STOPPING CORROSION BEFORE IT STARTS

Integrating experimental tests and high-performance computing models helps Lawrence Livermore understand the onset of corrosion and stop it before it starts.

CORROSION is a part of everyday life. From cars and home appliances that rust to roads, bridges, and other infrastructure that crack and pit, materials eventually begin to deteriorate and need to be replaced. Corrosion not only has a huge economic impact for households, industries, and governments, it is also a critical factor in nuclear weapons stockpile stewardship. Materials used for weapon components stored in potentially corrosive environments can crack, break, or fail over varying time frames.

Research has been largely focused on corrosion's later stage conditions rather than addressing the problem early on, when steps to mitigate the degradation can be most impactful and effective. In a new approach, Lawrence Livermore researchers recently completed a Laboratory Directed Research and Development Program Strategic Initiative project that focused on understanding the initiation of corrosion, specifically pitting initiation and chemical degradation in moisture- or hydrogen-rich environments at their earliest stages. The team integrated state-of-the-art multiscale computer simulations, in-situ characterization, and data science to paint a fuller picture of the timescales and evolution of corrosion.

Led by Brandon Wood, director of Livermore's Laboratory for Energy Applications for the Future, this project has filled many gaps in understanding the onset of corrosion in multiple materials. Wood says, "Looking at what's been done in the past for predicting and modeling corrosion over the lifetime of materials, the work has been mostly empirical. Data sets are collected under quasi-controlled conditions but result in many unknowns. The older studies also relied on traditionally manufactured materials as well as conventional processes and conditions, which aren't so relevant today given the advances in materials science and technology." To fill in the gaps, Wood and his team chose three research thrusts representing different materials classes and degradation modalities: aqueous corrosion of aluminum, hydriding of titanium, and corrosion of additively manufactured stainless steel. The team conducted experiments at the atomistic, compositional, and microstructural scales, using a variety of spectrometry and microscopy techniques to characterize the materials' surfaces as they corroded and degraded.

However, the experimental work only told one part of the tale. High-performance computing (HPC) simulations were developed to model the evolution and impacts of corrosion over time, and machine-learning (ML) tools were needed to analyze the data. The surprising results of the multidisciplinary project have attracted the attention and interest of many academic research institutions, national laboratories, and government and industry stakeholders also seeking to predict—and one day prevent—corrosion.

Aluminum Meets Acid

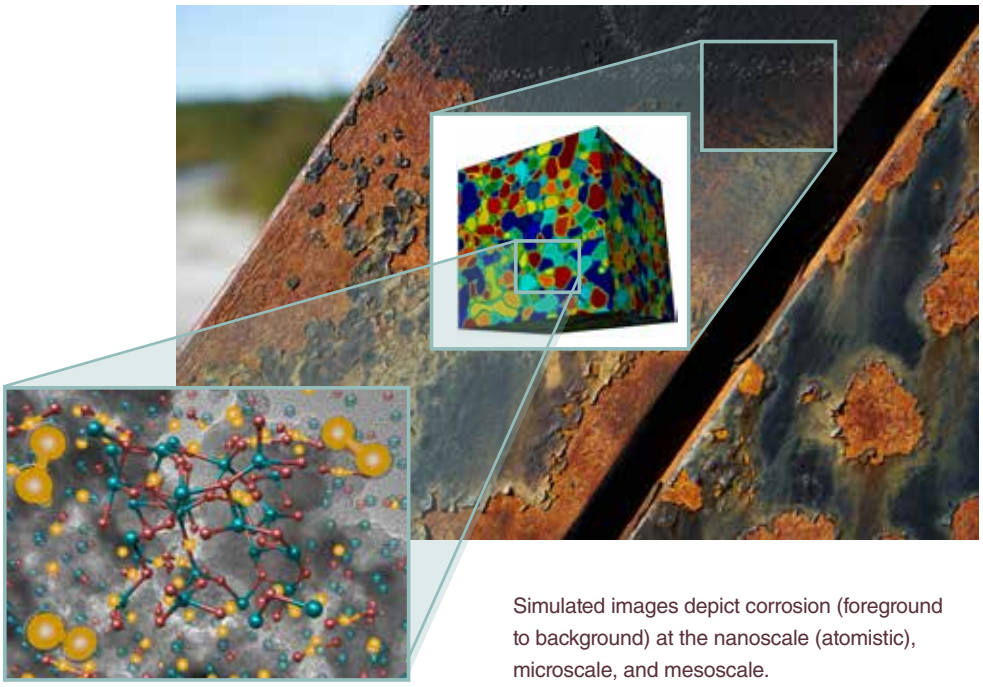
Aluminum is used across everyday and industrial needs, from aluminum foil and kitchen utensils to building materials and aircraft construction. As such, aluminum corrosion impacts nearly everyone in some manner, whether they realize it or not.

