# Developing Icephobic Surfaces for Aircraft Industry Applications

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## Abstract

Current deicing technology in aircraft industries employs either air or fluid based methodology. Thermal and bleed air technology utilize heated air to remove ice from planes in order to minimize hazardous conditions on an aircraft surface. Commonly, antifreeze is applied repetitively to the aircraft which is both time intensive and environmentally toxic. This study aims to improve the deicing process by using alternative surface solutions to both minimize the interfacial shear strength of smaller ice lengths and minimize the surface interfacial toughness in order to initiate crack propagation of larger area-independent ice sheets. By measuring the force required to remove various ice lengths from a surface, the relative ice adhesion strength can be calculated to a range where deicing technology becomes area independent. Surface design also allows for the possibility of using organic polymers which match the thermal hysteresis properties of antifreeze but are not environmentally toxic as shown by differential scanning calorimetry analysis. Product design improvements will limit ice adhesion strength and interfacial toughness while employing a fabrication process for surfaces with practical industrial applications.

## Background

The Aviation Accident Database of the National Transportation Safety Board reports that 228 aircraft accidents occurred because of icing from 2006-2010 with 40 accidents occurring during the flight. Apart from documented accidents, ice buildup on an airplane wing interferes with the normal airflow over a plane wing which reduces thrust and lift with weight and drag, undesirable for an airplane. It is clear that icing is a present threat to aircraft technology, leading to hazardous and sometimes fatal accidents.

Current deicing technology focuses on one of two aspects of the icing process: delaying the formation of ice (anti-icing) and facilitating the detachment of ice that has already formed (ice shedding). One anti-icing process for larger aircraft is a “bleed air” system where hot air is fed onto critical surfaces to halt ice accreditation. An alternative method is achieved by placing thermal coils to warm up the plane surface similar to a heated oven. These two anti-icing technologies, while effective in many cases, are limited to larger aircraft and may have overheating concerns. Not to mention, they require additional power to maintain during flight.

One common fluid de-icing technology uses antifreeze to chemically break down ice on vulnerable surfaces. These antifreeze molecules utilize thermal hysteresis properties to inhibit the growth of ice crystals at temperatures below the ice freezing point. While thermal hysteresis can effectively reduce ice freezing temperature, antifreeze molecules, which facilitate this hysteresis, have several negative environmental effects. Antifreeze is made up primarily of ethylene glycol or propylene glycol which creates metal contamination through corroding acid and would have health effects to the central nervous system if ingested. If possible, surfaces should aim to use safe chemicals without these harmful effects.

Clearly there are improvements to be made to these deicing technologies. My research aims to develop a deicing technology that does not rely on active energy input, human intervention and result in negative environmental consequences. Thus, we have focused on developing a one-time surface technology which aims to facilitate both deicing and anti-icing. Two main approaches include reducing interfacial shear strength and reducing interfacial toughness.

Interfacial shear strength ($\tau$) generally reflects the sliding resistance between two surfaces. A low interfacial shear strength means that ice can slip off the surface more easily, a preferable approach for this project. The apparent ice adhesion strength between the polymer surface and the ice is the force required to remove the ice (calculated on ice rig) / initial bonded area (variable with ice length). Given the scale-independent properties of these samples, the true ice adhesion strength is related to (G/t)^(1/2). Generally speaking, the shear modulus (G), lowers ice adhesion strength regardless of surface chemistry.

In a more generalized sense, surfaces with both a low interfacial shear strength ($\tau$) and low interfacial toughness ($\Gamma$) facilitate de-icing but in different ways. A surface with low $\tau$ helps with spontaneous ice delamination at small ice areas. At larger ice areas, a surface with low $\Gamma$ facilitates propagation of an interfacial ice crack. Additionally, a surface with thermal hysteresis properties, chemically addresses the freezing point of ice which can help stop ice adhesion at the start of the icing process.

Natural deep eutectic solvents (NADES) have demonstrated biomolecular activity, physiochemical properties, and component properties. In order to utilize these components under thermal hysteresis, a mixture of natural metabolites were combined under a specific molar ratio in order to melt under the eutectic point. A eutectic point essentially means that under a certain combination of materials, they will melt from liquid to entirely solid all at once, bypassing semi-liquid, semi-solid states at every other composition. This eutectic point also effectively lowers the freezing point of a system. Given that there are natural non-toxic combinations of materials which can be combined under their eutectic combination, there is potential to use these as surface materials which can effectively delay ice accumulation. At least 39 aqueous NADES species have been described in the literature and demonstrate the potential for water to be utilized in these systems.

