

Improving Surface Properties of Materials



SwRI researchers are using advanced processes and diamond-like carbon (DLC) coatings to reduce wear and strengthen materials

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In many cases, the failure of a mechanical component in modern machinery starts at the surface. Wear (abrasion, galling and erosion), corrosion (including pitting, crevice and galvanic), and fatigue are all surface-related phenomena. To increase machinery reliability or meet ever-increasing challenges for higher loads, speeds and productivity, new base materials are being developed. However, developing a new material takes a long time and is costly.

One alternative is to improve the surface properties of materials. Heat treatment has been used for thousands of years. “Surface engineering” is the term commonly used for nearly all surface treatments, including coatings. Surface engineering is a cost-effective way to increase the surface hardness or other functionalities while maintaining the desirable properties of the base material such as toughness. For instance, to make gears more wear-resistant in automobiles, steel might be replaced with a ceramic material. However, ceramic is too brittle,

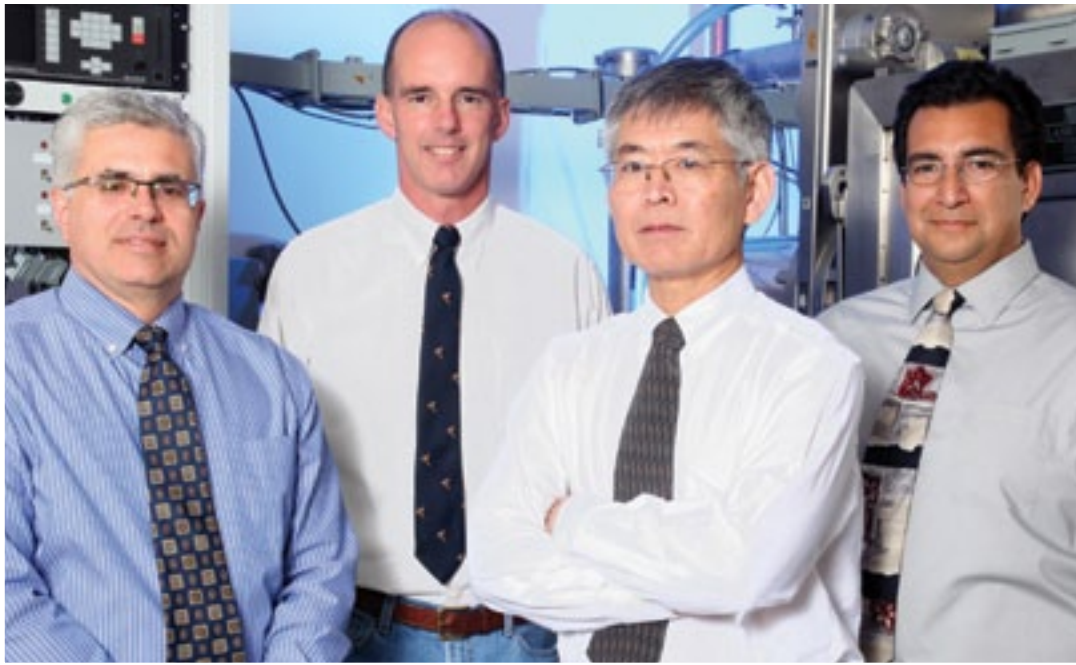
and the ceramic gears may simply lose their teeth in acceleration. This presents an opportunity to put a ceramic coating on the outer surface of the gears to improve wear resistance while retaining the underlying toughness of the base metal.

Diamond is the hardest material obtainable today. It shows the highest resistance to nearly all types of wear and has a low coefficient of friction in many environments. It is inert and resistant to various types of corrosion. Thanks to modern technologies, large-area diamond coatings have been deposited on selected materials. But diamond coatings cannot be applied to every component that experiences wear and corrosion.

There are two primary problems that hinder the broad application of diamond. First, the deposition temperature (greater than 1,300 degrees F) is too high for most engineering materials, including steels. Second, diamond coatings are very rough, and polishing them is arduous and costly.

