New approach to dealing with biofilms and biofouling

A surface coating developed by Duke researchers detaches biofilms produced by bacteria and reduces biofouling.

PAST ARTICLES IN THIS COLUMN have discussed ongoing research to better understand how bacteria adhere to surfaces and form biofilms. This issue is important to users of metalworking fluids because bacterial contamination has been found to decrease operating life and can lead to health and safety concerns for workers monitoring these fluids.

In a previous TLT article, research detailing how a specific bacterium *(Caulobacter crescentus)* adheres to a system through a reversible, irreversible two-stage process was discussed.[1] In the first step, the bacterium will establish a low adherence to a specific surface to determine if it is the right location. Then a stronger polysaccharide-based adhesive is produced and secreted in the second step to enable the bacterium to remain on the surface in an irreversible manner for a long period of time. This natural adhesive has the performance attributes of super glue.

KEY CONCEPTS

- A new trilayer, laminate surface coating has the potential to detach biofilms produced by bacteria and barnacles from the hulls of marine vessels upon application of an external stimulus such as an electric field.
- In testing, 95% of a biofilm is detached after a voltage was applied over 200 on-off cycles.
- Air pressure applied through the presence of air channels was also used as an external stimulus to enable the coating to detach biofilms.

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A second problem involving bacteria is their presence on the hull of maritime vessels. Biofouling leads to an increase in the weight of the vessel, a decrease in speed and, as a consequence, an increase in fuel consumption and overall operating cost.

Xuanhe Zhao, assistant professor in the department of mechanical engineering and materials science at Duke University in Durham, N.C., says, "Two approaches are currently used to minimize biofouling. The surface chemistry of the vessel can be modified through the use of, for example, toxic materials that will kill the bacteria. But the problem is that toxic materials used in the coating have a negative impact on the environment."

Zhao continues, "A second approach is to physically modify the modulus, topography or roughness of the vessel coatings. Some benefits are found to limit the growth of specific microbes but over the long-term, this approach is not very effective."

Other options to deal with biofilms and biofouling are offered by nature because animals are constantly exposed to this problem. Gabriel P. Lopez, professor of biomedical engineering at Duke, says, "Nature has developed a clever way to minimize biofouling by the development of biological surfaces that clean themselves through dynamic deformation and motion. One obvious example is the presence of cilia in the respiratory tract of humans. Cilia expel foreign particles that can form protective mucous layers on surfaces in the lung."

Cilia also are used by marine organisms such as mollusks and corals. A third example is the periodic shedding of skin by animals such as lizards and snakes.

If a coating can be prepared that is similar in performance characteristics to what is done in nature, then a technique may become available that can minimize the presence of biofilms and biofouling in such applications as MWF systems and the hulls of maritime vessels. Such a technology has now been developed.

TRILAYER LAMINATE

Zhao and Lopez, along with fellow Duke researchers, have developed a surface coating that constantly deforms as a means to detach biofilms and eliminate biofouling. Zhao says, “We determined that two external stimuli can be used to activate the deformation.” The stimuli used are application of an electric field and the use of pneumatic networks fabricated into the coating.

A trilayer laminate coating was developed that involves the bonding of a silicone elastomer, rigid insulating substrate and a metal foil. Zhao says, “The silicone elastomer is currently used in this type of marine coating application. A rigid insulating substance was used to protect the silicone elastomer from the external stimuli used.”

> *‘We chose this bacterium because it has been isolated from marine biofilms and can be cultured to form nice biofilms. Cobetia marina is quite tenacious and forms very sticky biofilms.’*

The researchers applied the trilayer laminate coating onto a surface exposed to artificial seawater suspensions of the bacterium, *Cobetia marina*. The concentration of the bacterium in the suspension was $7x10^7$ cells per milliliter of fluid. Lopez says, “We chose this bacterium because it has been isolated from marine biofilms and can be cultured to form nice biofilms. *Cobetia marina* is quite tenacious and forms very sticky biofilms.”

Prior to applying an external stimulus, the bacterium was allowed to form biofilms on the surface coating for a period of four days. Once the electric field is applied and reaches a critical value, the surface coating deforms into a pattern of craters, leading to the removal of the biofilm. Figure 2 illustrates this process.

After applying a voltage over 200 on-off cycles covering a time frame of 10 minutes, over 95% of the biofilm is detached from the surface. Additional experiments were done with the induced electric field on undeformed surfaces to show that this stimulus itself is not responsible for detaching the biofilm.