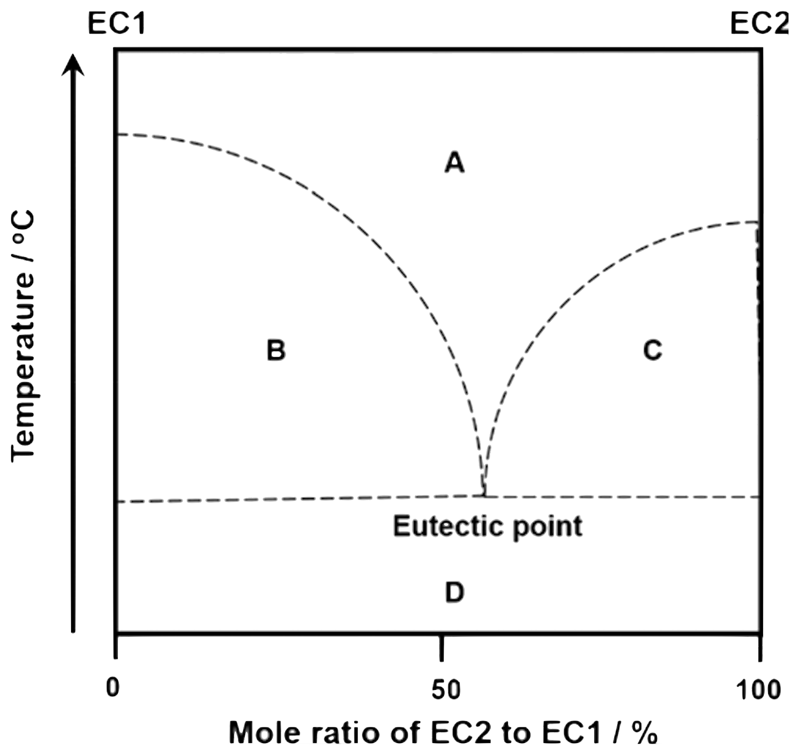


**Figure 5**. Eutectic point of two constituents demonstrating potential for a specific composition used to effectively lower the freezing point of water.

## Methods

### Push-Off Test

In order to test interfacial shear strength ($\tau$) and interfacial toughness ($\Gamma$) between the ice and surface, we have been utilizing the push-off test, the most commonly used measurement in deicing publications. With this methodology, we set up an ice rig designed to push off pieces of ice adhered to a cold surface as close to the interface as possible in order to obtain accurate measurements of pure shear stress over normal stress values. Once ice cubes are adhered, a force is applied tangentially to the ice and the maximum force required to dislodge ice is recorded. This process is repeated 5 times for each sample at increasing ice lengths.

Once the testing process is complete, the interfacial shear strength ($\tau$) is calculated as the maximum force required to dislodge ice divided by the interfacial area.

$$\tau\, ice = \frac{F}{A}$$

The surface shear strength can only be measured for area-dependent samples. In order to develop an ice-phobic surface which facilitates ice-shedding we are looking at $\tau$ < 100 kPa. However, given that the force required to remove ice is linearly increasing relative to surface area, even with an icephobic surface, large blocks of ice may require another strategy in order to facilitate ice removal.

In samples with area-independent properties, minimizing the interfacial toughness (Γ) can be measured by values at area-independent ice lengths. In these samples, the force required to remove adhered ice from large areas (a few cm2 or greater) is both low and independent of interfacial area. Once the ice rig data is collected, we view the critical length at which the force required to remove ice remains constant. This value is often between 8-12 cm for the current sample chemistry. Past this length, the interfacial toughness (Γ) is measured according to the following equation where Γ is the interfacial toughness, F is the critical force, h is the ice thickness, and E is the ice modulus.

$$\Gamma = \frac{(F\ ice)^2}{2Eh}$$

**Differential Scanning Calorimetry**

In terms of the anti-icing chemical properties of antifreeze, some natural deep eutectic solvents are able to capture hysteresis properties of antifreeze without impacting the environment. In order to measure the probability of these properties, differential scanning calorimetry analysis was employed to visualize phase changes at various temperatures. In this analytical method, a change in heat capacity of a material reflects a phase change. Evidence of thermal hysteresis was demonstrated when the phase change of water occurs below its typical freezing point. Practically, when the freezing temperature of water is lowered by a chemically altered surface, ice crystal formation is delayed which is a key anti-icing technology.

