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The Adhesion of Ice to Hydrophobic Surfaces

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Determinations have been made on the adhesional shear strength of ice formed against clean, highly polished steel, against close-packed monolayers adsorbed on steel, and against thin coatings of organic polymers painted on metal surfaces. The adsorbed monolayers reduced the shear strength by about one third of that for ice against clean steel. The values of the shear strength for the different monolayers were approximately the same despite a wide difference in the chemical constitution of the adsorbates. The monolayers also had the effect of changing the character of the breaks from clearly cohesional, ductile fractures from clean steel to apparently adhesional, brittle fractures from the monolayers. On lightly abraded steel the results were quite different from those on the highly polished surfaces—the adhesion was noticeably higher and the breaks were cohesional for both clean and monolayer-coated abraded surfaces. The shear strength against the organic coatings ranged from values equal to that of ice against clean steel to values 70 to 80% lower. These results showed no simple correlation with the water contact angle on the organic coatings.

The appearance of the ice separated from the various substrates was examined by forming plastic replicas against the ice surface. These replicating solutions etched the ice to reveal crystal structure and crystal lattice defects. The etching features showed the ice lattice to be highly defective near the substrate. Use of the replica-etchant technique and microscopic examination of the organic polymer coatings has revealed two mechanisms by which ice-release coatings operate—air entrapment at the ice/coating interface and the cohesive failure of the coating itself.

INTRODUCTION

The separation of ice from surfaces against which it has formed is a complex and generally misunderstood process. Some empirical studies of the problem have been made in an attempt to design ice-release coatings and these efforts have produced genuine improvements in practical operations. Unfortunately, accidental changes in the formulation of useful ice-release coatings or changes that have been deliberately made to improve their resistance to environmental degradation have resulted in a loss in ability to release ice. These detrimental alterations in the coatings could be avoided if there were a better understanding of the fundamental factors that determine the adhesive strength of ice-solid bonds.

Some tentative conclusions about the process of ice release can be drawn from previously reported work. It has been determined (1) that the adhesive strength of ice calculated from the thermodynamic work of adhesion of ice to even a low-energy solid such as Teflon is considerably higher than any experimentally determined adhesive strength. The explanation for this discrepancy between theoretical and experimental adhesive strength is that there are lattice flaws and microcracks present in the interfacial region from which fracture can initiate at forces much less than that necessary to overcome intermolecular attractions. Consequently, in attempting to understand the results of adhesion tests it is important to have a clear picture of the defect structure at or near the interface. In this connection Raraty and Tabor found that in shearing from clean steel the ice undergoes plastic deformation (2). This conclusion implies that the lattice defects of interest are dislocations which under external stress slip

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and pile up to generate microcracks from which fracture then initiates (3).

The subject of lattice defects in the ice is enormously complex but pertinent to the understanding of fundamental adhesional behavior. Previous work has done little but underline the complexity of the problem. In an earlier publication from this Laboratory (4) it was reported that the adhesional shear strength of ice from clean steel was lower by a factor of two than the bulk shear strength of ice formed under the same experimental conditions. This difference might be explained by the presence of strain near the interface as a result of the difference in the thermal coefficients of expansion of steel and ice. However, such an explanation may be too simple. Crystalline solids at temperatures just below their melting point can dissipate strain by various processes of recovery and recrystallization whereby the strain energy is redistributed by polygonization and grain growth (5). This relaxation of strain would tend to strengthen the interface, but the fact that the ice/steel interface was weaker than bulk ice suggests either that the recrystallization does not take place or that the slip and shifting of the ice lattice during recrystallization gives rise to interfacial defects that weaken the interface. In seeking answers to these complex problems it is found that little is known about the defect structure of ice near interfaces, although much has been learned about the defect structure of bulk ice (6). The only work on the relation between defect structure and the adhesive strength of ice appears to be that of Jellinek (7). This author has determined the adhesional strength of ice to steel both in tension and shear and analyzed the data statistically assuming various models for the defect distribution near the interface. This approach does not present a clear picture of the distribution of flaws because in order for the mathematics to be manageable the models must be unrealistically simple.

A number of workers have found that there is a rough correspondence between ice adhesion and the hydrophobicity (low surface energy) of the substrate. Raraty and Tabor (2), for instance, found the adhesional shear strength of ice to decrease progressively with increasing water contact angle on a series of polymer substrates. The simplest explanation of the effect of wettability is that air is entrapped in microscratches on the polymer surface leaving voids that weaken the interface (8). The ease of air entrapment and thus the number of voids will increase with increasing water contact angle. However, Raraty and Tabor suggested that air entrapment was not always an obvious explanation. They found that the adhesional shear strength of ice formed against a stearic acid monolayer deposited on cleaved mica was reduced by a factor of eight from that of ice against clean mica. They did not expect that on such a smooth surface there would be any appreciable entrapment of air. This interpretation ignores the fact that the surface of cleaved mica is not molecularly smooth but is composed of steps from one crystalline layer to the next and that air may still be trapped at these steps.

An alternate explanation of the effect of changing the substrate on the adhesional strength of ice has been offered by Jellinek (9) who suggests that a "liquid-like" layer of water exists at the interface even down to −15°C and that the thickness of this liquid layer is greater against hydrophobic surfaces than against hydrophilic surfaces. This suggestion was offered to explain the much larger adhesional strength in tension compared with the adhesional strength in shear. The surface tension of the liquid layer would have to be overcome in tension, while only frictional forces would be encountered in shear. The presence of a liquid layer becoming thinner and more viscous with decreasing temperature would also explain the linear increase in adhesion with decreasing temperature down to about −15°C found by Jellinek (9) and by Raraty and Tabor (2) for ice on clean steel. However, Jellinek found a change in adhesional strength with temperature for plastic substrates, while Raraty and Tabor did not. There has been a recent revival of theoretical support for the existence of an ultrathin water layer on ice (10), but the assumptions concerning the orientation of the water molecules at the interface made in developing the theory have been challenged (11). These difficulties in understanding the fundamentals of ice adhesion have not simplified the task of finding useful ice-release coatings. There has been some recent empirical success in this direction (12), but the discovery of promising coatings has come only at a high cost in time and effort. Therefore, it is most important that in any fundamental study of ice adhesion, technical coatings and surfaces having proved ice-release

properties should be examined in detail in an effort to identify the mechanism by which adhesion is reduced. Once identified, the mechanism can be utilized to design other ice-release coatings.

The purpose of the work reported here was not only to determine the adhesional strength of ice to various surfaces but also to examine in detail the substrate surface, the ice near the ice/substrate interface, and the ice surface that has been separated from the substrate. It is hoped that such information will shed some light on the mechanisms by which ice detaches from solid surfaces.

Although the work described here has been largely concerned with the development of new techniques for the study of the ice/solid interface and of ice fracture phenomena, the exploratory observations made with these techniques have already provided valuable research leads.

EXPERIMENTAL PROCEDURE

Materials

The test plates against which the ice was formed were all 1 in. square and 1/4 in. thick. The substrate materials included close-packed monolayers deposited on clean, highly polished stainless steel plates and various polymer coatings applied to clean, abraded brass plates. The surfaces of the steel plates on which the monolayers were deposited had been polished to a mirror finish and were cleaned just prior to use by wet metallographic polishing with 0.05μ alumina powder. Studies were also made on monolayer-coated steel surfaces that had been given a final polish with 1.0μ alumina and on surfaces that had been abraded with "4/0" emery paper. Before adsorbing films on the abraded steel, the surfaces were cleaned by lightly polishing with the alumina powder slurry to remove any organic contaminants picked up from the binder in the emery paper.

Most of the monolayer-coated substrates were prepared by the method of retraction either from solution or from the melt (8). Monolayers of poly(methylsiloxane) were deposited by flooding a clean steel plate with the polymer oil and then repeatedly washing the surface with benzene to remove all but the firmly adsorbed siloxane polymer molecules. This film had a critical surface tension of 24 dynes/cm (8).

The polymer coatings studied are listed in Table 1. These commercial materials were applied according to the instructions given by the manufacturer. Coating H was applied by depositing onto the brass plate a thin film of the polymer dissolved in xylene hexafluoride and allowing the solvent to evaporate. The poly(vinylsiloxane) (coating K) was applied by evaporating a film of 20% vinyltrimethoxyethoxysilane in water made to pH 3 with glacial acetic acid and then drying at 120°C for 1 hr.

TABLE 1
Polymer Coating Characterization

Coating	Chemical Type
A	Poly(dimethylsiloxane), cross-linked, filled
B	Poly(dimethylsiloxane), cross-linked, filled
C	Poly(dimethylsiloxane), cross-linked
D	Poly(dimethylsiloxane), cross-linked
E	Poly(organosiloxane)
F	Poly(organosiloxane)
G	Polyurethane
H	Perfluorooctylmethyl methacrylate
I	Epoxy-poly(organosiloxane)
J	Poly(organosiloxane)
K	Poly(vinylsiloxane)

The distilled water used to form the ice was redistilled from a quartz still and had a conductivity of 1×10^{-6} ohm^{-1}. A part of the dissolved air was 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 (4). The test rig is shown schematically in Fig. 1 with the ice block on the test plate. Ice had been formed on the test plate in a clean, Teflon-coated foil mold. 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

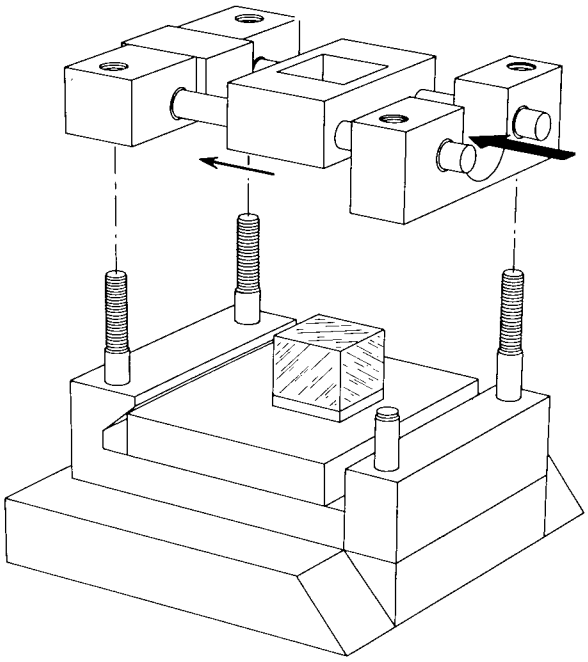

Fig. 1 — A schematic drawing of the adhesive shear test apparatus

have reached completion, resulting in the ice within 1/4 in. of the interface being clear and free of gas bubbles. The test rig was designed so that there would be a 0.10-in. clearance between the ice holder and the test plate beneath. The foil around the ice in this space was stripped away and the ice sheared from the substrate by applying force against the ice holder with a hydraulic ram. The mechanical resistance of the rig with no ice present was subtracted from the shear force reading. 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 Lucite (poly(methyl methacrylate)) or Formvar (poly(vinylformal)) in ethylene dichloride at about 2% of polymer by weight. The solvent had been percolated through Florisil absorbent to remove water and polar contaminants. The replica 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 optical methods were used to study the replicas and also the surface texture of the substrate. The electron microscope was used in some cases, but more frequently the examination was done through a polarization interference objective (13) on an incident-light microscope. The polarization interference method was supplemented by examination with an ordinary incident-light objective with asymmetric illumination produced by partial obstruction of the incident beam. The positioning of the obstructing barrier at about the plane of the illuminator diaphragm produced a shadowing effect that was particularly helpful in resolving surface structure at 400X magnification and greater. The shadowing was most uniform if the end of the stop was cut in the form of a semicircle concave to the remaining aperture.

