Ice Adhesion to Hydrophilic and Hydrophobic Surfaces

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ABSTRACT

The adhesional shear strength has been determined for ice formed against polished steel, monolayers adsorbed on steel and thin plastic coatings painted on metal surfaces. The adsorbed monolayers reduced the shear strength to about one-third of that for ice on clean steel. The monolayers also had the effect of changing the character of the breaks from clearly cohesional to apparently adhesional failure. The shear strength from the plastic coatings ranged from values equal to that of ice against clean steel to values 70 to 80% lower. The reduction in shear strength did not correlate with the water contact angle on the coatings but was usually found to be due either to air entrapment at the ice/coating interface or to cohesive failure of the coating itself.

The ice separated from the various substrates was examined microscopically by forming plastic replicas of the ice surface. These studies helped determine the mechanism of failure and, since one of the replicating solutions was also an ice etchant, much was learned about the crystal structure and the crystal defects of ice near surfaces. The ice lattice was found to be highly defective near the substrates and this is discussed in connection with the "liquid-like," behavior of interfacial ice.

INTRODUCTION

ICE ADHESION research has been motivated by interest in the surface properties of ice and the need for practical icephobic coatings. Empirical studies aimed at designing ice-release coatings have produced genuine improvements in practical operations. Unfortunately accidental changes in the formulation or in the method of applying these coatings often result in a loss of their ability to release ice. These detrimental alterations in the coatings might be avoided if there were a better understanding of the fundamental factors that determine the strength of ice-solid bonds. In addition to their practical im-

plications, ice adhesion investigations have revealed that ice near interfaces may have some unusual properties.

The factors known to influence ice adhesion can be divided into those related to the substrate and those related to the interfacial properties of ice. With regard to the substrate, there exists a rough correspondence between ice adhesion and the hydrophobicity of the surface against which the ice is formed. Raraty and Tabor, for instance, found the adhesional shear strength of ice to decrease progressively with increasing water contact angle on a series of polymer surfaces [1]. However, even though adhesion to hydrophobic surfaces is usually less than to hydrophilic surfaces, the adhesion to a solid with as low a surface energy as Teflon is seldom negligible, i.e., weak enough that the ice releases under its own weight. The adhesional strength of ice to Teflon is slightly more than half the value for ice sheared from hydrophilic metal surfaces [2]. In a study of ice adhesion to lubricated surfaces, strong adhesion was observed even when the contact angle of water on a metal under oil was as high as 160° [3]. Ford and Nichols [2] demonstrated that at temperatures near −20°C low adhesion to hydrophobic plastics usually results from large differences between the thermal coefficients of expansion of ice and substrate. At temperatures above −10°C, differences in thermal expansion are less important and the adhesion is stronger.

The interfacial properties of the ice also affect adhesion behavior. Raraty and Tabor [1] and Jellinek [4] concluded that ice near the interface undergoes plastic deformation when sheared from both hydrophobic and hydrophilic surfaces. Jellinek found that the adhesional strength of ice was substantially lower in shear than in tension. He explains this difference by postulating that ice near interfaces has liquid-like properties between 0°C and −13°C and that this liquid layer fails easily in shear but not in tension.

In this paper measurements are reported for the adhesion of ice to both hydrophilic (high surface energy) and hydrophobic (low surface energy) surfaces. Replication and etching techniques were used to examine the separated ice surfaces for fracture markings and to determine their crystal structure. The results agree with much of the previous work although there are some interesting differences.

EXPERIMENTAL PROCEDURES

Materials:

The test surfaces against which the ice was formed were highly polished stainless steel plates or various polymer coatings applied to clean brass plates. These plates were 1 in. square and ¼ in. thick. The steel plates were polished to a mirror finish and were cleaned just prior to use by wet metallographic polishing with 0.05μ alumina powder. A few observations were made on steel

that had been given a final polish with 1.0μ alumina or had been abraded with a fine (4/0) emery paper.

Monolayers of octadecylamine, stearic acid and perfluoroundecanoic acid were absorbed on the steel plates by retraction from solution or from the melt. Adsorbed films of polydimethysiloxane were deposited on steel by flooding clean plates with the polymer oil and then rinsing with benzene to remove all but the firmly adsorbed polysiloxane molecules.

The commercial coatings used are listed in Table 1. Each was applied to the brass plates according to the instructions given by the manufacturer.

The ice was formed from water that had been redistilled from a quartz still and had a conductivity of 1×10^{-6} ohm^{-1} cm^{-1}. Dissolved air was partly removed by boiling at reduced pressure.

