. Theory predicted that the initial stage of straining would increase the dielectric constant, loss, and relaxation time by unpinning of the dislocation line. In higher straining the segment length becomes shorter because of the dislocation intersection and thus reduces the values disproportionately because the dielectric constant is proportional to the square of segment length while loss depends on the fourth power of segment length. The measured results indicate that the theory is generally correct though simplification in the theory has caused some discrepancy (16) (Fig. 4).

Charged dislocations can also help explain electromechanical interactions observed in ice such as extrinsic piezoelectricity (17, 18) and charge generation (19).

Mass Transfer Along the Interface—Mass transfer in the interface not only is a controlling factor of dislocation motion but also contributes to the macroscopic process of ice adhesion in the effect of surface roughness as pointed out previously. Mass transfer is also an important mechanism in the adhesion of snow and ice particles (sintering) because it can change the contact area and neck size between these particles (20).

The values of self-diffusion in bulk ice seem pretty well established (21, 22, 23, 24), although there are problems in interpreting the mechanism. No published surface mass transfer values are available yet. We have conducted 2 types of measurements, and the results will be published in the near future.

Four mechanisms can contribute to mass transfer along a surface. Surface self-diffusion is a mass transfer mechanism restricted to molecular migration along the surface without penetrating into the bulk. Mass transfer can also proceed through the bulk material when initiated from the surface and terminated onto a different part of
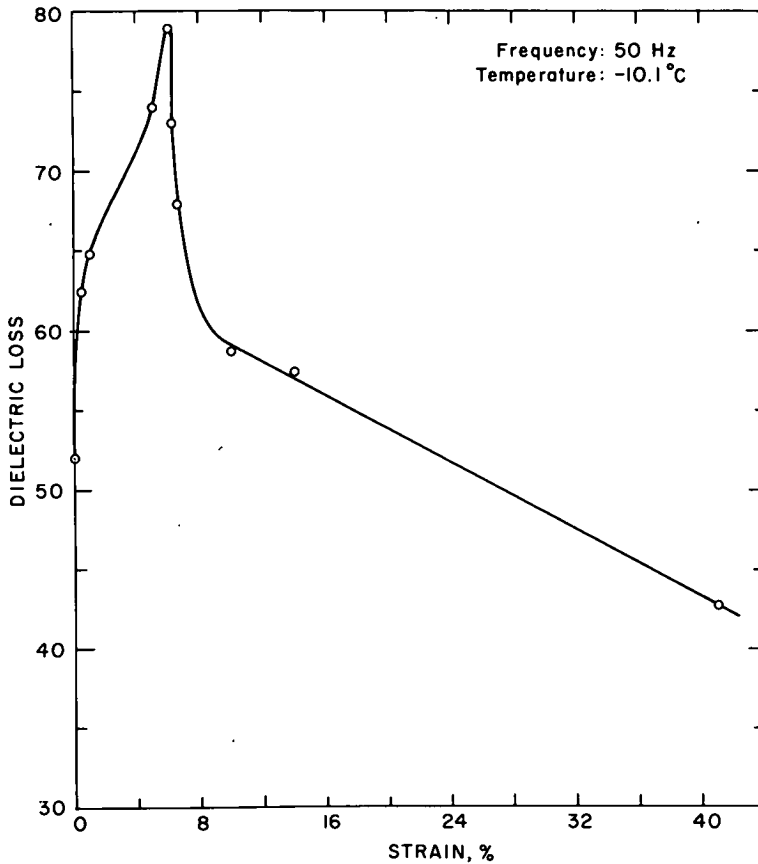
Figure 4. Dielectric loss versus strain in an ice single crystal.

the surface. If the surface of the ice is exposed to the atmosphere, a similar process can proceed as evaporation from the surface, diffusion through the atmosphere, and deposition onto another part of the surface. The fourth mechanism appears when the surface is curved. If a viscous layer covers the ice surface, flow will be initiated by the pressure difference caused by the curvature (25). The 2 independent measurements employed make it possible to distinguish among these mechanisms and assess the contribution from each mechanism. The 2 measurements are as follows:

1. Decay of strain-freely produced grooves. A system of sinusoidal grooves formed on a solid surface will decay or flatten according to the following equation (25):

$$A\omega^4 + B\omega^3 + B'\omega^3 + C\omega = K \qquad (1)$$

where $\omega = 2\pi/\lambda$ (ω is the frequency and λ is the wavelength of the periodic grooves); A, B, B', and C are constants related to the surface diffusion, volume diffusion, diffusion through the atmosphere, and viscosity respectively; and K is the decay constant. A close study of the frequency dependence, ω, can reveal the contribution of each mechanism. However, a determination of the surface diffusion constant, A, is very difficult by this method because of the high contribution of the other mechanisms in the temperature and wavelength range of the experiment. Thus, a radioactive tracer method was required to separate the mechanisms.