Lawrence Livermore's researchers sought to understand and predict several aspects of aluminum degradation such as aluminum's surface dissolution rate in corrosive solutions, the effect of aluminum's microstructure—which depends on processing conditions—on its susceptibility to corrosion, and the source of deterioration in surface oxides that form natively to protect the metal. While working with such a commonly used material with well-known properties may seem straightforward, the team realized early on that they would need to establish several parameters around the experiments and simulations to answer their questions. The team opted to work with pure aluminum instead of more commonly used aluminum alloys because alloys are much more complex systems with many more factors that are difficult to control in experiments and simulations. "We wanted to establish a baseline for aluminum's corrosion timescale and kinetics, which meant we needed to use the simplest system within the simplest environment," says Chris Orme, staff scientist. The simplest environment was determined to be the one in which the researchers could easily control and analyze the effects of changes to the corrosive solution on the material—varying only the pH of the solution in which the aluminum was submerged, in this case.

Orme and postdoctoral fellow Seongkoo Cho developed a titration system to adjust the pH levels of the solution by increasing

and decreasing acidity levels on submerged aluminum samples. In doing so, they could measure corrosion rates in chemistries that develop in cracks and other occluded environments. Semi-closed environments, such as cracks, create a positive feedback loop of corrosion and acidity that leads to even more aluminum corrosion as the solution becomes increasingly acidic. The acidity produced during corrosion can worsen pre-existing cracks, pits, and crevices, exacerbating degradation. As the pH was lowered from neutral pH to acidic pH, the protective oxide normally present on the metal surface began to dissolve, and the corrosion rates increased. As the corrosion tests with different pH levels were taking place, electrochemical impedance spectroscopy was used to analyze the thinning oxide layer on the corroding aluminum, providing valuable insights into the variation of corrosion rates with changes in pH. At the lowest pH values, the metal was essentially bare, creating a good model system for comparisons to more detailed atomistic simulations.

One factor the team sought to better understand was the role that grain orientation, regions, and boundaries play during corrosion. Aluminum's grain structure is polycrystalline, meaning that it has a microstructure composed of randomly oriented grains separated by grain boundaries. Grain orientations can be viewed using a technique called electron backscatter diffraction, a method that maps grain orientations across the surface. Each grain orientation has a slightly different arrangement of atoms—some more tightly bound, others less tightly bound, depending on their number of nearest-neighbor atomic bonds—resulting in slightly different corrosion rates. Orme and her team were particularly interested in understanding the differences in corrosion rates between grain orientations, something that has been overlooked in the past. Orme says, "Typically, corrosion studies yield an average corrosion rate instead of looking closely at the differences between grain orientations. We wanted to know whether the corrosion rate tracked with the local bonding environment—the number of nearest neighbor bonds the atoms had due to their grain orientation—or whether something more complicated was going on."



Simulated images depict corrosion (foreground to background) at the nanoscale (atomistic), microscale, and mesoscale.

Neighborhood Effect

What the team found was rather unexpected. Under the aqueous corrosion experiments, the pure aluminum exhibited galvanic corrosion, an electrochemical process in which one metal normally corrodes preferentially when in electrical contact with a different metal due to the presence of an electrolyte. In Livermore's research, however, galvanic corrosion was occurring on a microscale between the grains of aluminum with no other metal playing a role.

The team correlated the grain orientation maps with confocal microscopy, an optical imaging technique that can measure height changes across a surface on the microscale, to know the corrosion rate of each grain of their metal surface. "We had expected to find that the grains with the best bonding environments would have the slowest corrosion rates because they have more nearest-neighbor atoms holding on to them, while the grain orientations with more isolated and loosely bound atoms would corrode more quickly," says Orme. "This is true of other metals, such as nickel-based alloys, but this was not what we found for pure aluminum." Instead, the team observed galvanic corrosion, where the dissolution rate of one metal grain was influenced by the presence of another metal grain in its neighborhood.

However, cooperative effects such as these are difficult to quantify. By converting the orientation and height maps into a spatial network and subjecting them to graph neural network ML algorithms, data scientist Tim Hsu was able to analyze interactions among hundreds of grains as the pH balance of the solution changed, enabling him to demonstrate how the grains interacted. Using the ML model, the team could compare corrosion rate predictions of any one grain when they either included or excluded information about the size and orientation of the neighboring grains. The team found they could significantly improve the ability to predict corrosion rates by including information about the surrounding grains, what they have called

the "neighborhood effect" to mean that any given grain's neighbors had a strong impact on the corrosion rate. In addition to the surprise of galvanic corrosion with only aluminum, the team determined that their hypothesis about the relationship between bond strength and corrosion rates had been incorrect. Rather, galvanic corrosion reversed the relative corrosion rates making the grains with the highest local bonding the most likely to corrode.