To overcome these problems, researchers have developed an alternative coating — diamond-like carbon (DLC). Like

diamond, DLC is a carbon-based material, but unlike diamond, which has a crystalline structure, DLC has an amorphous structure without the crystalline grains. DLC obtained its name because it resembles diamond in many ways. It exhibits comparatively high hardness. The hardness of diamond is 100 gigapascals (GPa). DLC varies from 15 GPa to 50 GPa (for example, the hardness of fully hardened tool steels is 6 to 9 GPa). Moreover, a DLC coating is very smooth compared to diamond; thus, it can protect both the coated component and the surface that is its counterpart. Similar to diamond, the coefficient of friction of DLC is low, and DLC has good corrosion resistance. DLC can be deposited at room temperature, making it suitable for application to steels, aluminum alloys and even polymers. In addition, DLC can be “doped” with many elements for various purposes, such as silver and titanium oxide for antibacterial applications, gold for higher oxidation resistance and fluorine or other elements for low surface energy for de-icing and self-cleaning.



Researchers in SwRI's Materials Engineering Department are developing and investigating advanced coatings for a variety of applications. The team includes (from left) Institute Scientist Dr. Michael Miller, Manager Dr. Kent Coulter, Program Director Dr. Ronghua Wei and Engineering Technologist Christopher Rincon. Miller specializes in the structural analysis of organic, inorganic and polymeric compounds. Coulter, who manages SwRI's Surface and Materials Chemistry Section, specializes in vacuum-coated thin films for advanced materials applications. Wei's primary focus is developing new plasma surface engineering technologies. Rincon is responsible for the daily operation of the Surface Engineering Facility and its equipment.

SwRI plasma immersion ion deposition technology

Currently, deposition processes for DLC coatings can be categorized as either physical vapor deposition (PVD) or plasma-enhanced chemical vapor deposition (PECVD). In PVD, one technique referred to as sputtering is where carbon is obtained from a solid source,

such as a graphite target that is biased, and argon ions are accelerated to the surface to knock off "sputter" carbon that is collected on the part as a coating. In the PECVD process, carbon is obtained from a gaseous source, such as acetylene or methane. In general, a DLC coating obtained from a PVD process is hydrogen-free and harder than its counterpart from a PECVD pro-

cess. The PVD coating usually has more stress, which can lead to the coating delaminating; therefore, an interfacial layer is often needed to increase adhesion, or a thinner DLC coating is applied to avoid film spallation. The biggest limiting factor for PVD is that it is a line-of-sight process. It is difficult to coat three-dimensional components uniformly. To achieve a uniform deposition, complicated sample manipulation is required. The significant advantage of a PECVD process comes from the inherent non-line-of-sight nature of the process. In PECVD, multiple three-dimensional parts can be coated uniformly without manipulation because the carbon source is from a gas or gas mixture, which goes everywhere in the deposition system.

Researchers at Southwest Research Institute (SwRI) have been developing various DLC coating processes using a plasma immersion ion deposition (PIID) process originated at the University of Wisconsin and Los Alamos National Laboratory. PIID is an advanced version of PECVD. Its main advantage is the use of a pulsed glow discharge to deposit coatings. This process allows the coating to be applied to multiple components in a large-scale chamber, which lowers the cost of the coating. Other advantages include low-temperature deposition and minimized arcing, resulting from the short voltage pulses used during the deposition.

For the PIID process, parts are placed in a vacuum chamber. When the chamber is pumped down to a low pressure ($\sim 10^{-6}$ Torr), a gas is fed into the chamber to typically about 10 to 15 millitorr. A pulsed train of negative voltage is applied to the parts, and a pulsed-glow discharge plasma is generated in the vacuum chamber. Because the parts are pulsed, the voltage also draws the ions to the part's surfaces. Depending on the ion species (precursor gases), either ion sputter cleaning (if argon is used) or deposition of DLC can



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These images show components being processed in the PIID system: (left) coated components and (right) automotive parts.