Methods:

The measurements of adhesive shear strength were made at $-6°C$ using the apparatus and techniques developed by Ford and Nichols [2]. The test rig is shown schematically in Fig. 1 with the ice block on the test plate. Ice was formed in clean, Teflon-coated foil molds. A hard wax was used to seal the foil around the outside edges of the test plate. Care was taken to prevent this wax from contaminating the test surface and the water. Approximately 15 min after the water had been added, it had supercooled to about $-3°C$ to $-4°C$ and crystallization was started by nucleating with a tiny frost crystal. The ice was then allowed to stand overnight. During this time, the recrystallization processes appeared to have reached completion; the ice within ¼ in. of the interface was clear and free of gas bubbles. The test rig was designed so that there would be a 0.01-in. clearance between the ice holder and the test plate beneath. The foil around the ice in the 0.1 in. space was stripped away

Table 1. Polymer Coating Characterization

| Coating	Chemical Type
A	Dimethylpolysiloxane, cross-linked, filled
B	Dimethylpolysiloxane, cross-linked, filled
C	Dimethylpolysiloxane, cross-linked
D	Dimethylpolysiloxane, cross-linked
E	Polyorganosiloxane
F	Polyorganosiloxane
G	Polyurethane
H	Perfluorooctylmethylmethacrylate
I	Epoxy-polyorganosiloxane
J	Polyorganosiloxane
K	Vinyl-polyorganosiloxane
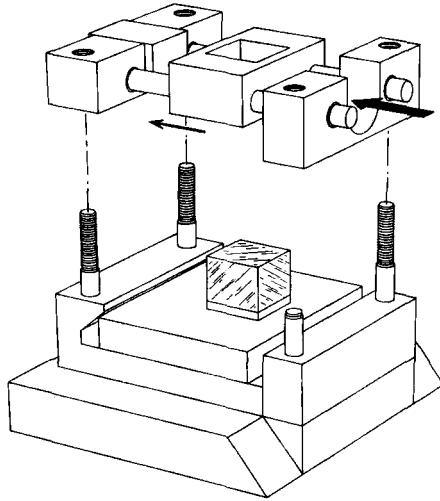
Figure 1. Adhesion test apparatus.

and the ice sheared from the substrate by applying force against the ice holder with a hydraulic ram. In general, four determinations were made on each test plate, and then the test surface was renewed and four more determinations made. The shear strength reported was the average of these eight measurements.

Thin plastic replicas were made of the ice surface sheared from the substrates, and these replicas were examined microscopically. The replicating solutions were either water-saturated Lucite (polymethyl methacrylate) solutions in ethylene dichloride or Formvar (polyvinylformal) in ethylene dichloride that had been percolated through Florisil absorbent to remove water and polar contaminants. In both cases the polymer concentration was about 2%. The solutions were precooled to $-6°C$ and applied to the surface with a cold medicine dropper within 20 sec after the ice had been sheared from the block. When dry, the plastic replicas were transferred to microscope slides by placing the plastic-coated ice surface against the slide at room temperature and allowing the ice to melt. Both types of replica films adhered well to clean microscope slides.

Various methods were used to study the replicas and also the surface texture of the substrates. These methods included electron microscopy and incident-light microscopy using a polarization interference objective [6]. Light microscopy was also used with asymmetric illumination produced by partially obstructing the incident beam.

This technique created a shadowing of the image that was helpful in resolving surface structure at $400 \times$ and greater.

The freezing process for ice forming against steel surfaces was observed with a polarizing microscope fitted with a cold stage. Steel cylinders ¾ in. in

diameter and with the upper surface highly polished were placed on the stage and the polished surface covered with a water film about ¼ in. thick. The freezing of the water was observed in incident light.

Contact angle measurements were made on the substrates at 25°C by the sessile drop method with a telescope goniometer.

RESULTS

Adhesional Shear Behavior:

The adhesional shear strength of ice to adsorbed films on polished steel are compared with the shear values from uncoated steel in Table 2. The effect of interposing the adsorbed, hydrophobic films was to (a) reduce adhesional shear strengths by about one third and (b) to change the character of the break from cohesional-adhesional to apparently adhesional (i.e., more than 95% of the failure appeared to occur between the ice and substrate). There was no correlation between the shear strengths and the minor variations in water contact angles on the monolayer coated surfaces. In using the phrase, "adhesional failure," it is not implied that the failure occurred exactly at the ice/substrate interface. Instead, it is meant to distinguish breaks where no visible ice was left on the substrate from breaks that had obviously occurred through the ice. It is worth noting that the apparently adhesional breaks

Table 2. The Adhesion Shear Strength of Ice to Clean and Monolayer-Coated Surfaces of Highly Polished Steel at —6° C

Monolayer Present	Water Contact Angle (deg)	Shear Strength (psi)	Type of Break
None	0	135	adhesional-cohesional
Octadecylamine	104	71	adhesional
Stearic acid	104	87	adhesional
11-H-perfluoroundecanoic acid	97	91	adhesional
Polymethylsiloxane	103	91	adhesional

Table 3. The Effect of Surface Roughness on Ice Adhesion to Monolayer-Coated and Clean Steel Surfaces at —6° C

Monolayer Present	Shear Strength (psi) polishing method		
	0.05µ alumina	1.0µ alumina	"4/0" emery paper
Polymethylsiloxane	91	86	130
Octadecylamine	71	93	
None	135		182

paralleled the interface so well that the ice consistently replicated any minor surface scratches or pits on the steel.