A modified polarizing microscope was used to examine the ice/substrate interface directly. An incident-beam microscope body tube, monochromatic light source, polarizer, analyzer, and a cold stage were mounted on a vertical optical bench. Steel cylinders 3/4 in. in diameter were fitted into a cavity on the cold stage, and the ice was formed on the upper polished surface of the cylinder. Observations of the ice/steel interface were made through the ice.

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 effects of surface constitution on the ice-solid bond were examined by adhesional shear measurements on ice formed against clean, polished stainless steel, against various close-packed monolayers adsorbed on polished steel, and against different polymer coatings expected to show ice-release properties. Further measurements were made to examine the relation of the surface texture of the metal base to ice adhesion

on both clean and monolayer-coated surfaces. The effect of prolonged water exposure on ice adhesion to polymer coatings was also explored. In all of the experiments, attention was given to whether failure occurred at the interface (adhesional failure) or whether it occurred within the ice (cohesional failure). Breaks were recorded as adhesional if more than 95% of the failure appeared to occur between the ice and substrate. Those surfaces that failed adhesionally gave faithful ice replicas of even minor surface characteristics of the substrate. In order to examine the separated ice surfaces in minute detail, plastic replicas were made of the ice and the replicas examined microscopically. The results of the replica study were complex and will be presented separately for the sake of clarity.

The adhesional shear strengths of ice to clean polished steel and to polished steel coated with four different chemical types of close-packed monolayers are shown in Table 2, together with water contact angles for each surface and an indication of whether the failure was adhesional or cohesional. Each table entry represents the average of eight trials. The effect of interposing the monolayer was (a) to reduce adhesional shear strengths by approximately one third and (b) to change the character of the break from cohesional-adhesional to purely adhesional. The water contact angles of all the monolayers were nearly the same, and there was no correlation between the minor variation in contact angles and the corresponding minor variations in adhesional shear strength.

Contact angle measurements on the monolayer-covered steel after successive shear tests indicated that the monolayers had undergone some disturbance. On an octadecylamine monolayer, after four successive tests, the contact angles for water and methylene iodide had declined about 10°. These changes in contact angle are compared with the corresponding shearing forces in Fig. 2 which shows that there was no progressive change in the adhesive force with the decline in contact angle.

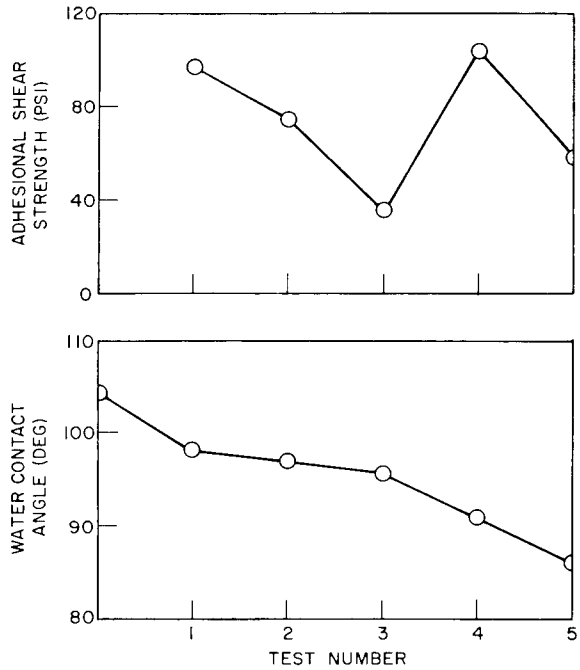

Fig. 2 — A comparison of the progressive change in water contact angle with adhesional shear strength for successive shear tests of ice from an octadecylamine monolayer on polished steel

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 (°)	Shear Strength (psi)	Type of Break
None	0	135	Adhesional-cohesional
n-Octadecylamine	104	71	Adhesional
Stearic acid	104	87	Adhesional
11-H-Perfluoroundecanoic acid	97	91	Adhesional
Poly(dimethylsiloxane)	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) for Three Different Polishing Methods*		
	0.05μ Alumina	1.0μ Alumina	"4/0" Emery Paper
Poly(dimethylsiloxane)	91	86	130
n-Octadecylamine	71	93	–
None	135	–	182

*See Fig. 3.

The effect of surface finish on the adhesional shear strength of ice to freshly prepared steel surfaces and to monolayer-covered steel surfaces having different microtextures is shown in Table 3. The roughness of the surfaces can be judged from the electron microscope photomicrographs in Fig. 3. There was a notable increase in adhesion in going from the alumina-polished surface to the surfaces abraded with emery paper, regardless of whether or not the surfaces were covered with an adsorbed monolayer. The surfaces polished with different size alumina powders did not give a significant difference in adhesion despite the greater roughness of the surface polished with the 1.0μ powder (Fig. 3). The failure from the abraded surfaces, unlike the separation from the polished steel, was always cohesional-adhesional, even when coated with an adsorbed monolayer.

The experiments with polymer coatings provided a wider range of solid surface energies, as reflected in the 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 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 clean, polished stainless steel.

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

Coating	Water Contact Angle (°)	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-adhesional
J	108	122	Cohesional-adhesional
K	93	126	Cohesional

*This break, while it did not involve cohesional failure of the ice, did give evidence of cohesional failure in the coating film.

An important requirement of a useful ice-release coating is that it withstand long exposure to water before freezing without an increase in adhesional strength. A few of the coatings were tested for their ability to withstand exposure to water, and they showed wide differences in behavior. Two poly(organosiloxane) coatings from the same manufacturer (E and F in Table 1) were

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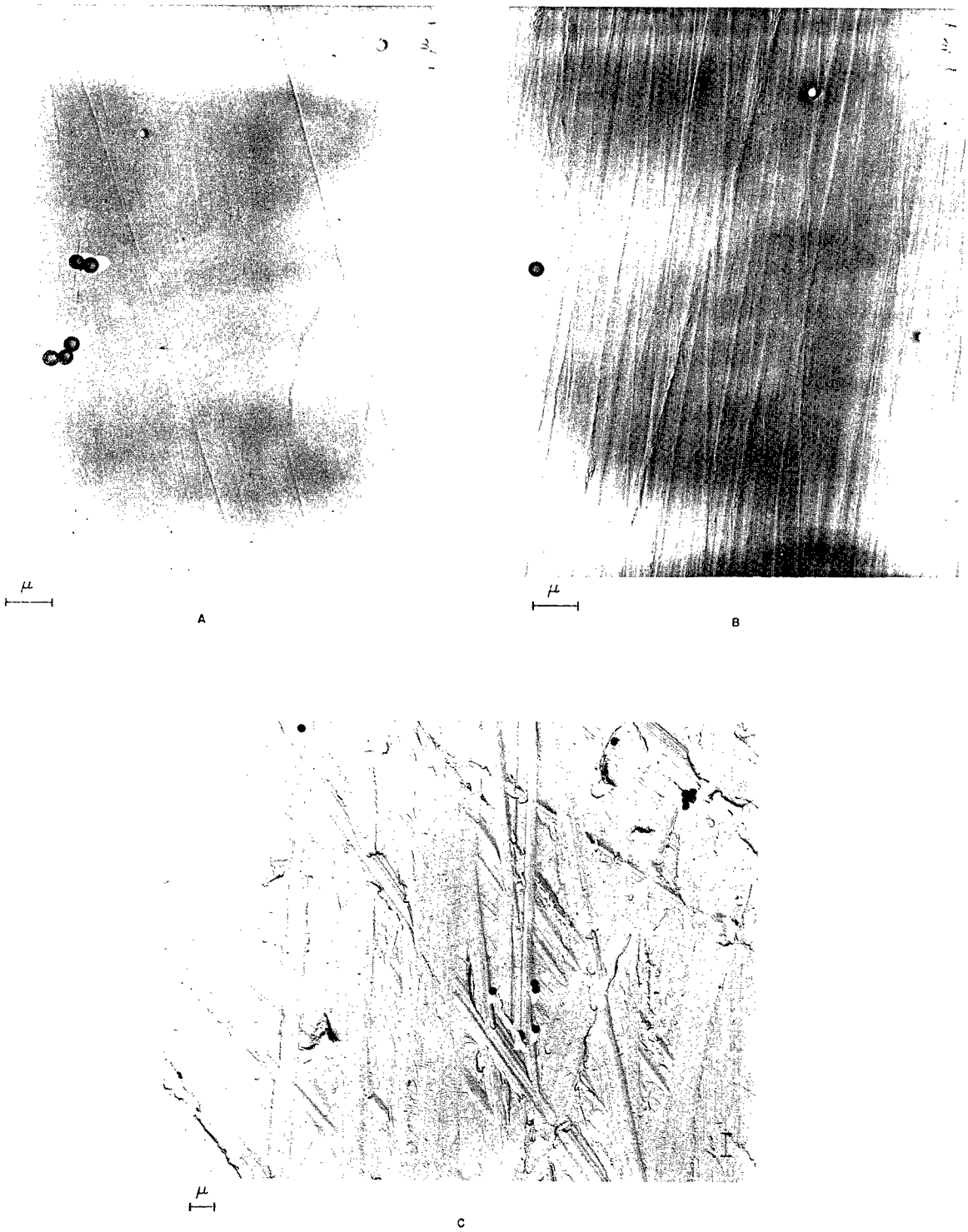

Fig. 3 — Electron microscope photographs of stainless steel surfaces polished with 0.05μ alumina powder (A), 1μ alumina powder (B), and abraded with "4/0" emery paper (C)

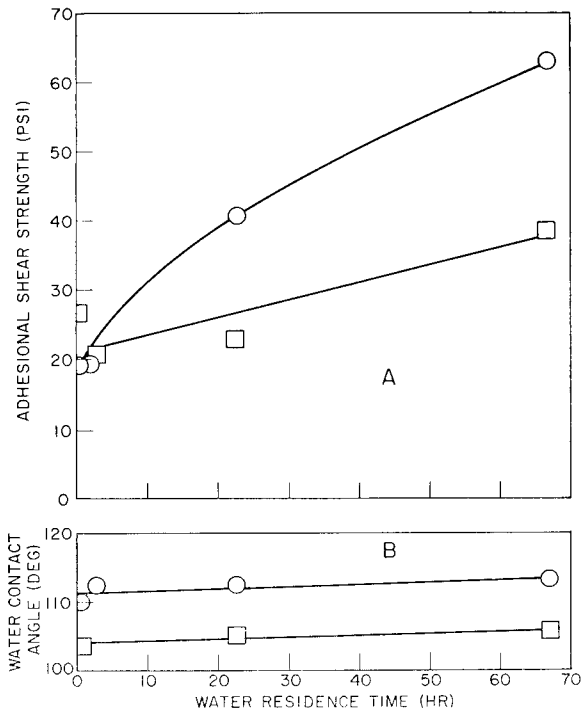

Fig. 4 — The change in adhesional shear strength (A) and water contact angle (B) with residence time for water on poly(organosiloxane) coating E (○) and poly(organosiloxane) coating F (□)

tested, and the results are given in Fig. 4. In one case the adhesional shear strength increased considerably over a 64-hr period, while for the other there was relatively little increase in shear strength. There was no significant change in the water contact angle on either of these polymer coatings after water exposure. It is interesting that the coating which had the greatest loss in ability to release ice had evidently undergone a permanent change during the 64-hr exposure experiment. When ice was later re-formed on the test surface with a minimum exposure to water, the adhesional shear strength was as high as when the water had remained for 64 hr before freezing.