**Results**

Our group began by testing a series of polymeric surfaces to determine which allowed for low interfacial toughness properties.

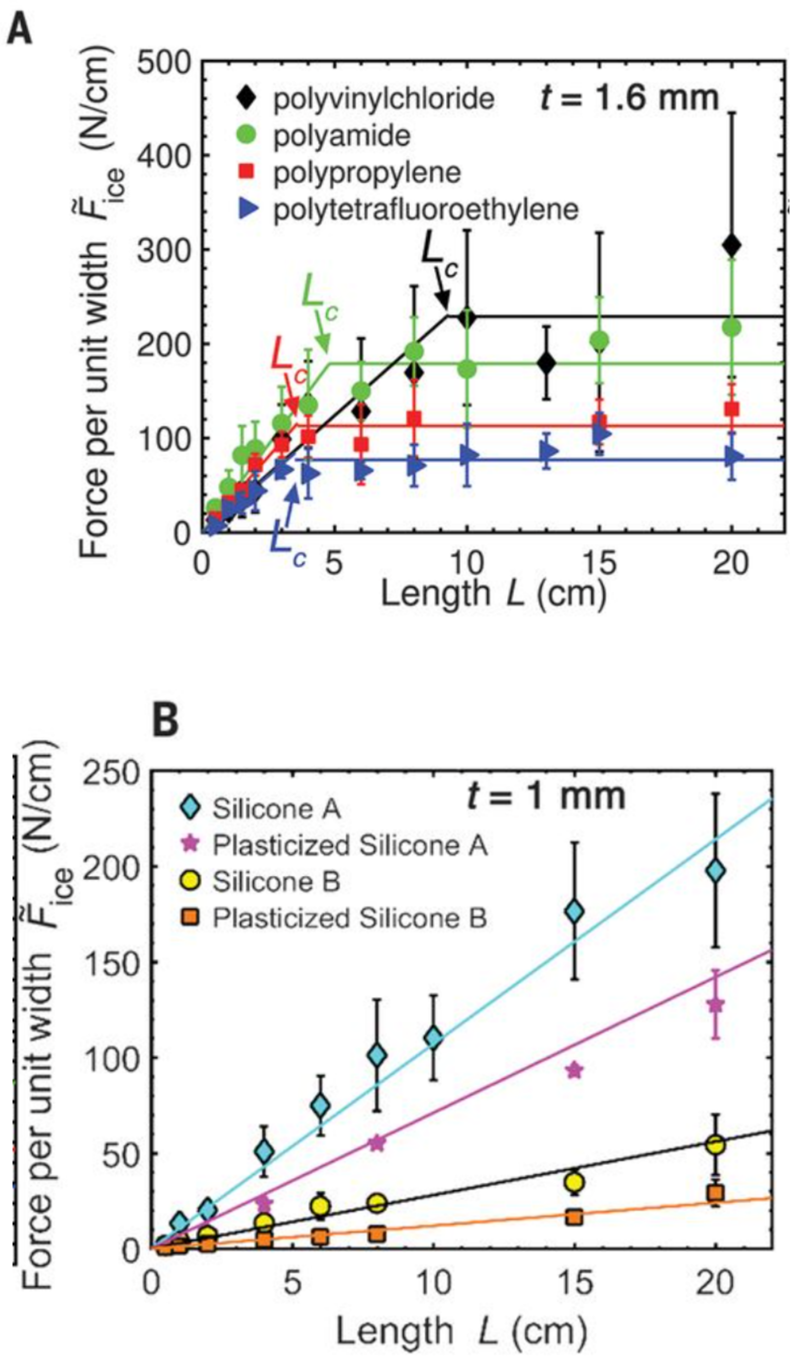


**Figure 1.** A comparison of force required to remove adhered ice for low interfacial toughness surfaces that exhibit area independent properties and other surfaces that do not exhibit these properties.