Contact angle measurements on the monolayer-covered steel after successive shear tests indicated that the monolayers had undergone some disturbance. On an octadecylamine monolayer, the contact angles for water and methylene iodide had declined about 10° after four successive tests. There was no progressive change in the adhesive force with this decrease in contact angle.

The effect of surface finish on the adhesional strength of ice to hydrophilic steel surfaces and to steel covered with adsorbed films is shown in Table 3. The different steel surfaces were examined by electron microscopy. At a magnification of 20,000 $\times$ the highly polished steel (0.05μ alumina) showed only an occasional surface scratch but the steel polished with 1.0μ alumina had a dull mirror appearance and the electron microscope showed many parallel scratches separated by less than 0.5μ. The abraded surface (4/0 emery paper) was visibly scratched and in the electron microscope showed deep, criss-crossing furrows.

The surfaces polished with 0.05μ and 1.0μ alumina did not give a significant difference in adhesion despite the greater roughness of the surface polished with the 1.0μ alumina. On the other hand, there was a notable increase in adhesion in going from the alumina-polished surfaces to the surfaces abraded with emery paper, regardless of whether the surfaces were covered with an adsorbed film. The failure from the abraded surfaces, unlike the separation from the polished steel, was always cohesional-adhesional, even when the steel was coated with a film.

The experiments with polymer coatings provided a wider range of water contact angles and a wider range of adhesion strengths than did the monolayer experiments. These results appear in Table 4 in the order of increasing

Table 4. Adhesional Shear Strength of Ice to Organic Polymer Coatings on Brass at −6°C

Coating	Water Contact Angle (deg)	Shear Strength (psi)	Type of Break
A	111	9	adhesional
B	113	11	adhesional
C	111	15	adhesional
D	111	17	adhesional
E	111	22	adhesional
F	106	45	adhesional
G	80	70	cohesional-adhesional
H	118	74	adhesional
I	96	93	cohesional
J	108	122	cohesional-adhesional
K	93	126	cohesional

adhesional shear strengths. Five coatings gave shear strengths substantially lower than those obtained with close-packed monolayers. These five surfaces exhibited water contact angles slightly higher than those formed for the monolayers, but within the five there is again no clear correlation between contact angle and shear strength. This lack of correlation between contact angle and adhesional strength is further emphasized by the fact that for the coating with the highest contact angle noted, 118°, the ice adhered as strongly as to the monolayer-coated surfaces; to another coating with a contact angle of 108° the ice adhered almost as strongly as to hydrophilic, polished stainless steel.

An important requirement of a useful ice-release coating is that it withstand long exposure to water before freezing without an increase in ice adhesional strength. A few of the coatings were tested for their ability to withstand pre-exposure to water, and they showed wide differences in behavior. Two polyorganosiloxane coatings from the same manufacturer (E and F in Table 1) were tested. In one case the adhesional shear strength increased by a factor of more than three after 64 hours contact with water, while for the other the increase was less than a factor of two. An interesting feature of this experiment was that in neither case did the water contact angle for the polymer coatings change as a result of the prolonged immersion in water.

The Freezing Process:

A knowledge of the manner in which the ice freezes, including any recrystallization processes it may undergo, is important in understanding adhesion behavior. When the supercooled water is nucleated, ice forms in an open network of crystal plates. After standing overnight the solidification is complete and the ice is clear in the ¼ in. adjacent to the bottom and sides of the mold. The interior of the block contains a characteristic pattern of air bubbles which extends to the ice/air interface. Observations of the mode of freezing made with a polarizing microscope revealed that ice forming in a ¼-in. layer of water on polished stainless steel blocks appeared first as long dendritic needles and plates which slowly re-formed into polygonal grains. Simultaneously, air bubbles appeared and migrated upward. There was no apparent difference in the freezing process on clean steel from that on steel coated with a monolayer of stearic acid or poly(dimethysiloxane).

Morphology of Sheared Ice Surfaces:

Thin plastic replicas were made of the (subzero) ice surfaces that had been sheared from the various substrates. These replicas were intended to reveal any fracture markings on the ice that would help establish the mechanism of failure. Two replicating solutions were used, a water-saturated,
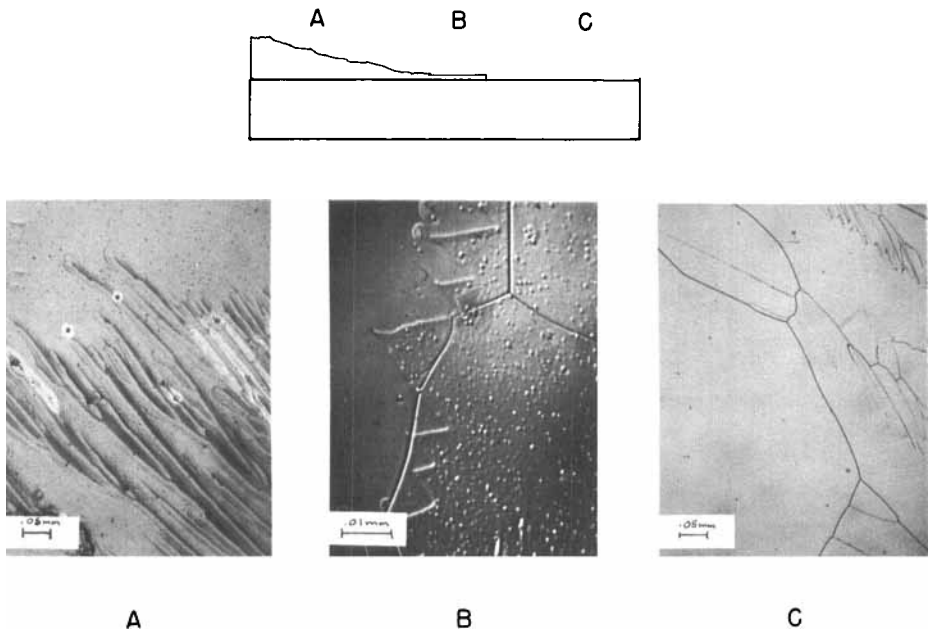
Figure 2. Profile of ice left on clean steel. The photomicrographs show three regions of a Lucite replica of the ice that had sheared from this surface at the points identified in the profile diagram.

Lucite-ethylene dichloride solution and Formvar in dry ethylene dichloride. The Lucite solution was used primarily to replicate surface markings since the dissolved water inhibited the etching action of the solution except for a weak etching of grain boundaries. The dry Formvar solution was used as an etchant which, when the solvent had evaporated, formed a replica of the etched surface. The etched features helped to establish the crystal structure and the crystal defects of the ice.

a. Replicas of ice sheared from clean steel. In Figure 2 a sketch is given of the profile of ice left on a clean, polished steel test plate showing the three types of fracture regions typical of these breaks. Using the low-etching, water-saturated Lucite solution a replica was made of the ice surface that had separated from this test plate, and in Fig. 2 photomicrographs are given for characteristic fracture regions on the replica. In region A the fracture took place some distance from the interface, and the replica showed the ice to be quite rough and generally characterized by "river markings" (Fig. 2A). These markings frequently appear on the fracture surfaces of crystalline solids [7]. In region B the fracture was close to the interface but still discernibly cohesional. The ice surface was extremely smooth in this region as can be seen in the photomicrograph (Fig. 2B) taken along the boundary between region B and region C. Note the saw-tooth edge of the ice along this boundary. Region C corresponds to an area where failure appeared to be
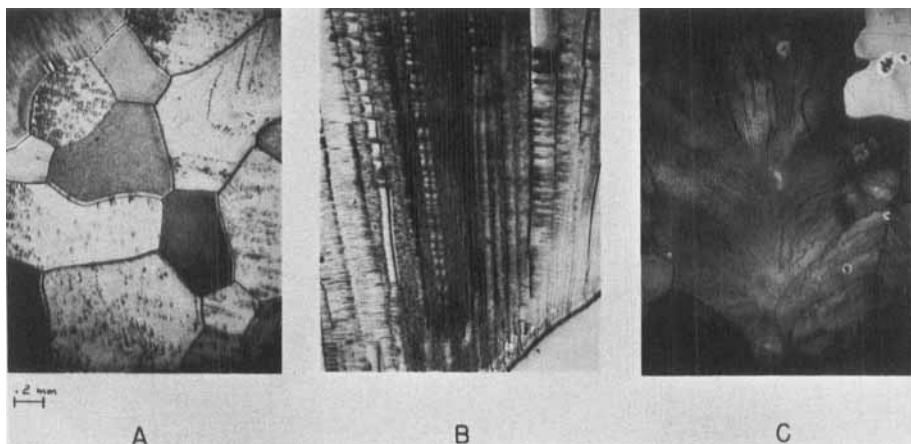
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Figure 3. Photomicrographs of Formvar replicas of separated ice surfaces. (A) Columnar polyg-onal grains and etch pits, (B and C) dendritic crystals sometimes found between ice and substrate.

adhesional. Replicas of this region gave no evidence of fracture markings. The connected lines in Fig. 2B and C are grain boundaries (the etching action of the Lucite solution had not been completely inhibited by saturating it with water).

b. Replicas of ice sheared from adsorbed films on steel. The Lucite rep-licas of the ice that had separated adhesionally from the adsorbed mono-layers on steel showed no evidence of fracture markings. On the other hand, replicas taken of these surfaces using the Formvar etchant-replicating solu-tion showed a profusion of etch pits and deeply etched grain boundaries.