The Freezing Process

The manner in which the ice freezes, including any recrystallization processes it may undergo, is important in understanding adhesion behavior. Observation of the freezing of the ice test specimens indicated that when the ice is nucleated it forms an open network of crystal plates. After standing overnight the solidification is complete and the ice is clear in the 1/4 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 1/4-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(dimethylsiloxane).

Replica Study of Sheared Ice Surfaces

Thin plastic replicas were made of the ice surfaces that had been sheared from the various test substrates. The purpose of these replica studies was to reveal any fracture markings on the ice surface that would help to establish the mechanism of failure. The choice of replicating solutions, Lucite and Formvar in ethylene dichloride, was made not only because of their ability to reveal fracture marking but also because of their ability to etch and replicate crystal grain boundaries and dislocation etch pits. These etching features provide a great deal of information about the crystal structure and the lattice defects of the separated ice surfaces. The etchant-replicating solutions operate by the selective solution of water molecules from along grain boundaries and from around line and screw dislocations, vacancies, impurities and other lattice defects. At times it was desirable to replicate the fracture markings on the ice surface without the coincident production of etch patterns; in this case it was only necessary to presaturate the solution with water. This device worked best with the Lucite solution; the presence of the water inhibited the etching action of the solution except for a weak etching of grain boundaries.

The dry Lucite and Formvar replica solutions consistently produced two general types of etching features, etch pits and what is here referred to as "furrowed etching." Examples of the etch pits produced by the dry Lucite solution are given in the top row of Fig. 5, and examples of the furrowed etching produced by this solution are given

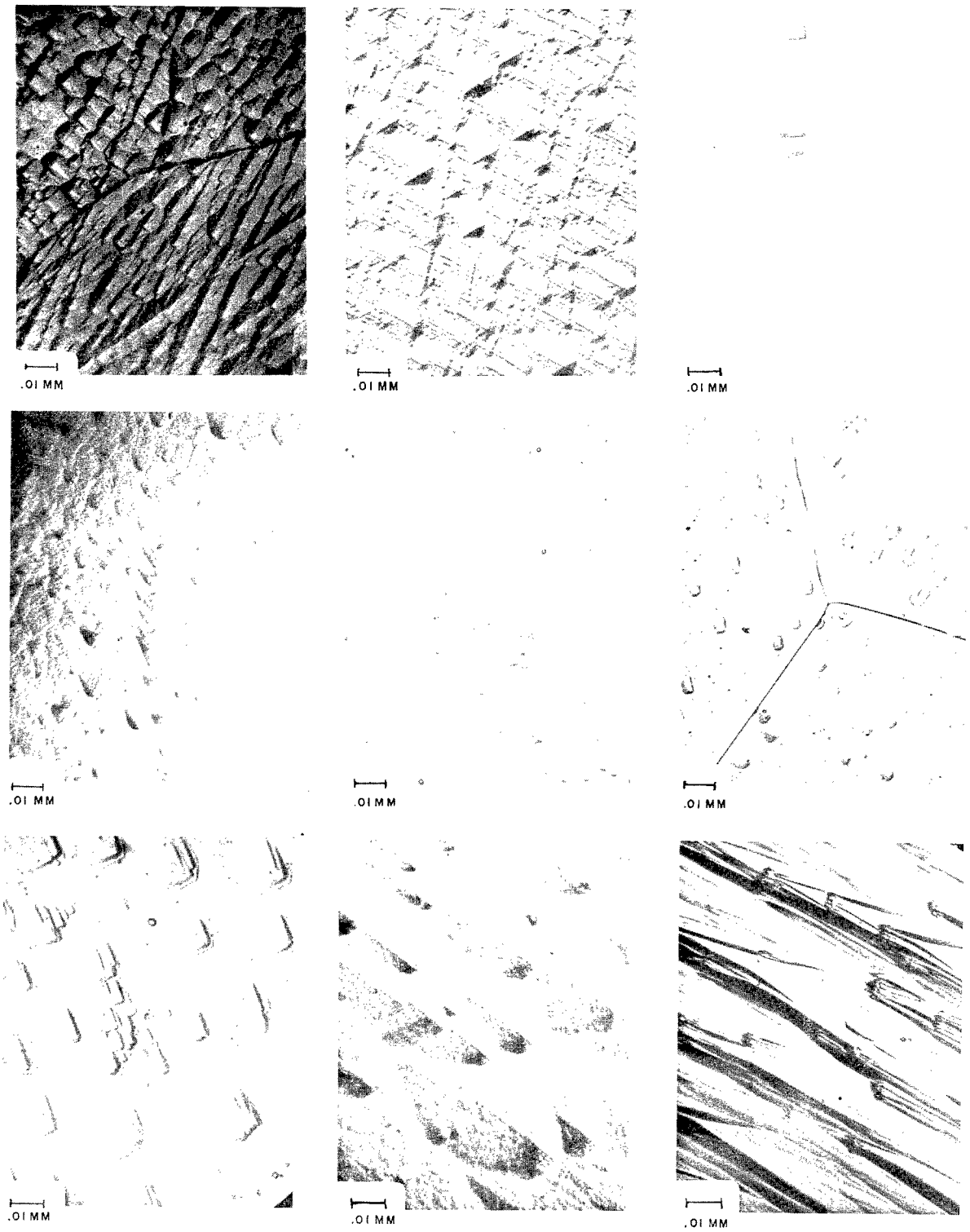

Fig. 5 – Selected photomicrographs of ice etch pits produced by dry Lucite replicating solution (top row) and dry Formvar replicating solution (below)

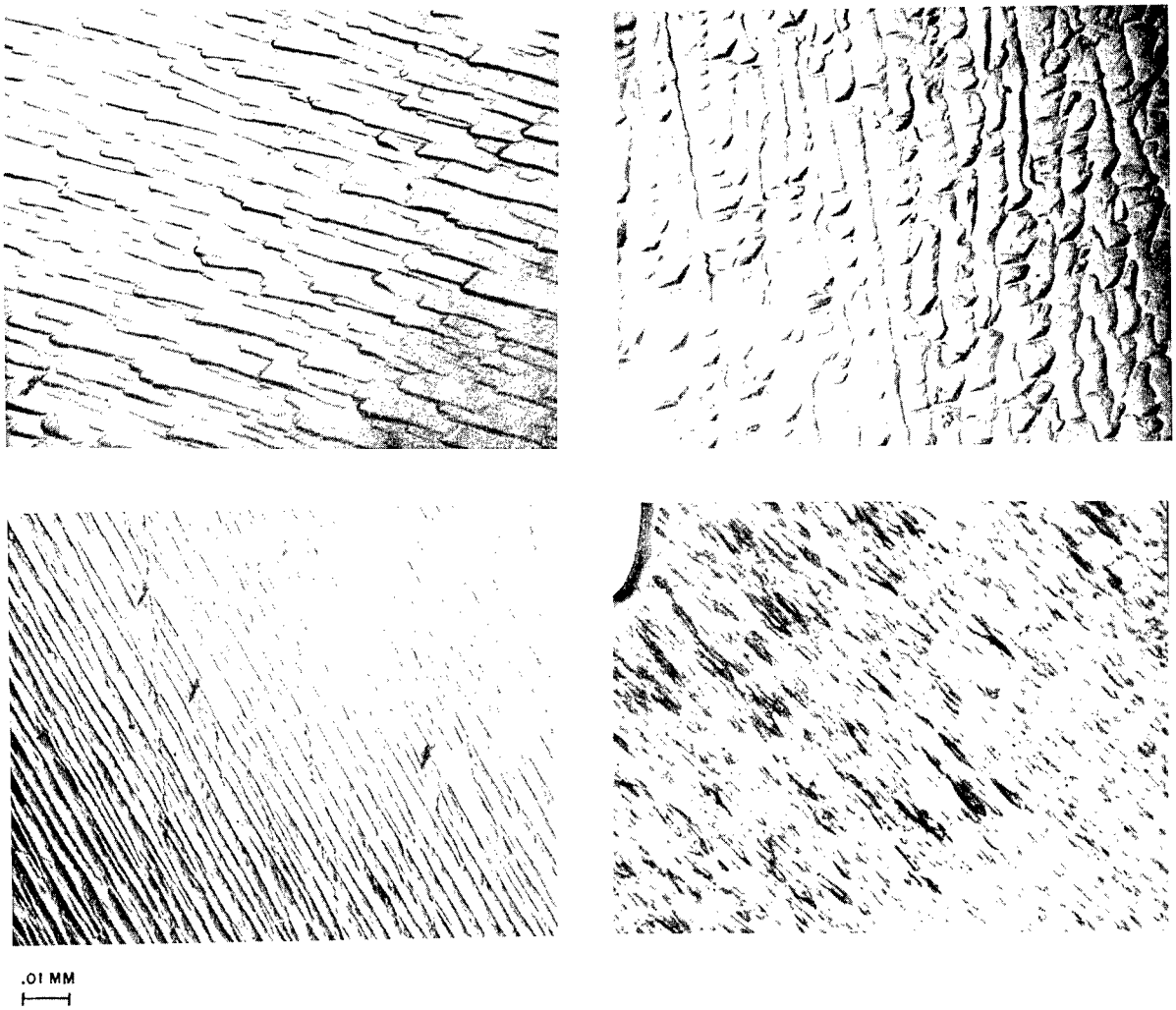

Fig. 6 — Selected photomicrographs of furrowed etching produced by dry Lucite replicating solution

in Fig. 6. The Formvar solution produced etch pits such as are shown in Fig. 5, and it produced furrowed etching nearly identical to that formed by the Lucite. In general, the Lucite produced fewer types and a lower density of etch pits and more sharply defined furrowed etching than did the Formvar solution. For either replicating solution, the etch pits in any individual grain were identical in shape and orientation; the furrowed etching was uniform over the entire grain. The various types of pits and furrow patterns were repeated in different grains on the same surface, but adjacent grains never had identically shaped and oriented etching features.