The experimental research team partnered with Lawrence Livermore's HPC researchers to develop more predictive, physics-based models, but integrating the two fields was challenging. Anh Pham, researcher and quantum simulations expert, says, "Experiments are always more complex because the real systems are so complicated. Many factors, such as the different types of ions, solutions, and surface oxides, aren't typically included in computer simulations. Even though simulations offer tremendous insight into the corrosion process and what can be done to mitigate it, we also had to simultaneously make our computer models much more complex while simplifying and better controlling our experiments to find a middle ground that provides accurate information in a more cost-effective way than running many quantum simulations." The team developed new HPC capabilities and multiscale models to show how the grain orientation changed the corrosion rates and to directly predict rates of dissolution and oxide formation from quantum mechanics, going beyond simple textbook thermodynamics. These capabilities were used not only to recreate the surface height maps of locally varying corrosion, but also to reveal the key competing mechanisms and origins of the observed grain dependencies on corrosion rates. ML algorithms analyzed hundreds of grains at a time as the pH balance of the solution changed. By integrating atomistic modeling with data science and experiments, the team developed models that showed the rates of aluminum corrosion in solutions of varying pH. These simulations will be used in future research aiming at more accurately predicting the corrosion process.

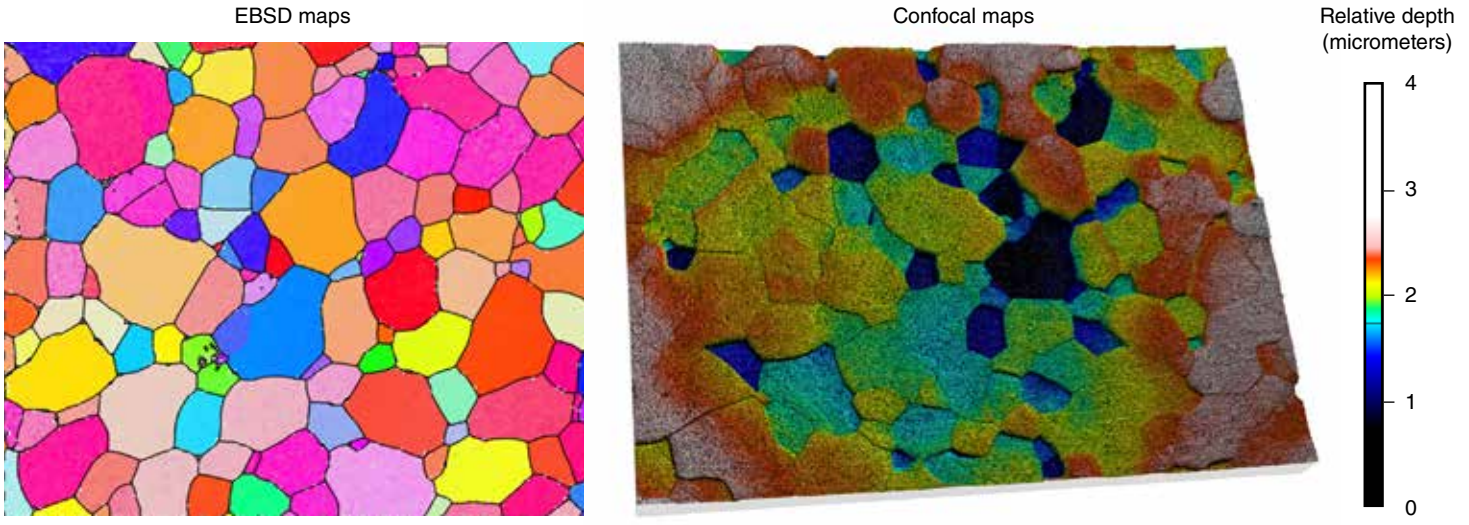
Hydrogen-induced Failure

Used for commercial and industrial applications such as spacecraft, automobiles, sporting goods, and mobile phones, as well as for military hardware, titanium is a material synonymous with strength and resilience. Yet titanium can fall prey to corrosion over time.

Livermore researchers placed their primary focus on the roles of surface oxide features and metal microstructure in initiating hydrogen-induced degradation of titanium as hydrogen permeates through the surface oxide layer and the formation of the undesired phase (i.e., hydride) is affected by the metal microstructure. While the oxide acts as a natural barrier to outside elements that can impact the chemistry of the metal, Wood says, "We needed to understand how the metal itself impacts what is in the native oxide film, and then how that native oxide film is impacted by the environment." Hydrogen-induced corrosion, or hydriding, can lead to embrittlement, fractures, cracking, and ultimately failure of titanium materials, which presents a serious problem for many of its uses, including national security and transportation purposes.