As shown in Figure 1A, surfaces like polyvinylchloride, polyamide, polypropylene, and polytetrafluoroethylene have low interfacial toughness. These surfaces have a critical force which is represented by the plateau of force required to remove ice past the critical length. Surfaces that do not contain this property are those shown in Figure 1B, which include variations of silicone.

Next we developed a low interfacial toughness coating which allows for scale independent ice removal from a spray-on fabrication method. This fabrication method is easily applicable to industry since it is thin for structural flexibility and automated for processing consistency. Since this surface coating focuses on toughness, it was tested exclusively in the area-independent regime to find the toughness and subsequent critical force as shown in Figure 2.

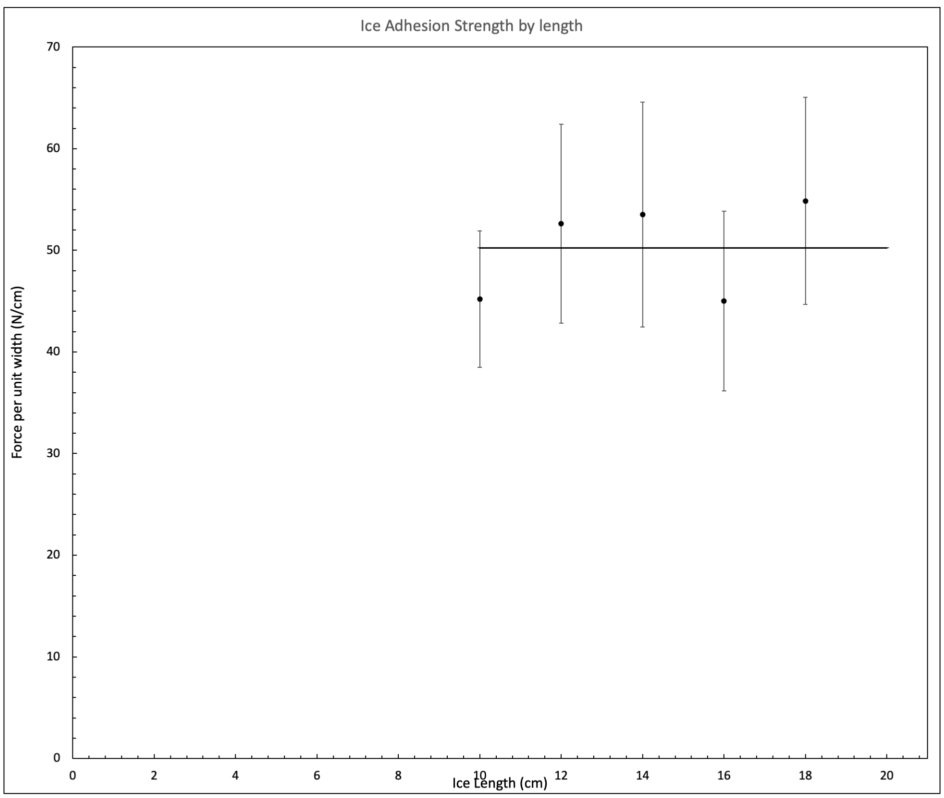


**Figure 2.** Force summarization of low interfacial toughness (LIT) coating system past critical length of ice adhesion showing a low interfacial toughness surface.

One of the surface designs includes a bilayer surface relying on the combination of two materials with greatly differing elastic moduli to form a bilayer laminate composite surface: M-3115 Polyurethane (E = 26.4 kPa) and Desothane (E = 2.4 GPa). This surface design demonstrates a unique combination of both low interfacial toughness and low ice adhesion strength which may address the issue of ice shedding in industry at both large and small scales. Additionally, these polymers are non-toxic and have excellent adhesion properties.