Direct evidence that the etch pits correspond to regions of lattice strain is presented in Fig. 7. In Fig. 7A the strain around an air bubble in the ice was revealed by etch pits. The remaining three photomicrographs show lines of etch pits along scratches on the surface of ice crystals. The furrowed etching has not been related to specific lattice strains or defects.

The replica study of the ice sheared from the monolayers on polished stainless steel gave no evidence of fracture markings—the replicas produced by water-saturated Lucite solution were devoid of any feature except where the grain boundaries had been etched. On the other hand,

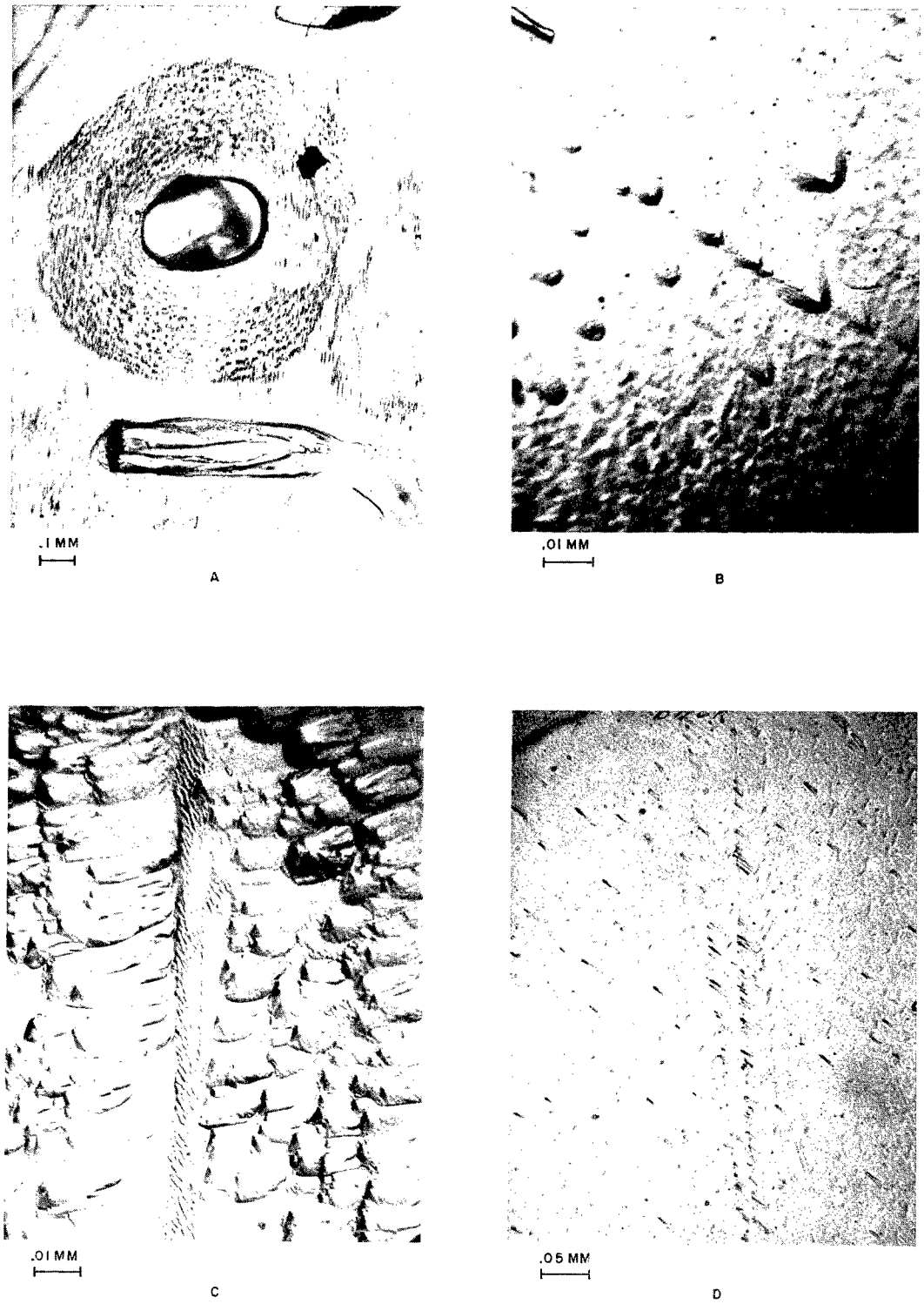

Fig. 7 — Examples of association between ice crystal strain and etching features: (A) etch pits produced by Formvar solution around air bubble; (B, C, and D), etching produced by Formvar solution along scratch marks on ice surfaces

the dry Lucite and Formvar etchant-replicating solutions produced a profusion of etch pits and furrowed etching on these ice surfaces. Photomicrographs of typical regions on these etchant replicas are given in Fig. 8.

Examination of the replicas for these ice surfaces sheared from the monolayers provided a reasonably clear picture of the crystal structure of the ice near the solid interface. The principle structural feature was the presence of small columnar grains such as those in Fig. 8A. 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. The photomicrograph in Fig. 9A was taken of a replica formed on such a cleaved surface, and it can be seen that the grains near the interface had dimensions in the vertical direction comparable to their dimensions parallel to the interface, *i.e.*, Fig. 8A. Frequently patches of thin dendritic growth were interposed between the columnar grains and the substrate. The two types of dendritic growths that have been observed thus far are illustrated in Figs. 8B and 8C. It was generally found that the occurrence of these thin sheets of crystals did not measurably affect the adhesional shear strength.

In examining the replicas formed against cleaved ice surfaces, it was found that 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. An interesting demonstration of this difference between bulk ice and ice formed at a water/solid interface is given in Fig. 9B. A block of ice was formed with a strip of Teflon-coated aluminum foil 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, that is, there was a distinctly greater amount of etching than was observed for interior ice. The similarity in the amount of etching on replicas of the three forms of interfacial ice is somewhat surprising since in the case of the ice/solid interface the ice had been subjected to externally applied shearing forces, while the ice at ice/air and ice/oil interfaces had not. The ice/air interface was produced by freezing small pools of water. The ice/oil interface had been created by placing water in the adhesional test apparatus on a film of squalane, a hydrocarbon oil, that had been spread over a polished steel test plate. Since the water did not displace the oil film, the ice block could be sheared free with a negligible force. Any oil remaining on the ice was rinsed off using cold ethylene dichloride.

Some interesting information was obtained from the replicas formed against ice that had sheared from clean, polished stainless steel by cohesional-adhesional failure. In Fig. 10 a sketch is given of the profile of ice left on a clean steel test plate showing the three types of fracture regions typical of these breaks. Using the nonetching, water-saturated Lucite solution, a replica was made of the ice surface that had separated from this test plate, and in Fig. 10 photomicrographs are given for the different 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. 10A). These markings frequently appear on the fracture surfaces of crystalline solids (14). 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. 10B) taken along the boundary between region B and region C. The area of the replica corresponding to region C, where the failure was adhesional, was identical in all respects to the replicas of the ice that had sheared adhesionally from the adsorbed monolayers.

Replicas made of the ice that had separated by cohesional-adhesional failure from the abraded steel surfaces were covered with line markings that were evidently connected with the abrasion scratches on the steel test plate. Along with these unusual line markings, these replicas showed the same etching features and fracture markings observed for ice sheared from polished steel. An example of the line markings can be seen in Fig. 11A which, on comparison with Fig. 11B,

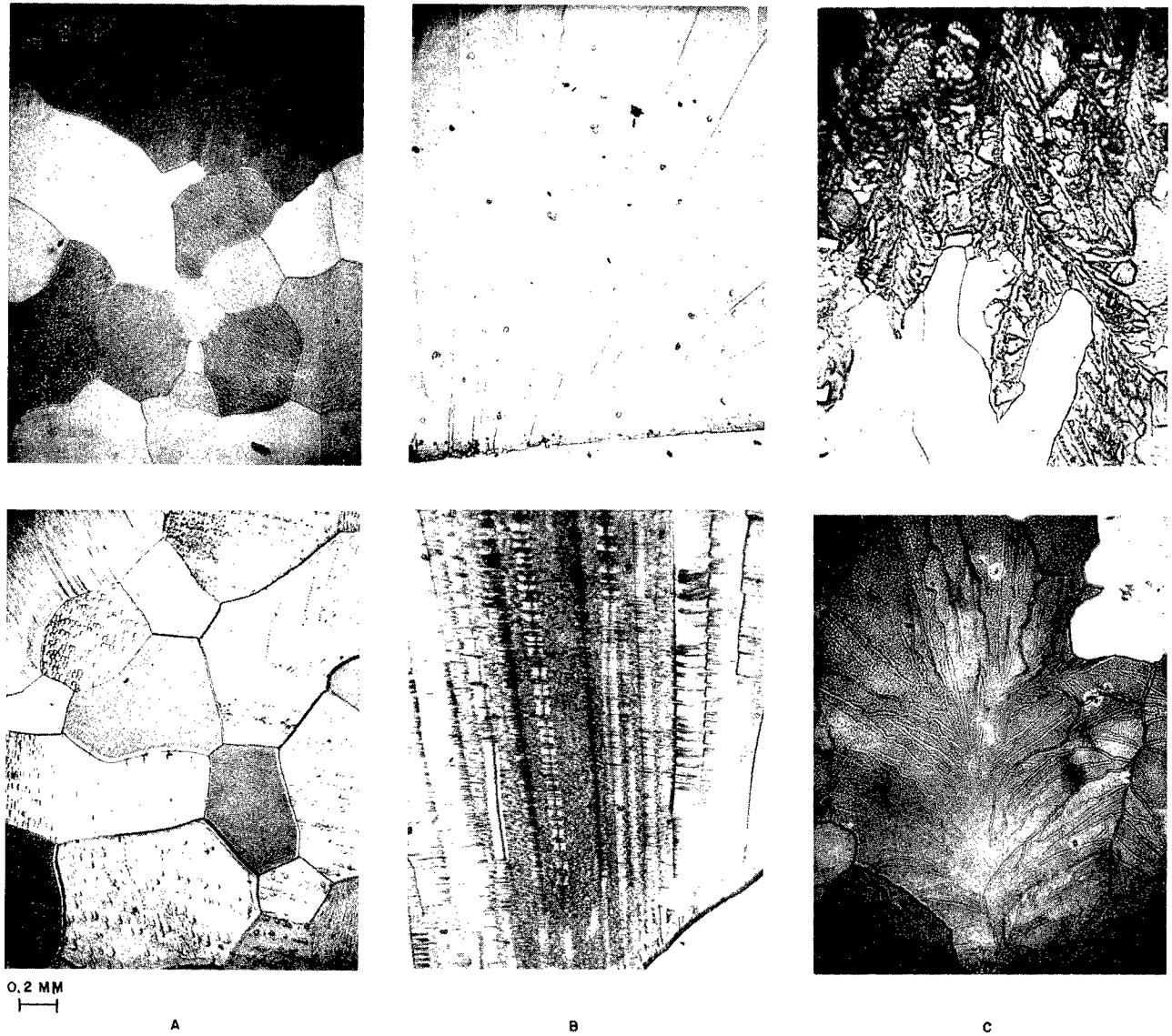

Fig. 8 — Photomicrographs of Lucite (upper) and Formvar (lower) replicas of separated ice surfaces illustrating columnar polygonal grains (A) and frost growth (B and C)