Preparation of air channels also was conducted to enable air pressure to be used to deform the surface. In this experiment, biofilms of *Cobetia marina* were grown on the surface in combination with adult barnacles seen in maritime applications. An air pressure of 3 kPa created 23% surface strain and led to the successful detachment of the biofilm. To achieve the same result with the barnacles, a higher pressure of approximately 15 kPa was needed.

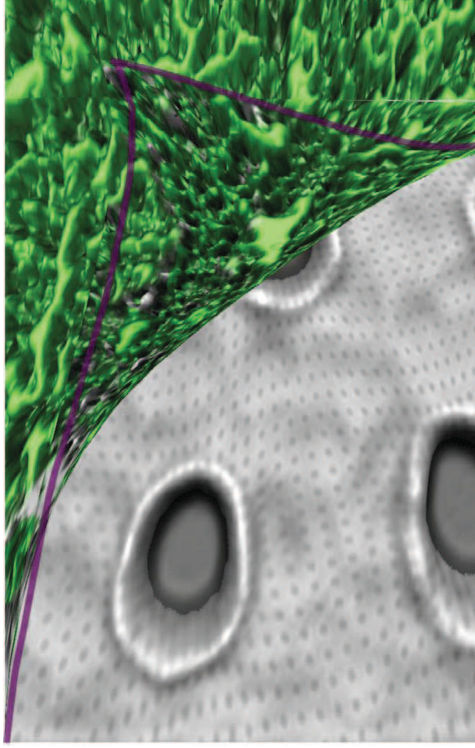

Figure 2 | **Deformation of a surface coating prepared with a trilayer laminate by an external stimulus leads to the formation of craters that facilitates the detachment of biofilms and, as a consequence, reduces biofouling.** *(Courtesy of Duke University)*

The researchers are looking to license this technology. Further details can be obtained by contacting Rob Hallford, Jr., of Duke at **rob.hallford@duke.edu.** Additional information on this research can be found in a recent article[2] or by contacting Zhao at **xuanhe.zhao@duke.edu.**

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2. Shivapooja, P., Wang. Q., Orihuela, B., Rittschof, D., Lopez, G. and Zhao, X. (2013), “Bioinspired Surfaces with Dynamic Topography for Active Control of Biofouling,” *Advanced Materials*, DOI: 10.1002/adma.201203374.

Low-temperature production of crystalline silicon

A more efficient, low-temperature process uses a liquid-metal electrode for preparing crystalline silicon.

CRYSTALLINE SILICON IS A VERY IMPORTANT RAW MATERIAL due to its use in semiconductor electronics applications such as computers. Another use for crystalline silicon is in solar cells that capture energy from the sun.

Research has been ongoing to find ways to reduce the cost of solar cells to enable this form of energy to become more competitive. In a previous TLT article, work conducted to develop a solar coating or paint was described.[1] Quantum dots prepared from cadmium sulfide and cadmium selenide were coated on titanium dioxide nanoparticles and applied to a conductive surface to form a solar paint. This more cost-effective approach produced a coating that converted solar energy to electricity and has potential to be commercialized.

KEY CONCEPTS

- Carbothermal reduction is an expensive and energy-intensive process used for preparing crystalline silicon.
- A potentially more efficient, low-temperature electrodeposition process has been developed to prepare crystalline silicone.
- The key to the process is the use of a liquid-metal electrode that acts to reduce the silicon precursor and solubilize the silicone until it reaches a supersaturated state that leads to crystallization.

One of the major reasons for the high cost is the energy-intensive process known as carbothermal reduction used currently to prepare crystalline silicon. While silicon is readily available as silicon dioxide (or silica) in about 40% of the earth's crust, the conversion to crystalline silicon is very inefficient. Stephen Maldonado, assistant professor of chemistry and applied physics at The University of Michigan in Ann Arbor, Mich., says, “In a multisequence fashion, carbothermal reduction converts silica initially to raw silicon, then metallurgical grade silicon and finally to crystalline silicon. The process takes place at temperatures well in excess of 1,000 C in an electric furnace. One other problem is that undesirable byproducts such as carbon dioxide are also formed.”