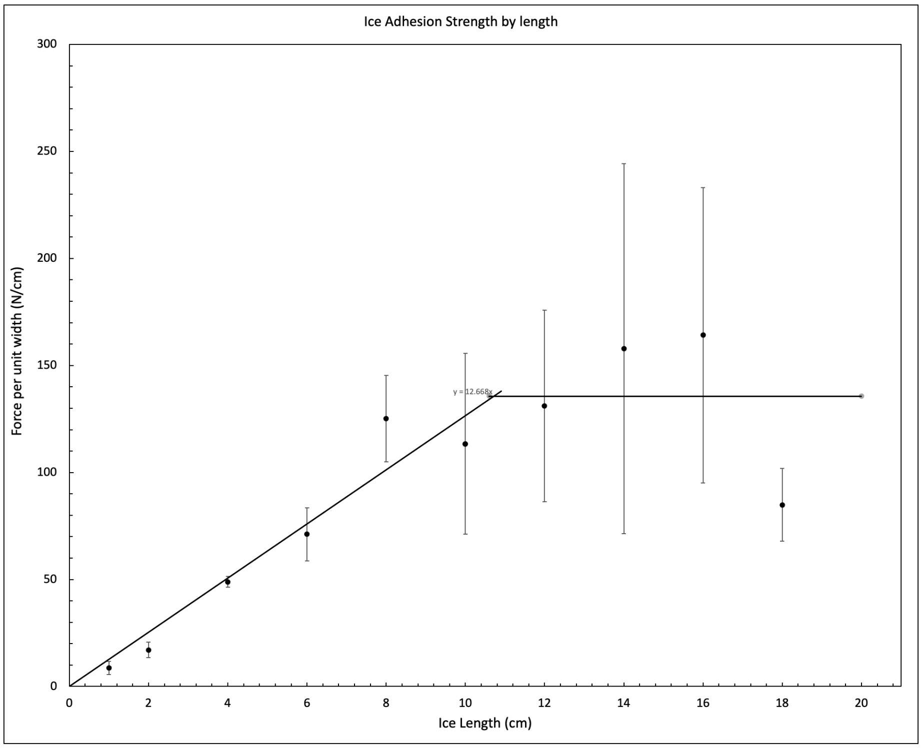


**Figure 3.** Force summarization of M3115-desothane bilayer system demonstrating critical length of ice adhesion after which force becomes area independent.

In another surface chemistry, a Polytetrafluoroethylene (PTFE) film was inserted between the base and capping layer. PTFE has extremely hydrophobic properties which allow it to form gaps between the bilayer surface. These gaps can facilitate buckling of ice and are able to target deicing using a novel  surface mechanism.