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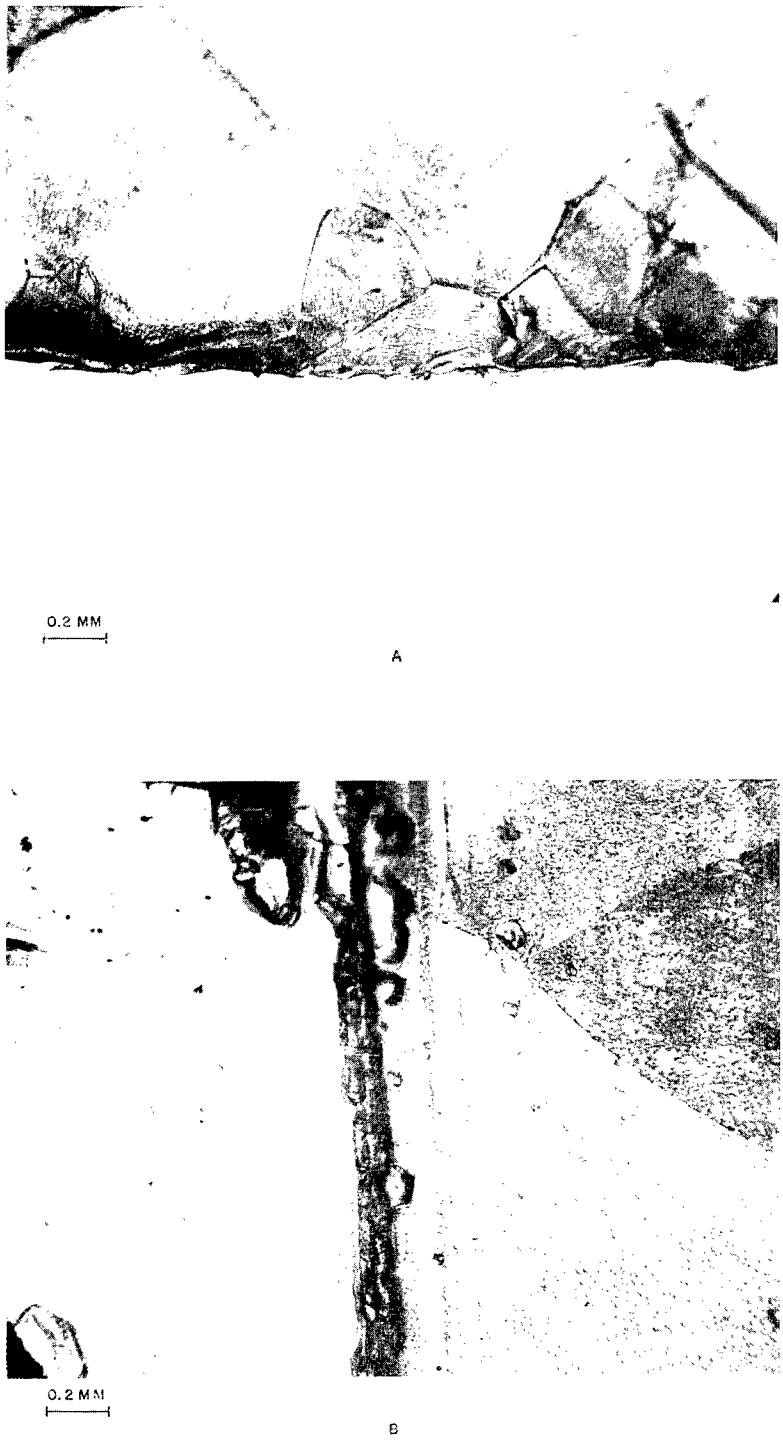

Fig. 9 — Photomicrographs of Formvar replicas of cleaved ice surfaces: (A) a cleavage plane perpendicular to an ice/solid interface; (B) a comparison of etching on cleavage faces formed by (right) separation from a Teflon surface and by (left) cleavage of bulk ice

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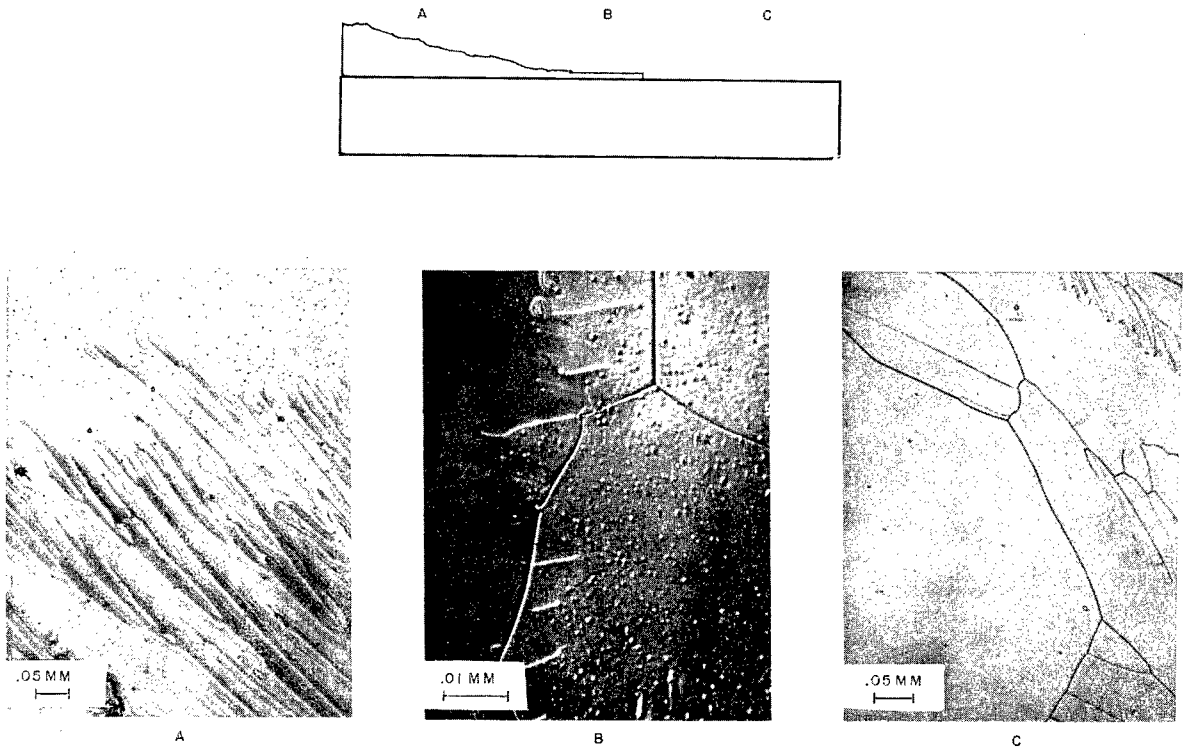

Fig. 10 — The profile of ice left on clean stainless steel showing regions of a Lucite replica of the ice that had sheared from this surface

reveals the similarity in distribution of these markings with that of the abrasion scratches on an abraded test plate. These line or scratch markings on replicas formed from the nonetching, water-saturated Lucite solution indicated on close examination that the ice had been broken and cracked along the scratches. On the replicas formed by the etchant solutions the line markings were frequently but not always composed of etch pits (Fig. 11C). In Fig. 11D the lines can be seen to cross grain boundaries with no change in direction.

The description of the replicas made on the ice surfaces sheared from the polymer coatings will be simplified if the last five coatings (G through K) listed in Table 4 are considered first. The adhesional shearing forces required for the removal of ice from these coatings were equal to or greater than the forces necessary to shear ice from the close-packed monolayers on polished stainless steel. The replicas of the separated ice surfaces showed no markings or etch pits that had not been seen on the replicas of ice removed from the adsorbed monolayers on steel. These results, then, are what might have been predicted for low surface energy coatings from the experience with monolayers.

The replica study of the other coatings in Table 4 (A through H) and an examination of the coatings themselves resulted in some particularly interesting observations. Replicas of the ice surfaces sheared from the first four polymer coatings (coatings A through D) all showed evidence of wide areas of tiny air bubbles as in Figs. 12A and 12B. The distribution of the bubble-like features was not entirely random; they were clustered in various places over the replica, and within each cluster they tended to be grouped within certain grain boundaries. Microscopic examination of the surfaces of the polymer coatings revealed that all four had a distinct microroughness but that the roughness of the polymer coatings containing a particulate filler (Fig. 12C) was different from the surface roughness of the