A second approach used to prepare crystalline silicon is electrodeposition that involves reducing an oxidized form of the desired element onto an electrode in the presence of an applied voltage. Maldonado says, “Electrodeposition of silicon has been tried at low temperatures and high temperatures. In the former case, the silicon produced is too impure and is amorphous, which means that high-temperature annealing and purification is still required in the same fashion as carbothermal reduction. High-temperature electrodeposition (temperatures > 700 C) can be done, but has not proven efficient enough to supplant carbothermal reduction reactions.”

> *‘High-temperature electrodeposition can be done, but has not proven efficient enough to supplant carbothermal reduction reactions.’*

A need exists for a more efficient process to prepare crystalline silicon at low temperatures. Such a process has now been developed.

LIQUID-METAL ELECTRODE

Maldonado and his fellow researchers have determined that crystalline silicon can be prepared at low temperatures through an electrodeposition process using a liquid-metal electrode instead of a traditional electrode. He says, “We have been working with liquid-metal electrodes as a means for reducing dissolved species in solution and for recrystallization applications through a process known as electrochemical liquid-liquid-solid. In our current work to produce crystalline silicon, we are working with a liquid gallium electrode.”

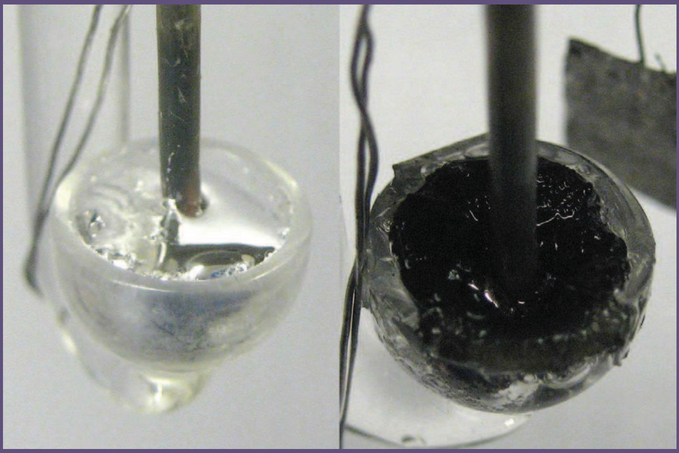

Figure 3 | **The liquid gallium electrode *(shown on the left)* is covered with crystalline silicon *(shown on the right)* through a low-temperature electrodeposition process.** *(Courtesy of The University of Michigan)*

The researchers used a two-compartment electrochemical cell to effect the deposition of silicon. Silicon tetrachloride was utilized as the oxidized silicon precursor. The system was pressurized at 400 psi to offset the volatility of silicon tetrachloride, and the gallium electrode was placed in propylene carbonate with 0.2 M tetrabutylammonium chloride.

Experiments were conducted at temperatures ranging from ambient up to 200 C. A deposition current of 20 mA cm^{-2} was used.

As shown in Figure 3, electrodeposition of the silicon on the gallium electrode was achieved through reduction of silicon tetrachloride. In this particular case, the silicon present on the gallium electrode in Figure 3 was formed at a temperature of 100 C after two hours.

The process takes place in four steps. Initially, gallium reduces silicon tetrachloride to silicon. The newly formed silicon dissolves in gallium until it reaches a supersaturated state when it will spontaneously form nuclei that come out of solution in the last step as crystals.

> *‘In a similar fashion to preparing crystalline rock candy from a super-saturated aqueous solution of sugar, we are using gallium as a crystallization solvent to expedite the crystallization of silicon.’*

Maldonado says, “In a similar fashion to preparing crystalline rock candy from a super-saturated aqueous solution of sugar, we are using gallium as a crystallization solvent to expedite the crystallization of silicon.”

The lowest temperature where crystalline silicon was obtained was 80 C. Maldonado adds, “This result is significantly better than the previous low temperature by at least 500 degrees.”

Several factors were studied to determine how to optimize the process. Maldonado says, “We found that increasing the temperature leads to bigger crystals. But moving to high pressure did not lead to better crystallization of silicon. The biggest factor of all is the type of liquid metal used to solubilize the silicon. Besides gallium, a second common liquid metal that can be evaluated is mercury. But there are lots of other options that we intent to study in this wide open field.”

Future work will also evaluate the use of another silicon source because silicon tetrachloride is too susceptible to hydrolysis. Maldonado says, “We believe that 80 C is not the lowest temperature that can be used to generate crystalline silicon. Ultimately, our goal is to find reaction conditions for preparing crystalline silicon at room temperature.

Further information can be found in a recent article[2] or by contacting Maldonado at **smald@umich.edu.** **TLT**

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