The Formvar replicas of adhesionally separated ice provided a reasonably clear picture of the crystal structure of the ice near the solid. The principal structural feature was the presence of small columnar grains such as those in Fig. 3A. The shape of these grains in a plane vertical to the interface was established by cleaving an ice specimen normal to the ice/substrate interface and then applying an etchant-replicating solution to the cleaved surface. It was found that the grains near the interface had dimensions in the vertical direction comparable to their dimensions parallel to the interface. Frequently, patches of thin dendritic growth were interposed between the columnar grains and the substrate. The two types of dendrite growth that have been observed are illustrated in Fig. 3B and C. The occurrence of these thin sheets of crystals did not measurably affect the adhesional shear strength.

In the replicas formed against cleaved ice surfaces, the bulk interior ice generally showed a much lower density of etch pits than did the ice that had sheared from the adsorbed monolayers on steel. A demonstration of this dif-ference between bulk ice and ice formed at a water/solid interface is given in Fig. 4. A block of ice was formed with a strip of Teflon-coated aluminum foil
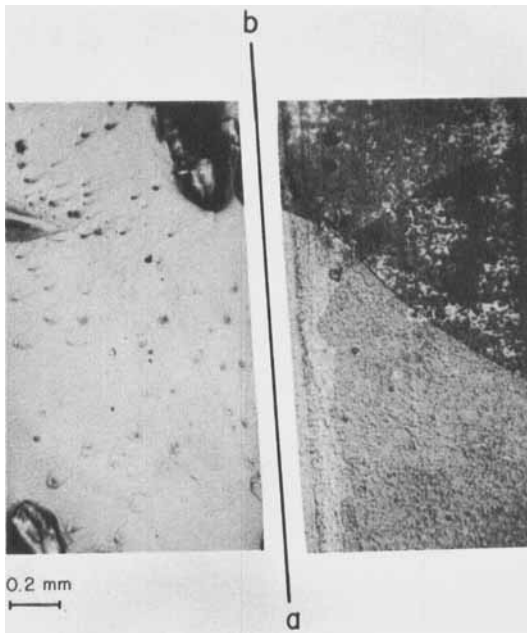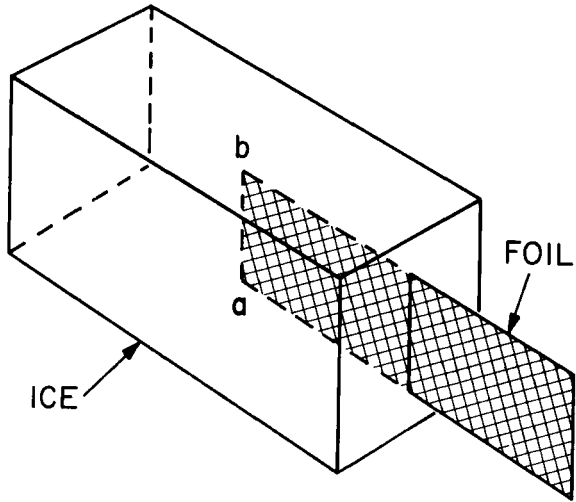
254

Figure 4. A comparison of the etching on an ice surface produced by fracture along a plastic-coated metal foil (right) and that on a fracture surface formed in bulk ice (left). Sketch shows foil frozen in ice block before fracture. The replica was damaged along a-b so this section was cut from the photograph.
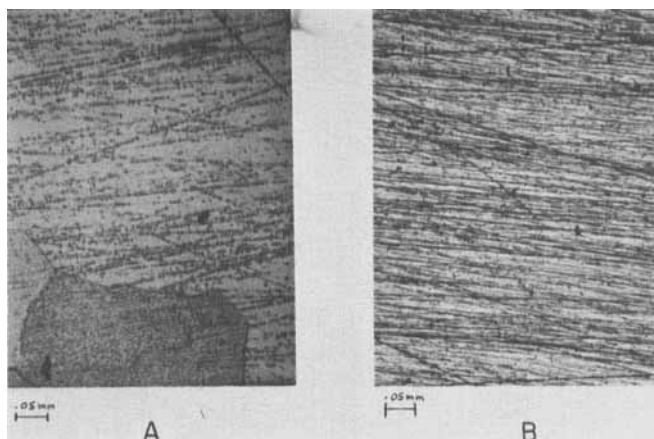
Figure 5. Similarity between the line markings on ice as replicated by the Formvar-ethylene dichloride etchant (A) and the scratches on the abraded steel substrate observed microscopically (B). Note in A that the lines are comprised of etch pits.

extending part way through it. The block was split by forcing a crack to run along the foil and into the bulk ice. The Formvar replicas taken where the foil ended and cleaved ice began, show a considerably greater number of etch pits where the ice had been in contact with the foil than where the ice had been cleaved. This difference between interior ice and interfacial ice was examined further by replicating ice surfaces that had formed at air/water and oil/water interfaces. In both instances, the density and type of etch pits were comparable with those of ice that had formed at water/solid interfaces; there were more etch pits than had been found on surfaces cleaved from interior ice.