The SwRI PIID coating chamber allows multiple components to be coated simultaneously, thus lowering the cost of the coating.

be performed (if a carbonaceous gas such as acetylene is used). Typically, to ensure good adhesion of the coating, components are sputter-cleaned with argon first. Then, without breaking vacuum or interrupting the discharge, deposition can proceed by gradually reducing the argon flow and increasing the acetylene flow to form the desirable DLC coating. Further improvement of DLC coating of ferrous materials can be made by depositing an adherent bond layer such as silicon, silicon carbide or silicon nitride, using various silicon-containing precursors before the DLC deposition.

DLC coating performance

Because of the smoothness and hardness of DLC coatings, their sliding wear resistance is very high. SwRI researchers have deposited DLC coatings on various materials including steels, aluminum alloys, titanium alloys, magnesium alloys, various ceramics, glass and polymeric materials including polycarbonate and Teflon® for applications that experience sliding wear such as parts in reciprocating motors or pumps.

The corrosion resistance of DLC stems from three sources: carbon is a

relatively inert substance, the coatings can be applied pinhole-free, and DLC coatings are typically resistive and suppress the transport of electrons at the coating surface. In some applications, DLC coatings are being evaluated as replacements for toxic chromium plating.

Erosive wear occurs when solid particles or water droplets impinge on a surface at high speeds. The erosion rate of a material depends, among other factors, on the incident angle and the particle speed. At a higher angle and a higher pressure (higher particle speed), the DLC coating is removed along with the protection it provides.

Hydrophobicity, or water resistance, of a material surface is a physical property that can be characterized by the water contact angle. When the angle is less than 90 degrees, the surface is hydrophilic. When the angle is greater than 90 degrees, the surface is hydrophobic. If the angle is greater than 150 degrees, it is super-hydrophobic. Surfaces with super-hydrophobic properties have many applications. The self-cleaning nature of super-hydrophobic surfaces has been used for mirrors and lenses in telescopes and for solar arrays to avoid dust accumulation. A hydrophobic surface may also be ice-phobic and, therefore, may be used for deicing aircraft wings or high-voltage transmission lines.

“Standard” DLC films deposited using acetylene in the PIID process are slightly hydrophilic with a water contact angle of 70 to 90 degrees. Because the PIID process is a PECVD process, during the deposition of a DLC film, many other gases contain-

ing elements such as fluorine (F) and silicon (Si) can be included to form F-DLC or Si-DLC and others. Some surfaces of engineering components that were coated with DLC at SwRI have shown a water contact angle of up to 140 degrees. Though they are still not classified as super-hydrophobic, such as the carefully prepared surfaces in laboratories, they are sufficient for many practical applications. It is important to note that these coatings retain the high hardness nature of the “standard” DLC; therefore, they are much more robust in practical applications than many that use other processes.

Practical applications of the PIID technology

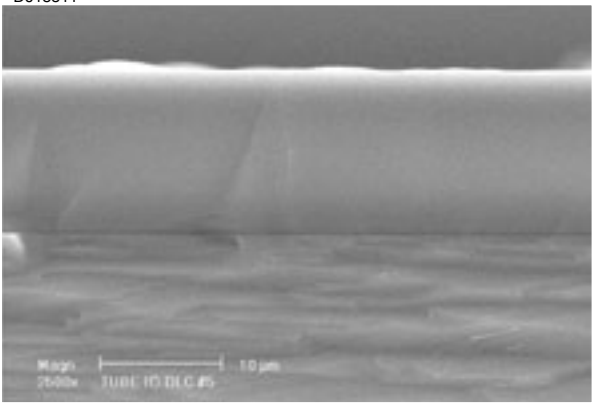
Using PIID technology, SwRI has been developing and transferring technologies for various DLC coatings with a wide range of practical applications. SwRI also has been further developing PIID-based coatings for other uses.