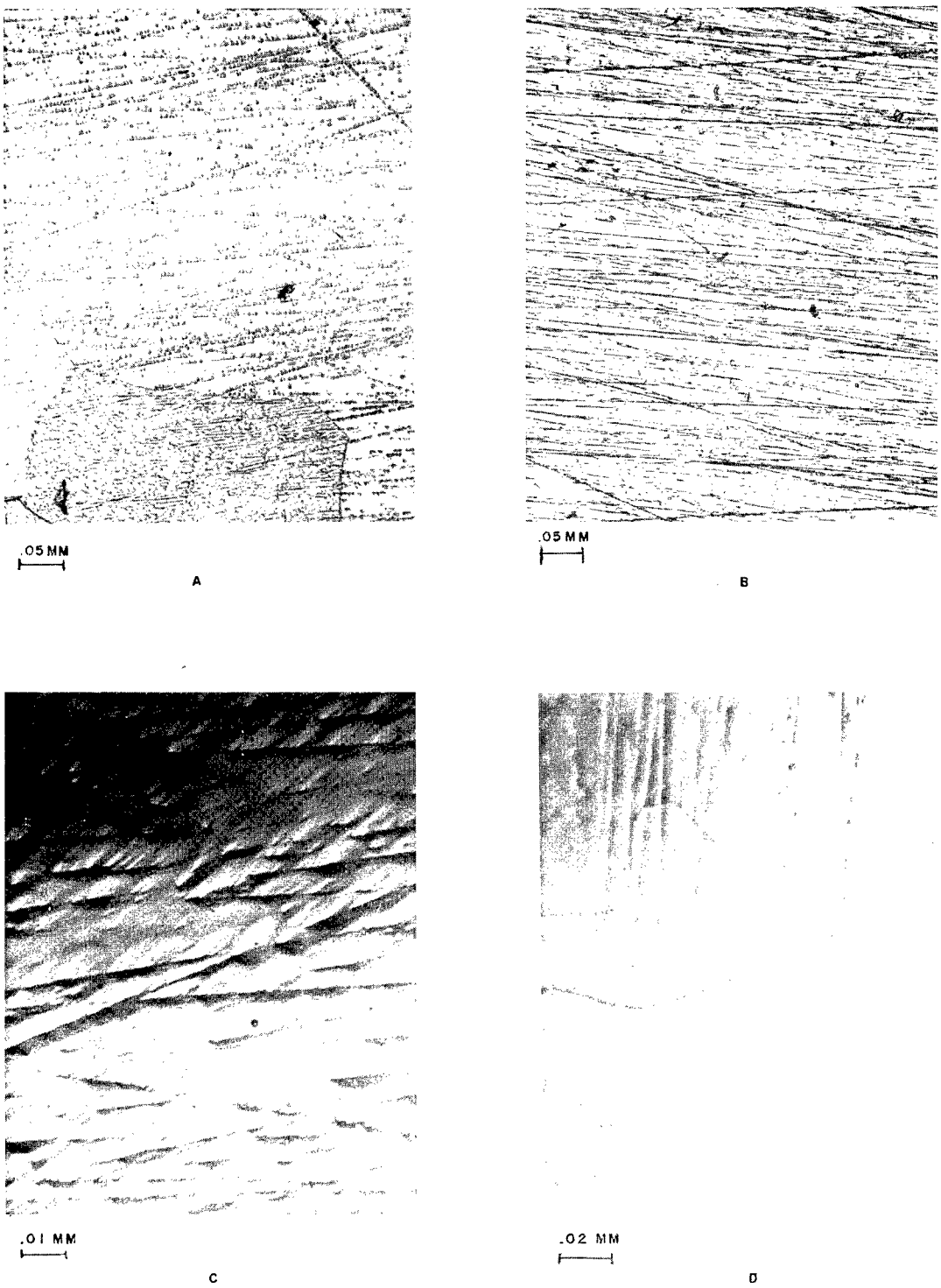

Fig. 11 — Photomicrographs showing the line markings on a Formvar replica (A) taken of an ice surface sheared from abraded steel (B). The line markings were frequently composed of etch pits (C) and they crossed grain boundaries (D).

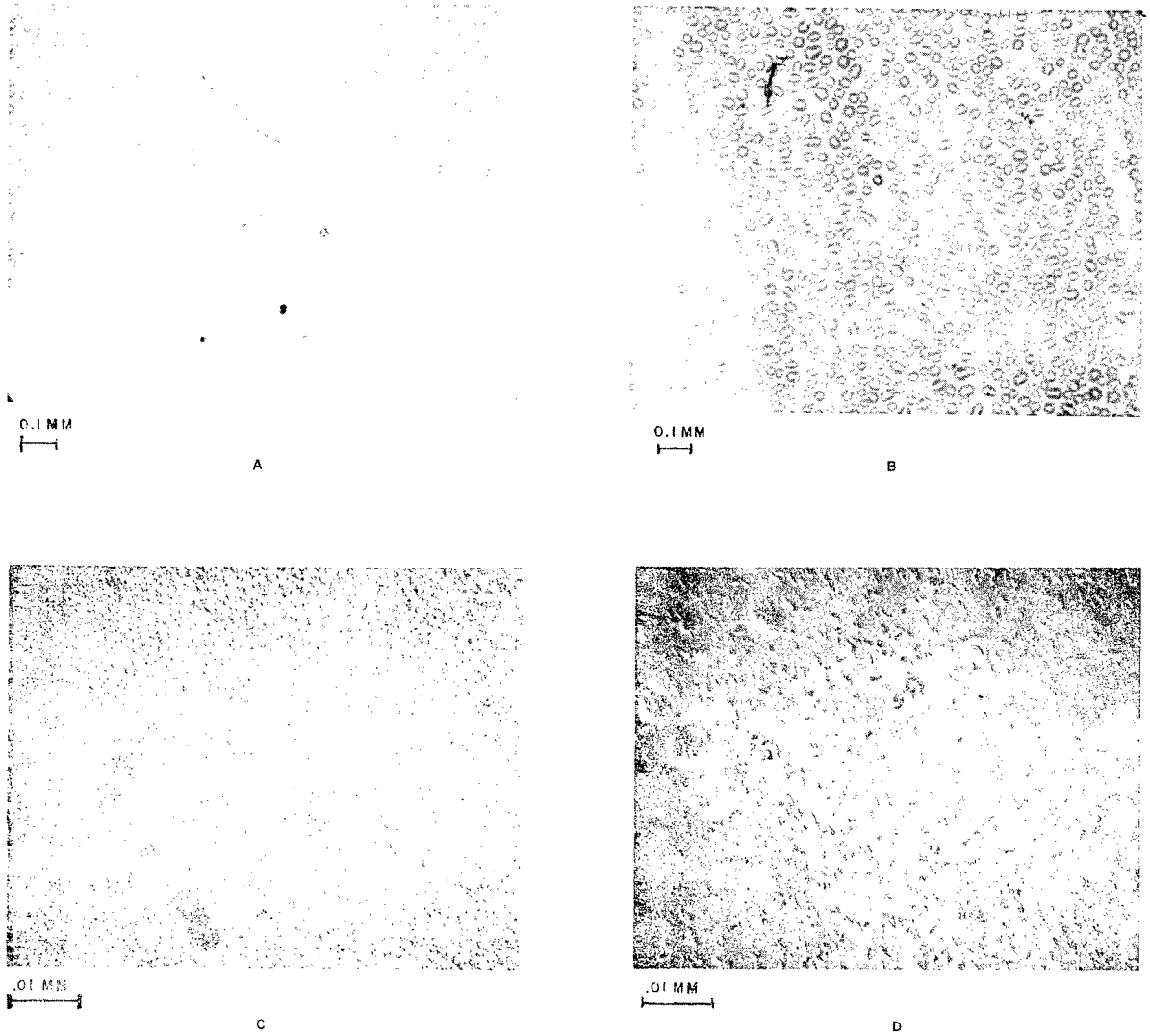

Fig. 12 — (A and B) Photomicrographs of bubblelike features typical of those found on Lucite replicas of ice sheared from coatings A through D; (C) interference photomicrograph illustrating the surface roughness of filled coatings A and B; (D) interference photomicrograph illustrating the surface roughness of coatings C and D

unfilled polymers (Fig. 12D). There was no obvious relation between the types of surface microroughness of the coatings and the amount or distribution of air bubbles at the ice/coating interfaces.

On the other hand, replicas formed of the ice sheared from coating E (Table 4) using the water-saturated Lucite solution had the usual grain boundaries but were also covered with tiny oil droplets (Fig. 13B) that could be smeared by rubbing the replica surface with a finger. Using the dry Lucite solution, the oil droplets were again observed but were usually resting within irregularly shaped etch patterns (Fig. 13C). These patterns are depressions on the replica, since their shadowing in Fig. 13C is the reverse of the shadowing of the oil droplets.

The remaining polymer coating (coating F) had a distinct microroughness, as can be seen from Fig. 14A. However, replicas of the ice sheared from this polymer surface showed no unusual fracture marking or etching features. Close examination of the water-saturated Lucite

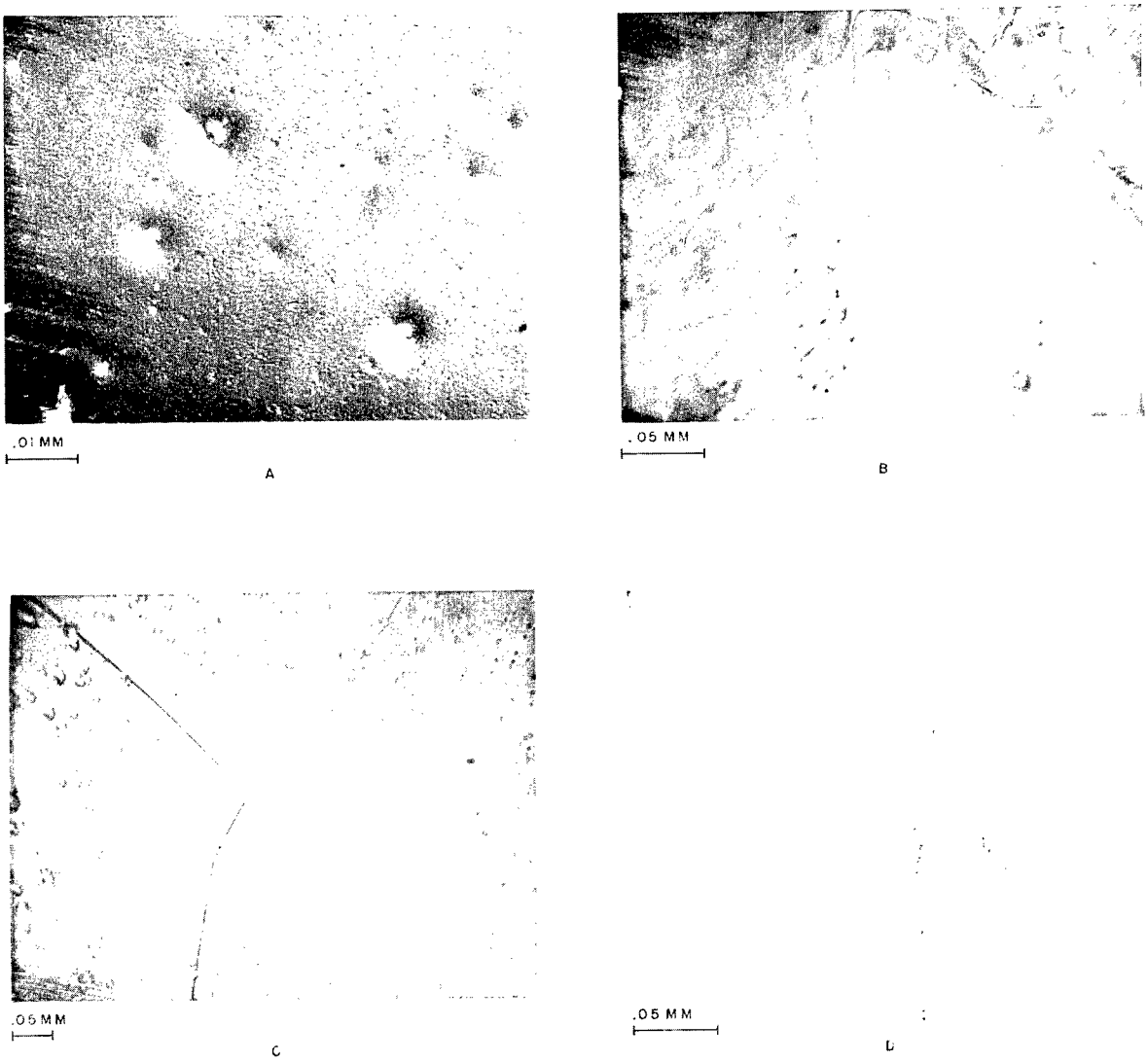

Fig. 13 – Interference polarization photomicrograph of coating E (A). Photomicrograph B is of a replica of ice sheared from this coating showing the flakelike outlines left on the ice and C and D show the oil drops found on the replicas.

replica did show that the ice had replicated the surface roughness of the coating which in turn was replicated by the Lucite. This fact is illustrated by comparing Fig. 14B, a replica of an ice surface sheared from coating F, with a similar replica, Fig. 14C, formed on ice sheared from an adsorbed monolayer on highly polished steel.