c. *Replicas of ice sheared from abraded surfaces.* Ice that had separated from the abraded steel by cohesional-adhesional failure gave replicas that were covered with line markings and these markings appeared to be related to the abrasion scratches on the steel. An example of the line markings on the replicas is compared in Fig. 5 with the scratches on an abraded steel plate photographed at about the same magnification as the replica. The comparison reveals the similarity in distribution of the replica markings and the abrasion scratches. The markings on replicas formed from the non-etching, water-saturated Lucite solution indicated that the ice had been broken and cracked along the scratches. On the replicas formed by the etchant solution, the lines were frequently composed of etch pits (Fig. 5) and can be seen to cross grain boundaries with no change in direction. Along with these unusual markings, the replicas showed the same etching features and fracture markings observed for ice sheared from polished steel.

d. *Replicas of ice sheared from the polymer coatings.* The description of these replicas is simplified if the last five coatings (G through K) listed in
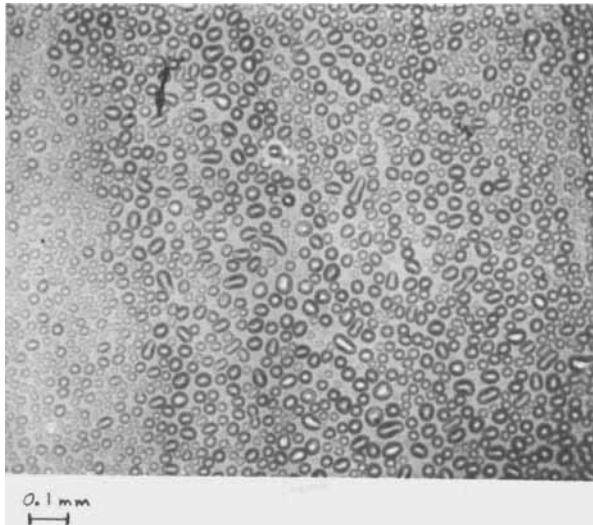
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Figure 8. Bubbles replicated by the non-etching Lucite solution on ice surfaces separated from coatings A-D.

Table 4 are considered first. For the ice separated from these coatings no markings or etch pits were observed that had not been seen on the replicas of ice from the adsorbed monolayers on steel. The forces required to remove ice from these coatings were equal to or greater than the forces necessary to shear ice from the adsorbed films. The results with the replicas, then, are what might be expected for low energy surfaces from the experience with the monolayers.

Replicas of the ice sheared from the first four polymer coatings (A-D) all showed bubble-like features that strongly suggested that tiny air bubbles had been trapped between the ice and coating. An example of these bubble-like features is given in Fig. 8. They were not evenly distributed over the replicas but were gathered in clusters. The polymer coatings themselves were examined microscopically and found to have a distinct microroughness. This microroughness was presumably due to a particulate filler the manufacturer had added. The appearance of this microroughness was distinctly different from the bubble-like features on the replicas of the ice surface so that the bubble-shaped features were not the result of the ice replicating the coating roughness.

Replicas of the ice sheared from coating E gave evidence that there had been a cohesional failure of the coating. Water-saturated Lucite replicas of the ice were found to be covered with tiny oil droplets that could be smeared by rubbing the replica surface. If the Lucite solution was relatively dry so that it had a slight etching action on the ice, then the oil droplets were again observed but were resting within irregular shaped patterns. These patterns were determined to be depressions on the replica and therefore must

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have been elevations on the separated ice surface—presumably small pieces of the coating had come off with the ice.

The remaining coating (coating F) had a slight but distinct micro-roughness and replicas of the ice sheared from this coating revealed that the ice had conformed to this microroughness. However, no bubble-like features were observed on these ice replicas.

DISCUSSION

Adhesion to Hydrophobic Monolayers:

The imposition of close-packed monolayers between ice and clean steel resulted in about a 30% reduction in the adhesive shear strength and a change in the apparent character of the break from cohesional to adhesional. Practically, this reduction in adhesion is not sufficient for useful ice-release. Fundamentally, the results emphasize that, although the work of adhesion of water to the monolayer covered surfaces is low (high water contact angle), this is not a sufficient condition for low adhesion.

The apparently adhesional failure from the monolayer covered surface indicated that the ice at or near the adsorbed film offered an easy path for crack propagation. On both the hydrophilic steel and the film covered steel, cracks initiated very near the interface (region C in Fig. 2). Invariably, the crack proceeded into the ice when the ice was formed against clean steel but continued close to the interface when the ice was formed against an adsorbed film. So close, in fact, that the separated ice surfaces replicated any minor scratches on the steel. Whatever the reason for preferential propagation near the ice/monolayer interface, it was too subtle to be revealed by the plastic replicas of the separated ice surfaces. Experience has taught that when an apparently adhesional failure occurs, it is usually due to a weak interfacial layer [8]. We can only speculate as to what interfacial defects might be responsible in the present case. It is possible that because of the large water contact angle air voids or very thin sheets of air were trapped at the interface but were too minute or too thin to be resolved by the plastic replicas. An alternate explanation is that there were crystal defects at the ice/monolayer interface in greater concentration than at the ice/hydrophilic steel interface.