2. Radioactive tracer method. Preliminary experiments gave scattered values presumably due to the surface defects introduced during the sample preparation. A method to produce strain-free flat surfaces on ice is essential to use this method properly. This new technique was recently established by our group and will be adapted to the tracer measurement.

A comparison of the groove decay results with the results of the preliminary tracer method show that the surface self-diffusion contribution (A in Eq. 1) is not appreciable in the temperature and wavelength range measured. Instead, the viscous flow term is the major mechanism, and diffusion through the atmosphere can contribute a smaller but comparable amount for groove wavelengths longer than 16 μm. More detailed studies are in progress.

Impurity Diffusion—Certain types of impurities such as hydrofluoric acid are known to soften ice crystals drastically. The effect appears very rapidly (11). A detailed study of HF diffusion suggested that its major mechanism is diffusion along the dislocation core. The higher concentration in the dislocation core can make the dislocation motion easier either by melting the core region and making a liquid core or by producing Bjerrum defects that reduce the resistance of dislocation motion through the solid.

There appears to be some hope to control the adhesive strength by introducing hydrofluoric acid in the interface region.

Breath Figure Study—The controlling factor of ice adhesion in some cases may be more macroscopic than molecular. A trace where ice was frozen on a substrate was observed by blowing warm breath onto the substrate after the ice was removed. Close microscopic study indicated that the fog on the undisturbed surface consisted of a relatively small number of uniform size droplets, while on the surface from where ice was removed the fog produced a larger number of droplets with a greater size distribution. This trace was very stable and remained for a few days. It can be washed away only by using a strong detergent and wiping with considerable force.

This fact may have indicated that the ice made contact with the substrate through the impurity layer at points where the droplets were formed. The adhesive force at the points where the droplets were formed can be stronger than at the other points that were covered by the impurities and may have contributed a greater amount to the total adhesion.

Practical Methods of Adhesion Control

The maximum adhesive strength can be determined as the weakest of the following parts: ice, substrate, or interface, while the van der Waals force limits the minimum between 2 solids. This minimum can be reduced to near zero if liquid exists in the interface and the rate of deformation is very slow.

Liquid Replenishing Lubricant—A layer of oil has been used to reduce the adhesive strength. The major disadvantage of this coating is its short life. Each ice separation reduces the oil thickness by half, which means about $\frac{1}{1,000}$ of the original coating thickness remains after 10 separations. One possible improvement is a water-repellent coating with a replenishing oil layer diffusing out to the surface. Some effort to synthesize this compound is in progress.

Solid Lubricant—There are some indications that a solid lubricant can reduce the adhesive force when the shear force is applied parallel to the interface. Abele and Parrott (26) noticed that snow adhesion onto vehicle tracks can be reduced by the application of flat black paint. One possible explanation of this finding is that the paint contains graphite as a pigment that serves as a lubricant. If this notion is correct, molybdenum disulfide can be a better ice release coating; the experiment is in preparation although preliminary indications have not shown a significant improvement.

Self-Straining Interface—Bascom et al. (1) observed straining in a freshly frozen ice substrate interface layer that later relaxed by recrystallization. Self-induced stress in the freshly frozen interface layer can reduce the external force required to fracture this layer. Certain substrate materials may reduce the adhesive strength by this mechanism and will be revealed by a better understanding of the defect process in this zone.

Application of Certain Types of Energy—The methods described are passive methods and are limited by the van der Waals force if no liquid exists in the interface (27). The
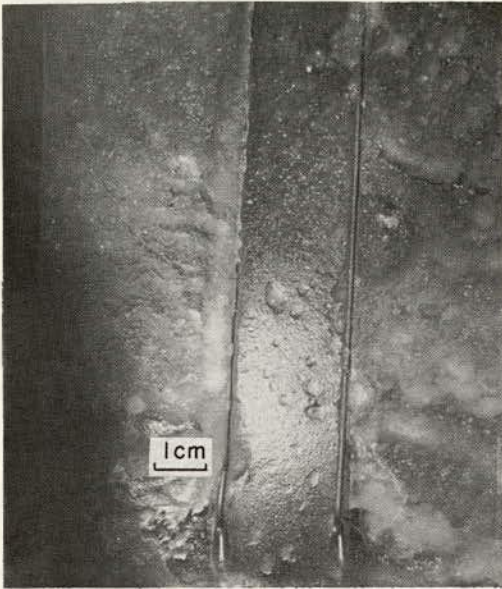
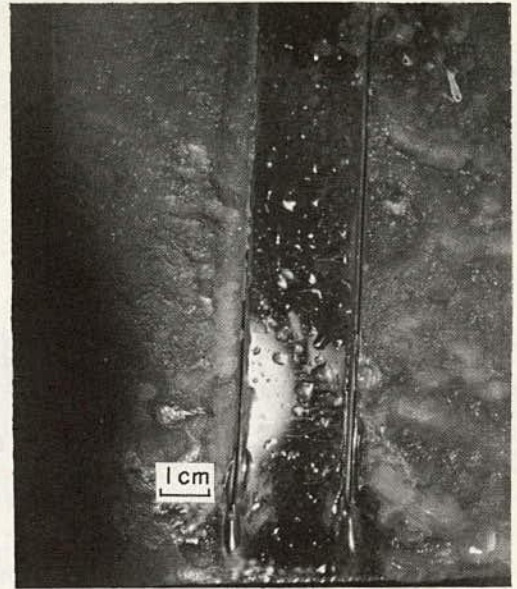Figure 5. Glaze formed between parallel electrodes.