DISCUSSION

Interpretation of the Etching Features

The etching technique described here can provide a considerable amount of detailed information about the crystal structure, strain, and lattice defects at ice surfaces. Such information

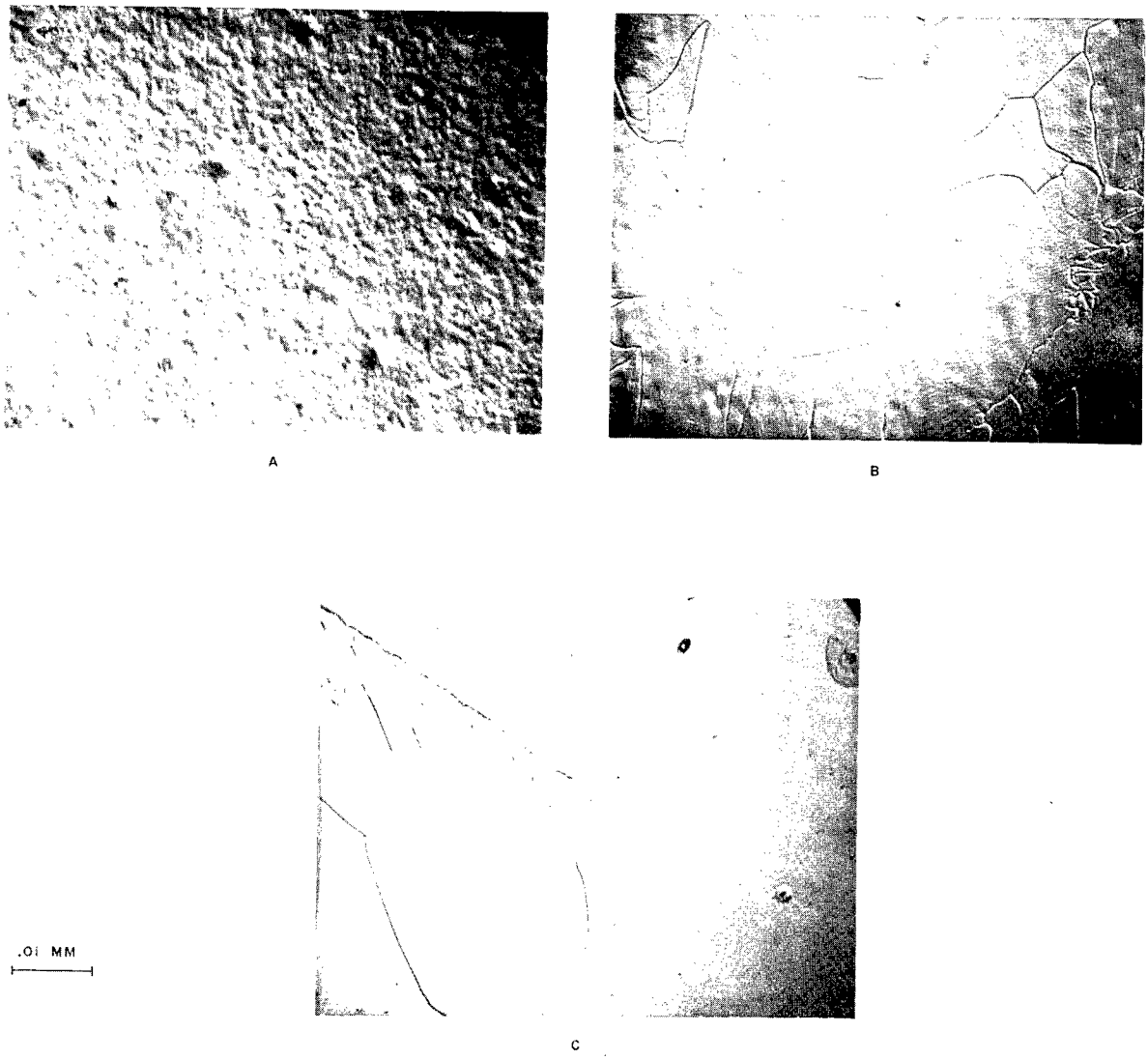

Fig. 14 — Interference polarization photomicrographs of coating F (A) and a Lucite replica of ice sheared from this coating (B) showing the replication of the substrate roughness by the ice (compare B with C, a Lucite replica of ice sheared from an octadecylamine monolayer on highly polished steel)

is invaluable for a study of ice adhesion. However, a substantial amount of exploratory work has yet to be done before it will be possible to interpret the etching features with confidence. The available information on the significance of the various etching features observed here is presented in the following paragraphs along with a few tentative conclusions about the condition of the ice near ice/solid interfaces.

It has been well established that by using the proper etchant and etching conditions it is possible to produce etch pits on crystal surfaces at the emergence point of dislocations (15). There are relatively simple experiments that can be performed to demonstrate that a given type of etch pit corresponds to a dislocation, and it is possible to determine the orientation of the slip plane in which the dislocation lies and its glide direction. There have been a few such studies made on ice crystals (16,17,18) using the Formvar etchant-replicating solution. The most extensive work has been that of Kuroiwa and Hamilton (17). They

have given indirect evidence that the etch pits correspond to dislocations and have been able in some instances to determine the slip plane. It is encouraging that the etch pits observed by these authors resemble some of the etch pits observed here. However, it would be most desirable to demonstrate a direct connection between the etch pits and dislocations in order to establish the reliability of the Formvar solution as a dislocation etchant. Also, a study should be made of the Lucite solution to determine how it differs from the Formvar solution and whether it has any value as a dislocation etchant.

The furrowed etching observed here has not been previously reported. Unlike the etch pits which appear at discrete points and along lines, the various types of furrowed etching were more-or-less continuous patterns. Presumably these patterns arise from the water molecules along certain crystal directions having a greater solution rate into the etchant than do the molecules in other directions. The particular pattern formed by a crystal grain would depend upon the orientation of these directions of more rapid etching with respect to the crystal surface; the failure of some grains to show furrowed etching implies that these crystal directions did not happen to be exposed to the etchant.

The only significance that can be confidently attached to the etching features thus far is that the amount of etching provides a gross indication of the degree of lattice strain and lattice deformation. Nonetheless, by assigning this limited significance, some useful conclusions can be derived from the etching studies presented here. First, it is quite clear that bulk interior ice is less strained and deformed than interfacial ice. This fact is demonstrated by the much smaller number of etching features on the replicas of cleaved interior ice than on the replicas of ice formed against air, a hydrocarbon oil, and an ice surface that had been sheared adhesionally from rigid solids. Secondly, there was little difference in the amount of etching features on the replicas of the ice formed at the different interfaces. Neither of these conclusions is particularly surprising. Eley has reviewed the subject of imperfections at crystal surfaces (19) pointing out the many sources of surface defects and the effect these defects may have on the adhesion of crystalline materials. Even in a homogeneous, single crystal the imbalance of intermolecular forces at an interface results in a surface stress which can be relieved by the formation of dislocations. The situation is enormously more complex in a polycrystalline material that has been subjected to various mechanical and thermal stresses and, as in the case of the ice test blocks here, has undergone various recrystallization processes. Admittedly, the defect structure of ice at ice/solid interfaces is complex, but once understood it may be possible to devise ice-release surfaces that operate by influencing this defect structure. Furthermore, the fundamental information obtained about the crystal structure and crystal lattice defects at ice/solid interfaces broadens our understanding of crystal interfaces and the adhesive behavior of crystalline solids. For these reasons the study of interfacial ice should be continued utilizing the etchant-replica technique to its fullest potential.

Adhesion to Hydrophobic Monolayers

The imposition of the close-packed monolayers between ice and clean steel resulted in about a 30% reduction in the adhesive shear strength and in a change in the apparent character of the break from cohesional to adhesional. From a practical point of view these results are not exciting because it has been shown that for the type of test used here the shear strength must be reduced by at least 80% in order for a surface coating to be considered a useful ice-release agent (12). However, it would be helpful to our general understanding of the fundamentals of adhesion if we had a clear explanation of the effect of the monolayers. In attempting to find an explanation it must be kept in mind that the values for the adhesional shear strength obtained on both clean and monolayer-covered surfaces were considerably less than values predictable from the thermodynamically derived work of adhesion. This discrepancy implies that the release of the ice occurred by the initiation of fracture from a pre-existing flaw at which the applied stress was concentrated. Evidently the stress-sensitive flaws at the ice/clean-steel interface were distinctly different from those at the ice/monolayer interface. Not only was there a difference in shear strength, but the character of the breaks was different. On clean steel the fracture was frequently cohesive and took place at least in part

some distance from the interface. The replicas of cohesive failure showed evidence of plastic deformation. From the monolayers, on the other hand, the ice separated at or extremely near the interface and showed no evidence of plastic deformation. Replicas of these ice surfaces gave no indication of fracture markings, and the etching features were comparable with those on the replicas of ice surfaces that had been separated from a thin film of hydrocarbon oil by a negligible shearing force. The fracture of solids is frequently classified as ductile if there is evidence that the solid underwent plastic deformation, *i.e.*, deformation beyond the elastic limit, or brittle if it can be shown that plastic deformation did not occur. It is therefore suggested that the ice sheared from the clean steel by a cohesive, ductile fracture but from the monolayer-coated steel by an adhesive, brittle fracture. This conclusion must be made with reservation. In separating from the monolayer-coated steel the ice may have undergone only a small amount of plastic deformation which, on the corresponding replica, may have resulted in only a few additional etch pits. The large population of etch pits already present on the replicas of the three forms of interfacial ice would have made it impossible to detect a small increase in the amount of etching on surfaces fractured from monolayer-coated steel.

The lack of a close correlation between the adhesional shear strength and the water contact angles on these monolayers reflects the fact that variables which do not affect the wetting characteristics of the surfaces do have a decided effect on the adhesion. Contact angle measurements would not reveal differences in the mechanical or thermal properties of the substrates or even small differences in surface microroughness, any one of which could seriously influence the adhesional shear strength.