The experiments on abraded steel demonstrate that surface roughness can substantially increase adhesional shear strength. Electron micrographs showed that these substrates had scratches approximately 1μ wide and 0.2μ deep. The replicas of the ice separated from abraded surfaces showed clearly that the ice in and around the scratches had been deformed and broken. The presence of the adsorbed polysiloxane on the abraded steel aided ice removal but did not prevent ice deformation. This ductile failure (plastic deforma-

tion) from the hydrophobic abraded steel contrasts sharply with the apparently brittle failure (no deformation) of the ice from the hydrophobic mirror surfaces. As already stated, failure from the mirror surfaces probably occurred through a plane of interfacial defects. It is probable that similar defects existed in the ice formed against abraded steel, but that because of surface roughness they were not coplaner and so did not offer a continuous path for crack propagation. Previous studies of ice adhesion have indicated ductile failure from both hydrophilic and hydrophobic surfaces [2, 4]. The deformation these workers observed can be partly attributed to surface roughness since most of their substrates had surface finishes comparable to the abraded steel studied here. However, these workers also used somewhat lower loading rates, 1-10 lbs/sec-in², compared to the 20 lbs/sec-in² used in the present study. At the lower loading rates the ice would have time to relax by dislocation slip and other micro-mechanical processes but when force is applied rapidly there is not enough time for crystal slip before fracture occurs.

Adhesion to Plastic Coatings:

Two mechanisms have been identified by which plastic coatings produce major reductions in ice adhesion: (a) air entrapment at the ice/substrate interface and, (b) cohesive failure of the substrate coating.

The entrapment of air at the interface was observed for only those coatings that had a rather specific microroughness. Evidently, this microroughness led to the type of air entrapment which Zisman [9] suggests may occur when a liquid exhibiting a high contact angle spreads over a rough surface. The air may have been trapped in sheets but then broke up into groups of microbubbles because of the instability of such flat air films. As a practical means of achieving ice-release, this mechanism would have limited usefulness. Its success depends on the manner in which the ice accumulates, which may vary in the field. For example, air entrapment is not likely to occur if the ice develops from the vapor or from fine spray deposition.

The evidence for a cohesive failure of the substrate in the case of coating E was the appearance of flake-shaped etch markings on the replicas of ice sheared from the coatings. There was usually a droplet of oily substance located within each of these flake markings on the replicas and these droplets are believed to be the result of some action of the replicating solution on the flake material. This mechanism of ice-release is more promising than air-entrapment because it does not depend on the mode of ice formation or on the properties of the ice. It does require that the coating fail by releasing thin flakes or platelets so that its ice-release properties will survive a reasonable number of ice removals.

The other coatings, with one exception, gave adhesional shear strengths equal to or greater than the 80 psi expected for a hydrophobic surface from the experiments with hydrophobic monolayers on steel. Two of these coatings (J and K) gave ice shear strengths comparable to clean steel and the ice failure was cohesional-adhesional. Possibly these substrates were penetrated by the water or had been rendered hydrophilic by contact with water. The exceptional coating (F) showed reasonably good ice-release but gave no evidence of air-entrapment or cohesive failure of the plastic. Whatever the mechanism of ice release, it could not in this case be identified from the replicas.

The Structure of Interfacial Ice:

To understand the properties of ice in the vicinity of interfaces it is helpful to consider the events that occur as the ice forms. Polarized light microscopy of thin layers of water freezing on steel revealed the initial formation of large crystals, but within a few hours these large grains had recrystallized into smaller polygonal grains. A similar recrystallization-polygonization process must have occurred in the formation of the ice test blocks. When the water in the mold was first nucleated a mass of large crystals developed but within 24 hours the etching study of the ice showed a predominance of small polygonal grains.

This recrystallization and polygonization process can lead to the accumulation of dislocations at ice surfaces, which explains the high surface density of etch pits. Polygonization occurs in any polycrystalline material when it is subjected to a steady stress [10]. Essentially, what occurs is that in adjacent, slightly misaligned regions of the large crystal grains, dislocation in one region slip toward those in the other and coalesce into new grain boundaries. Dislocation movement is greatly facilitated when the material is as close to its melting point as ice is at −6°C. Near the interfaces of the ice block, many of the dislocations may encounter the free surface where their motion stops so that they accumulate. Some dislocations will collapse into the surface to become steps if the interfacial bonds that must be displaced to form a step are not too strong. The driving force for dislocation movement in the present experiments was the stress produced by the difference in the thermal coefficient of expansion between ice and substrate. There are also small volume changes as the ice forms and cools to the test temperature. Stress was actually observed in the thin ice layers on steel as faint isochromatic lines of stress birefringence in polarized light. The isochromatic lines disappeared as the ice recrystallized.