Using the PIID process, SwRI has developed a method to deposit DLC coating on glass windshields of military “humvee” vehicles to improve their abrasion resistance. Abrasion tests applying alumina ball to uncoated and DLC-coated glass samples show a several-fold improvement of erosion resistance from a DLC coating that is only a few nanometers thick. Based on these results, hundreds of windshields were coated and delivered to the U.S. Marine Corps for field use. The final deposition process was later transferred to a commercial company. SwRI is continuing to develop



Using the hollow cathode discharge phenomenon, SwRI researchers have successfully coated curved pipes up to seven feet long and six inches in diameter.

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This image from a scanning electron microscope shows a cross section of a DLC coating.

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SwRI researchers have developed a method to deposit DLC coating on "humvee" windshields to improve their abrasion resistance.

more transparent and more hydrophobic coatings.

Even though many technologies are available to treat external surfaces, treating the internal surface of a bore is quite difficult. However, there are a number of applications that require internal surface coatings, such as aircraft landing gear, hydraulic cylinders, automotive engine cylinder liners, military gun barrels and pipes for transporting petroleum and chemical products. To deposit DLC on the inner diameter of a tubular structure, SwRI has developed its own patented and patent-pending techniques.

In a typical PIID process, if the negative voltage is applied on a short tube, a plasma is generated primarily inside the tube. This phenomenon is known as a hollow cathode discharge (HCD) as opposed to glow discharge generated around the parts in the "standard" PIID process. HCD is characterized by a high current at a low voltage. This is because the electrons generated inside the tube undergo many collisions before they can migrate out of the tube and be collected at the vacuum chamber wall. Because the plasma is generated in the bore of the pipe, the pipe does not need to be straight. Using HCD, SwRI researchers have coated curved pipes up to seven feet long and six inches in diameter. The coating is quite dense and adheres well to the steel.

To coat the inner diameter of longer pipes, a vacuum chamber is not a commercially viable option. However, for this process the pipe itself can be used as the vacuum chamber. Using proper vacuum and electrical isolation connections, the pipe can be integrated into the vacuum

pumping system. A pulsed voltage is then applied to the pipe, and a DLC coating can be deposited on the inner surface. However, if the pipe is longer than 20 feet, it is quite difficult to generate plasma more than a few feet beyond the ends of the pipe where electrons can be collected at ground. SwRI has developed innovative technologies by which pipes longer than 40 feet can be coated with DLC coatings.

If a tube greater than two feet long has a small diameter of less than one inch, for example, a plasma will not generate inside the tube using the HCD method. The SwRI team has developed a patented technology that uses a magnetic field to enhance the plasma inside the tube. Using this technology, tubes with an outer diameter of less than three-quarters of an inch by 10 feet long have had their internal diameters coated with DLC.

The intense plasma generated in the hollow discharge mode leads to a high deposition rate, which is useful for coating production. Using this principle, SwRI researchers developed a technique in which a meshed metal cage is used to enclose parts for high-rate deposition. Using this method, multiple components can be coated and a much thicker coating (10 to 20 μm) can be achieved. Additionally, short tubes can be coated on the inside and outside simultaneously, due to the high plasma density inside the cage. Using this method, SwRI has developed a deposition process for treating large air-compressor impellers of a type

used in chemical plants, on all surfaces, including the walls of the channels, for both increased erosion resistance and hydrophobicity to reduce build-up. This technology has been transferred to a Chinese commercial company, which operates a deposition system with a much larger volume than the one at SwRI. With the help of SwRI researchers, they have demonstrated the deposition process for coating three impellers, or 10 propellers, in one batch.

Conclusions

Using PIID technology, SwRI is addressing a broad market demand for increased wear and corrosion resistance and increased surface functionality for diverse markets such as oil and gas delivery, power generation, and automotive engines and drive trains. DLC is an established material known to supply superior surface quality, and it is the ability of SwRI's scientists and engineers to apply DLC onto industrially relevant parts with complex geometries that is generating demand for parts qualification and technology transfer. SwRI is actively engaged with approximately a half-dozen clients to set up facilities worldwide to utilize PIID as a high-value-added step in their manufacturing process.

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