Figure 6. Glaze removed between electrodes after application of 9,000 V/in. ac for approximately 5 sec.

large dielectric constant of ice makes the contribution of the van der Waals force even larger, while rapid mass transfer along the surface of ice makes a fast forming, extensive contact area and reduces the distance between the ice and substrate to the range necessary for van der Waals forces to act.

To overcome this limit may require some energy to initiate a minimum separation. The simplest method seems to be the application of mechanical force. However, the standard laboratory adhesion test using the tensile or shear mode attempts to obtain the maximum force, while practical procedures generally are a peeling or fracture method that requires considerably smaller effort. A more practical and reliable testing method is currently being searched for.

The thermal method is the other method widely used to remove ice. Its efficiency depends highly on the method of delivering the energy. Producing the heat directly in the interface layer will obviously be the best method. Electrical heating can concentrate the heat production in the interface if the substrate is an insulator. The application of sufficient ac voltage to a parallel electrode system can also produce heat in the interface layer. The voltage depends on the conductance in the layer and can be 9,000 V/in. for pure ice down to the order of 10 V/in. if the surface is salted. Unlike indirect heating, this system will turn off automatically when the surface is dry. An example is shown in Figures 5 and 6. A lucite plate that has one set of parallel electrodes was glazed by ice (Fig. 5). The layer of pure ice between the electrodes was melted and evaporated by an electric discharge of 9,000 V/in. ac in about 5 seconds. After the surface was dried no discharge occurred (Fig. 6).

Other possible methods such as infrared or radar are variations of the thermal method with a different procedure of energy delivery and can be classified either by introducing a liquid layer in the interface or by completely removing the ice by melting.

CONCLUSIONS

The problem of ice adhesion includes various aspects, and quick easy conclusions cannot be reached yet. Certain mechanisms may control one case while other mechanisms may become the controlling factor in another case. The data accumulated to

date seem too ambiguous to build a solid theory. Method of testing, surface treatment, effect of roughness, impurity layer on the surface, structure of defects—none is treated seriously in previous studies though all of them can affect ice adhesion. More careful studies are in preparation.

The only moderately successful way to reduce ice adhesion to date is to prevent the direct contact of ice with the substrate by a liquid lubricant. Some results obtained using high polymers indicate that low adhesive force may also be attributed to the impurity layer that shows more or less liquid properties. The main disadvantage of the liquid lubricant is its short life. A replenishing lubricant coating will, it is hoped, extend the life to a practical usable range. Other types of coating and treatment also have to be studied more carefully in the light of their influence on interface layer strength.

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Informal Discussion

R. P. Murrmann

How did you obtain the photographs of the ice-aluminum interface?

Ackley

The Lang technique is transmission, and a very thin slab of ice, $1/10$ mm or so, is gapped into this picture.

Murrmann

Is there any possibility that, when you prepared this, strain was introduced at the interface rather than by the freezing process?

Ackley

It was prepared by slightly warming the interface and letting it refreeze, so the volume change obviously introduces a strain. There was a possibility of mechanical strain being introduced also. We are refining the technique, but I do not think that the handling has been sufficient to account for the number of dislocations we have seen.

William F. Limpert

In your radioactive interface studies, did you ever run a test using sodium-22 below the eutectic point of sodium chloride-water?

Ackley

The tracer diffusion method we used was not ionic. We used a self-diffusion method—tagged water molecules. There is an experiment going on now under the direction of Dr. Weeks at USACRREL that involves freezing salt-ice, using very high concentrations, and modeling sea ice.

H. H. G. Jellinek

We did some work on sodium-22, but with diffusion into polycrystalline ice above the eutectic point. Above the eutectic point the grain boundaries are liquid—a saline solution—and below it they are solid, so the grain boundaries are influenced by temperature.

Limpert

Can you tell whether there is a liquid-like layer at the grain boundaries?

Jellinek

We have not done surface diffusion experiments. We have done diffusion through polycrystalline ice. Once you have attacked the grain boundaries, they would be liquid above the eutectic and solid below. So the diffusion coefficient at the eutectic point should not change suddenly to a lower value.