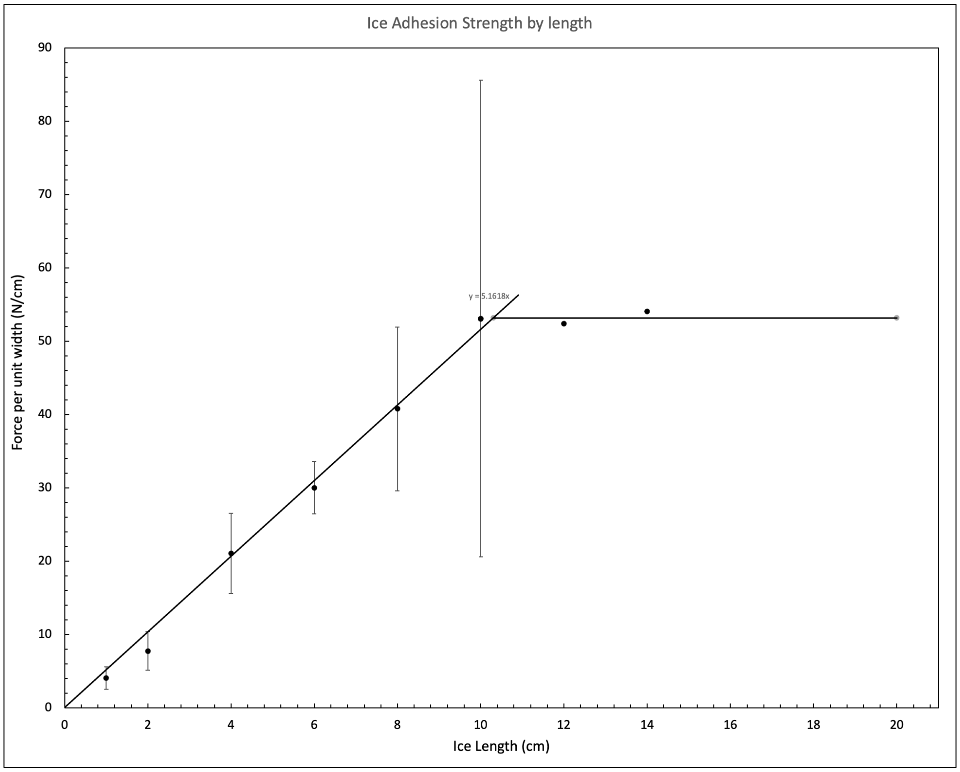


**Figure 4.** Force summarization of M3115-desothane bilayer system with PTFE film insertion.

**Table 1.** Comparison of bilayer surface chemistry interfacial toughness and interfacial shear strength properties

| Sample | Ice Adhesion Strength (kPa) | Critical Length (cm) | Critical Force (N/cm) | Interfacial Toughness (J/m^2) |
|---|---|---|---|---|
| LIT PDMS | – | ~10 | 50.24 ± 5.35 | 0.25 ± 0.053 |
| Regular Bilayer | 126.68 ± 8.06 | 10.6 ± 3.54 | 135.60 ± 36.08 | 0.63 ± 0.959 |
| PTFE Bilayer | 51.6 ± 12.88 | 10.3 ± 2.92 | 53.18 ± 0.84 | 0.28 ± 0.009 |

As shown in Table 1, the LIT (low interfacial toughness) coating and the PTFE bilayer perform similarly well in terms of low interfacial toughness characteristics. All three of these coatings have similar characteristics relating to critical length and surface area ice adhesion creating area independence. However, both the PTFE bilayer and LIT surfaces out perform the regular bilayer in terms of demonstrating less than half the critical force is needed to remove ice. Likely, the existence of voids has some impact on ice adhesion properties. While interfacial toughness is only around 0.3 J/m^2 higher in the regular bilayer, the critical force is more than double that of the PTFE and the bilayer coating. The impact of interfacial toughness in a surface is extremely consequential on the critical force of ice.

**Conclusion**

We have developed a methodology which can target three aspects of the icing process. At small scales, minimizing interfacial shear strength by targeting the shear modulus allows for rupture along the entire ice interface. When there are larger ice sheets which require larger amounts of force to remove, minimizing interfacial toughness can allow for area-independent ice crack propagation. Additionally, we can target the ice crystallization before it forms using chemicals which reduce the ice freezing point through the process of thermal hysteresis. By using natural deep eutectic solvents (NADES) we can mimic this property of antifreeze without harm to the environment.

Clearly, there is a wide range of potential for this technology usage in industry. Since a surface with low interfacial toughness has an area-independent critical force, when applied to an aerospace capability, these surfaces can remove large sheets of ice at the same force as those of the critical length. Additionally, the M3115, desosine and NADES materials do not contain the same toxicity concern as antifreeze molecules currently used in industry. Finally, these surfaces have the potential to be fabricated directly on a plane wing surface which could limit the human intervention necessary to de-ice a plane directly allowing for industry cost and time savings.

**Limitations**

Some considerations for testing and generating samples include potential sample fabrication and testing errors which may affect results. While the push off method is simple and widely used, this methodology may have limitations when the height of the ice rig is not exactly tangential to the interfacial surface and thus must be carefully monitored to maintain accurate results. Additionally, since the surface must be cooled in order to adhere to ice, occasional frost build-up is measured to ensure it does not significantly affect the results.

The bilayer surfaces that we have developed still have issues with complexity of fabrication processes and coating durability. While our samples were each tested at least 5 times at several ice lengths, there may be additional variation amongst their sample preparation. At a width of 2mm, these surfaces may have issues with thickness and application in the aerospace industry. Additionally, these samples have a complicated multi-step fabrication process in which mechanical properties can be greatly affected by the porosity and curing process. These surfaces still need to be refined to ease their application and use in the future.

**Future Directions**

In future research, it may be more industry efficient to utilize a spray coater to apply the de-icing agent onto the desired surface. Additionally, there are other possible surface combinations to be retested to continue to maximize ice-phobic surface properties. Perhaps, these surfaces should be tested for coating durability and by using other ice removal force tests such as force required to peel ice off the surface. These tests would allow for a more complete picture of the behavior of these surfaces on our desired application.

Finally, this research in ice adhesion and surfaces can be applicable to several other industries and purposes including but not limited to automotive, roofing, sidewalk, and building capacities where ice adhesion can be undesirable and hazardous. The ability to target ice adhesion from multiple angles allows for a broad level of improvement to surface technology which should continue to be developed for practical industrial applications.

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