Defects created at the interface by dislocations collapsing to form steps could explain the predominantly adhesional failures observed for ice separa-

tion from hydrophobic surfaces (mon-
olayers and plastic coatings). The in-
terfacial forces which inhibit the for-
mation of slip steps are weaker at the
ice organic boundary and thus allow
the development of more interfacial
defects than at the ice hydrophilic
steel interface from which the ice
broke cohesionally.

The high surface density of etch
pits observed here indicates that dur-
ing recrystallization many dislocations
slipped to the interfacial region but
because of insufficient stress were not
ejected from the crystal. Their pres-
ence has important implications for
the adhesional behavior of ice but be-
fore considering these implications,
note should be taken of the evidence

Figure 7. The appearance of the nearly hex-
agonal etch pits frequently observed on
replicas of ice surfaces separated from
solid substrates.

that these etch pits do indeed correspond to the emergence point of dis-
location lines. Previous experience with Formvar-ethylene dichloride solu-
tions has established this system as a dislocation etchant for ice [11, 12].
The etch pit shapes observed in this work closely resemble the etch pits
shown in earlier reports. It was noted in the present study that whenever
an ice surface was scratched, etch pits could be formed along the scratch
mark and in each crystal grain through which the scratch passed the etch
pits along the scratch had the same orientation and shape as the other etch
pits randomly distributed within that grain. This procedure is a simple and
useful means of producing and identifying dislocation etch pits. Additional
evidence is that none of the etch pits had perfectly hexagonal shapes. This
should be so because dislocations in ice are strongly restricted to the basal
plane [13]. Prismatic slip occurs only under relatively high stress. In order
for an etch pit to be perfectly hexagonal the crystal grain must be oriented
with the basal plane parallel to the surface in which case the dislocation
lines are in glide planes parallel to the surface so that their end points could
not intersect the surface. It was observed that about 20% of the crystal
grains showed no etch pits at all whereas adjacent grains were heavily
etched. Presumably, the unetched grains were oriented with the basal
plane parallel (C-axis perpendicular) to the surface. Among the etch pits
that were observed the predominant shape was a slightly but distinctly
distorted hexagon (see Fig. 7). This indicates that for these small polygonal
grains that formed against the substrates, the predominate orientation was

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with the basal plane parallel or very nearly parallel to the surface. A study of ice growth at water/aluminum interfaces indicates preferential growth with the C-axis normal to the surface [14]. Also, Pounder has observed a similar preferential orientation for ice crystals at ice/air interfaces [15].

With the evidence that there is a high dislocation density near ice/solid interfaces and that the glide plane (basal plane) of these dislocations is generally parallel to the interface, it is possible to explain why Jellinek [4] observed much easier plastic deformation in adhesional shear experiments than in tension experiments. In shear, the force is applied in a direction parallel to the planes in which the dislocations move with relatively small forces compared to the forces required in tension to obtain the same deformation by prismatic slip.

Jellinek further observed that deformation in shear became increasingly difficult with decreasing temperature and that ice formed against quartz deformed in shear more easily than ice formed against steel [16]. He explained these results by hypothesizing that a liquid-like layer exists at ice/solid interfaces similar to that proposed many years ago by Tyndall [17] and Faraday [18] at the ice/air interface. Jellinek [19] and also Fletcher [20] consider that the crystal structure of ice at all interfaces is distorted and that this distortion extends hundreds and even thousands of angstroms into the bulk ice. The present study indicates that ice surfaces are highly defective because of the accumulation of dislocations and it is for this reason that they show a liquid-like behavior. In identifying the unusual properties of interfacial ice with crystal defects, it might be better to refer to the interfacial region as being defect-rich rather than "liquid-like." The properties of ice surfaces are more like those of a weak solid than a liquid. The temperature and substrate dependence observed in Jellinek's experiments are not inconsistent with an explanation based on a high interfacial density of dislocations. The mobility of dislocations decreases sharply with temperature and this would affect both their accumulation at interfaces and their mobility in the interfacial region when the ice is sheared. The most probable effect of substituting quartz for steel is that for quartz, with its lower thermal conductivity, there would be a decrease in the rate at which the ice cools from 0°C to the test temperature. A lower cooling rate allows more time for dislocation movement and recrystallization. In some preliminary experiments here, a plastic spacer was placed between a steel substrate (coated with a stearic acid monolayer) and the base plate of the test rig. The spacer would have the effect of slowing the rate of cooling. With the plastic spacer, the adhesional shear strength at −6°C was 45 psi compared to the usual value of 80 psi obtained when the steel substrate was an integral part of the base plate. Furthermore, an etching study of the ice that separated from the insulated steel surface revealed an etch pit density at least one order of magnitude greater than when the ice was

sheared from steel surfaces integral with the base. The grain size was also considerably smaller. The experiment confirms that lowering the cooling rate favors the surface accumulation of dislocations and small grain formation by recrystallization and polygonization. These effects of cooling rate will be the subject of a future study.

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