A good deal more experimental work is needed before there can be an adequate explanation of how the monolayers reduced the shear strength and changed the character of the fracture. There are three interesting possibilities that deserve consideration in any future work. The first possibility is that the hydrophobic character of the monolayer-coated surfaces allows air to be trapped in the shallow microscratches as the water advances over the surface. Careful examination of the replicas provided no evidence for these voids, although they may have been so small as to be indistinguishable from the normal imperfections on the plastic replica surface. On the other hand, the replicas did show that the ice near the interface was highly defective, there being evidence for dislocations, grain boundaries, *etc.* The second possibility, therefore, is that the fracture of the ice from the steel may have been initiated from any of these lattice defects. It was not immediately evident that the defects at the ice/monolayer interfaces were any different or more numerous that at the ice/clean-steel interface. A more quantitative examination of the etching features might settle this question. A third explanation of the observations might assume that the size, orientation, and population of the critical flaws at the ice/solid interface are essentially the same for clean and for monolayer-covered steel and attribute the difference in adhesion to the reduction in the interfacial energy due to the adsorbed monolayer. The surface energy expended in separating ice from a close-packed organic monolayer is less than that needed to separate ice from clean steel or for ice to fracture cohesively; the force necessary to initiate a running fracture may well be less also.

The experimental approach necessary to distinguish the above mechanisms would have to be more sophisticated than that taken in the present study. A more quantitative measure of the lattice strain and lattice defects near the interface is needed and can in principle be obtained from the etchant replicas. A particularly important area of research as yet untouched in these studies is the effect of temperature and the thermal history of the ice on adhesion. Preliminary experiments have already shown that a small difference in cooling rate can have a large effect on the crystal structure of the ice near the interface and on the adhesion strength. Still another question that will have to be examined is whether the adhesional shearing forces measured represent the force necessary to initiate or to propagate a fracture. For any release or adhesive coating the desired property is that the flaws at the interface promote crack initiation with a minimum applied stress and that subsequent crack propagation take place spontaneously. Therefore it would be helpful to employ test methods that permit a study of fracture initiation and propagation along ice/solid interfaces (20,21).

The experiments on the abraded steel are interesting in that they demonstrate that an apparently slight surface roughness can substantially increase the adhesional shear strength. These substrates did not appear to be heavily roughened; they retained a dull mirror finish. However, the surfaces had a plowed appearance in the electron microscope with furrows about 2000A deep. The replicas of the ice separated from these abraded surfaces showed clearly that the ice in and around the scratches had to be deformed and broken to separate the ice from the steel. The presence of adsorbed monolayers on the abraded steel aided the ice removal somewhat. However, replicas of the ice sheared from the monolayer-coated, abraded steel exhibited markings which indicated that the ice in and around the scratches had been deformed. These results on abraded surfaces are comparable with those of Raraty and Tabor (2) whose steel substrates had been similarly abraded. These authors concluded that the ice underwent plastic deformation on removal from clean steel and to a lesser extent when removed from stearic acid monolayers deposited on steel. They did not study steel surfaces as smooth as the alumina-polished steel used in most of the work described here.

Adhesion to Thin Plastic Coatings

Two mechanisms have been demonstrated by which the application of air-drying coatings significantly reduces ice adhesion. They are (a) the entrapment of air at the ice/substrate interface and (b) the cohesive failure of the substrate coating. These results should be helpful in the design of ice-release coatings.

The entrapment of air at the interface as a mechanism of reducing adhesion is evidently related to the microroughness and the high water contact angle of the coating surface, as suggested by Zisman (8). However, there is evidence that under the condition of these experiments other factors besides roughness and wettability influence the massive entrapment of air. For instance, an attempt was made to imitate this combination of roughness and wettability by adding 0.05μ alumina powder to a perfluoromethacrylate polymer (coating H, Table 1). The addition of the alumina powder imparted a distinct microroughness to the dried coating, which without the powder had a microscopically smooth surface. However, the adhesional shear strength of ice to the roughened coating surface was as high as it was to the smooth coating. Replicas of the ice separated from the roughened surfaces showed only an occasional small group of trapped air bubbles. It is also curious that for those coatings that did show the massive entrapment of air the bubbles appeared to be restricted to certain regions of the interface. It is possible that air entrapment occurs initially for many surfaces but upon subsequent freezing of the water the air disappears from the interface, perhaps being expelled by the advancing ice front. It is not evident from the experiments described here how the air is expelled or what condition must be met to prevent its loss.

One of the more interesting results of these studies was the cohesive failure of one of the poly(organosiloxane) coatings (coating E, Table 1). The evidence for a cohesive failure was the appearance of oil droplets and flake-shaped etch markings on the replicas of ice sheared from the coating. Evidently, the coating lost flakes of itself to the ice, but it is not immediately clear whether the oil droplets came from the coating or are the result of some action of the replicating solutions on the flakes. This interpretive difficulty arises from the fact that the flakes on the separated ice surfaces should have left an impression on the wet Lucite replica as well as on the dry Lucite replica. Examination of the coating after ice removal also showed evidence that the coating film failed cohesively but did not reveal any details as to the failure mechanism. The experiments here did show that the coating continues to fail cohesively at a low shear stress for at least four successive tests. It speaks well for this mechanism of ice release that of all of the coatings examined in an extended laboratory testing program this was the only candidate to be selected for fleet trials (12). Coatings A through D, which released ice by air entrapment, are relatively recent developments and were not tested in the program. However, these latter materials require for their good release properties that the water come into contact with the surface in a manner that favors the entrapment of air. Also, the amount of entrapped air depends on how the ice freezes. Such requirements may seriously limit the usefulness of these and any other release coatings that

depend upon the manner in which the ice accumulates which, in the field, may be quite variable. The evidence thus far available suggests that the most promising ice-release coatings are those that fail cohesively and do not depend on the mode of ice formation or the properties of the ice.

One of the polymer coatings (coating F, Table 4) showed reasonably good ice-release properties, but the experiments did not reveal how the ice release was achieved. On the basis of the results on the monolayers, the adhesional shear strength for ice against a smooth, hydrophobic surface should be about 70 to 90 psi and the fractures generally adhesional in appearance. The adhesional shear strength of coating F was 45 psi, well below the range of the adsorbed monolayers. However, there was no evidence of air entrapment at the interface or of cohesive failure of the substrate. Indeed, the plastic replicas showed that the ice had conformed closely to the microtexture of this polymer film. This result suggests the existence of another as yet unidentified mechanism for ice release on which further experimental work is justified.

Three of the coatings, G, H, and I, gave adhesional shear strengths between 70 and 90 psi, and the breaks were generally adhesional so that their behavior was little different from that of the adsorbed monolayers. The remaining coatings (coatings J and K, Table 4) gave ice adhesional shear strengths nearly comparable to that of clean steel, and the failures were to a large extent cohesional. There is no ready explanation of why these surfaces showed such relatively poor release properties. One suspicion is that they permit the water to penetrate into the surface. In the course of studying the poly(vinylsiloxane) polymer (coating K), it was found that on this material, the hydrolysis product of a vinyltrialkoxysilane, the receding contact angle for water was much lower than the advancing angle and that both tended to decrease as the water remained on the surface. Such behavior suggests that the water attacks this coating and perhaps penetrates it. The mechanism of attack is not known. Water penetration may also explain the loss in ability to release ice observed on some of the polymer coating when the water was allowed to remain on the surface for long periods of time before freezing.

SUMMARY

An effort has been made to determine how the adhesional shear strength of ice is affected by the chemical and physical properties of the substrate surface and the condition of the ice near the ice/substrate interface. A number of techniques were utilized to examine the substrate and the ice microscopically: (a) a polarization-interference objective was used to reveal the microtexture of the substrate, (b) a replica-etchant technique was used to reveal the fracture marking, crystalline structure, and lattice defects of the sheared ice surface, and (c) the intact ice/substrate interface was examined through a polarizing microscope.

Measurement of the adhesional shear strength of ice to various surfaces and the application of the above techniques provided some interesting but only preliminary information about the adhesive properties of ice as follows: (a) The shear strength of ice formed and tested at −6°C against hydrophobic, close-packed monolayers adsorbed on highly polished stainless steel was only 30% less than the shear strength of ice in similar tests against clean, hydrophilic steel. Among the monolayers the shear strength was essentially the same, even though they presented to the ice quite different chemical constitutions, including close-packed methyl groups, close-packed ω-hydroperfluoro groups and dimethylsiloxane polymer chains. (b) The separation of the ice from clean steel was partly cohesive and occurred by ductile fracture. The breaks from the monolayers were apparently adhesional and occurred by brittle fracture. (c) On lightly abraded steel surfaces, which had a much greater microroughness than the highly polished steel, the adhesion was measurably higher and the fractures were cohesive and ductile for both clean and monolayer-coated substrates. (d) The adhesion to organic polymer coatings on brass plates generally paralleled the adhesion to the monolayers on steel. Some cases of much lower shear strength occurred when there was obvious entrapment of air at the interface or when the coating itself failed cohesively. For other coatings the adhesion was comparable to the adhesion to clean steel, and there was some evidence that the water penetrated the coating. (e) The replica-etchant technique and the use of the polarizing microscope showed the ice near the ice/substrate interfaces to be composed of small,

columnar crystal grains with occasional dendritic or frost growth. The ice lattice near the interface was also found to have a much larger amount of defects – presumably dislocations or vacancies – than did the bulk ice. The lattice defects appeared to be unevenly distributed among the crystal grains.

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13. ABSTRACT

Determinations have been made on the adhesional shear strength of ice formed against clean, highly polished steel, against close-packed monolayers adsorbed on steel, and against thin coatings of organic polymers painted on metal surfaces. The adsorbed monolayers reduced the shear strength by about one third of that for ice against clean steel. The values of the shear strength for the different monolayers were approximately the same despite a wide difference in the chemical constitution of the adsorbates. The monolayers also had the effect of changing the character of the breaks from clearly cohesional, ductile fractures from clean steel to apparently adhesional, brittle fractures from the monolayers. On lightly abraded steel the results were quite different from those on the highly polished surface – the adhesion was noticeably higher and the breaks were cohesional for both clean and monolayer-coated abraded surfaces. The shear strength against the organic coatings ranged from values equal to that of ice against clean steel to values 70 to 80% lower. These results showed no simple correlation with the water contact angle on the organic coatings.

The appearance of the ice separated from the various substrates was examined by forming plastic replicas against the ice surface. These replicating solutions etched the ice to reveal crystal structure and crystal lattice defects. The etching features showed the ice lattice to be highly defective near the substrate. Use of the replica-etchant technique and microscopic examination of the organic polymer coatings has revealed two mechanisms by which ice-release coatings operate – air entrapment at the ice/coating interface and the cohesive failure of the coating itself.

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