Because commonly used titanium alloys in industrial applications are too complicated to work with due to very complex surface oxide chemistry, Livermore researchers under the titanium

Through the use of electron backscatter diffraction (EBSD) and confocal maps, researchers track the surface height differences due to corrosion across aluminum samples. Each color in the maps represents a different surface height level. Areas of color or grain regions consist of multiple individual grains bonded together.



hydriding thrust worked with pure titanium that can serve as a representative model system. The team wanted to understand not just the initial hydrogen-surface interaction but also how hydrogen is specifically incorporated into the underlying metal at early stages. Tae Wook Heo, staff scientist, says, "What seemed like a simple question to answer was quite a big mystery, largely because the oxide on titanium has a very complicated and diverse structure at the atomistic level." That structure plays a role in how quickly or slowly the hydrogen can permeate the oxide and reach the titanium below, leading to material failure. Heo says, "We wanted to control the process of hydride formation, so it was vital to understand whether its onset depends on local microstructures and mechanical conditions and whether we could quantify the relationship between local features of the oxide and the onset of hydriding."

Like the aqueous corrosion thrust, an integration of experiments and computer simulations was necessary to capture the complex initial process of corrosion. However, the experiments were far more complicated and realistic than the early simulations. Heo says, "We needed to combine the two methods to fully understand hydrogen-induced corrosion at these initial stages, but we had to find an appropriate place where the two approaches can meet by simplifying experiments and incorporating beyond-ideal factors into simulations."

The researchers integrated a number of techniques and tools to evaluate and simulate the microstructure of the pure titanium, its surface titanium oxide layer, and the hydrogen distribution within both. First, Heo's team had to develop new multiscale models capable of resolving necessary features at both the microstructural and atomistic levels. ML and graph theory accelerated model generation, particularly for the disordered regions too complex to navigate using traditional approaches. The computational scientists incorporated advanced simulation techniques spanning molecular dynamics and kinetic Monte Carlo simulations, which simulate atomic arrangements directly with high accuracy, as well as continuum techniques that include phase-field modeling, in which atoms are approximated as continuously varying fields that evolve across much larger scales. Heo's team developed novel approaches to hand off parameters among these models, which then predicted how hydrogen should incorporate, distribute, and permeate upon contact with titanium and its oxidized surface.

To validate the model predictions, staff scientist Roger Qiu's team, including postdoctural fellow Yakun Zhu, used an ion beam sputtering deposition method and specialized thermal treatments to produce systematically varying titanium oxide films with physical properties resembling those of native oxides. The oxide layers and metal samples were imaged using multiple techniques, including transmission electron microscopy (TEM). In TEM, a beam of electrons is transmitted through a very thin (less than 100 nanometers thick) titanium sample to form an image, which is then magnified and focused onto an imaging device. TEM and companion techniques such as atom probe tomography, directly revealing atomic arrangements, provided exceptionally high-resolution images so the Livermore team could see the effects of corrosion on titanium and its oxide in much more detail than was typical in earlier research.

To study the local binding features of the titanium oxide and compare with the atomistic models, the Livermore team applied nuclear magnetic resonance spectroscopy, which observes local magnetic fields around atomic nuclei by exciting the atomic nuclei with radio waves. The resonance frequency changes based on the intramolecular magnetic field around the atomic nuclei, which tells researchers about the electronic structure of the molecule. The data generated from these techniques further refined the accuracy of the computer models and indicated how hydrogen interacts with the oxide layer at the atomistic, compositional, and microstructural scales.

Next, the Livermore team used a nuclear reaction analysis (NRA) tool, in collaboration with SUNY Polytechnic Institute, to study the hydrogen distribution and solubility. "Hydrogen is one of the difficult elements to probe experimentally due to its simple electronic structure," says Qiu. "A non-destructive nuclear reaction-based method such as NRA can provide accurate information of hydrogen depth distributions in materials without the need of a standard," says Qiu. These measurements were used to determine the dependence of hydrogen interactions with local structural features and defects. The results provided input for theoretical calculations and simulations to build a multiscale model of the way hydrogen inserts and permeates through the surface oxide, eventually forming a hydride in the metal underneath.

A major finding from the research was how the binding structure of oxygen determined the hydrogen interaction with the titanium oxide. Contrary to what the team expected, hydrogen did not distribute uniformly, but rather was very sensitive to the local chemistry and binding structure of the oxide. The surface oxides usually have a mixture of atomically ordered regions that are crystalline in addition to more disordered regions that comprise grain boundaries or amorphous layers. This complex, nonuniform structure contributed to a random initial onset of hydriding.

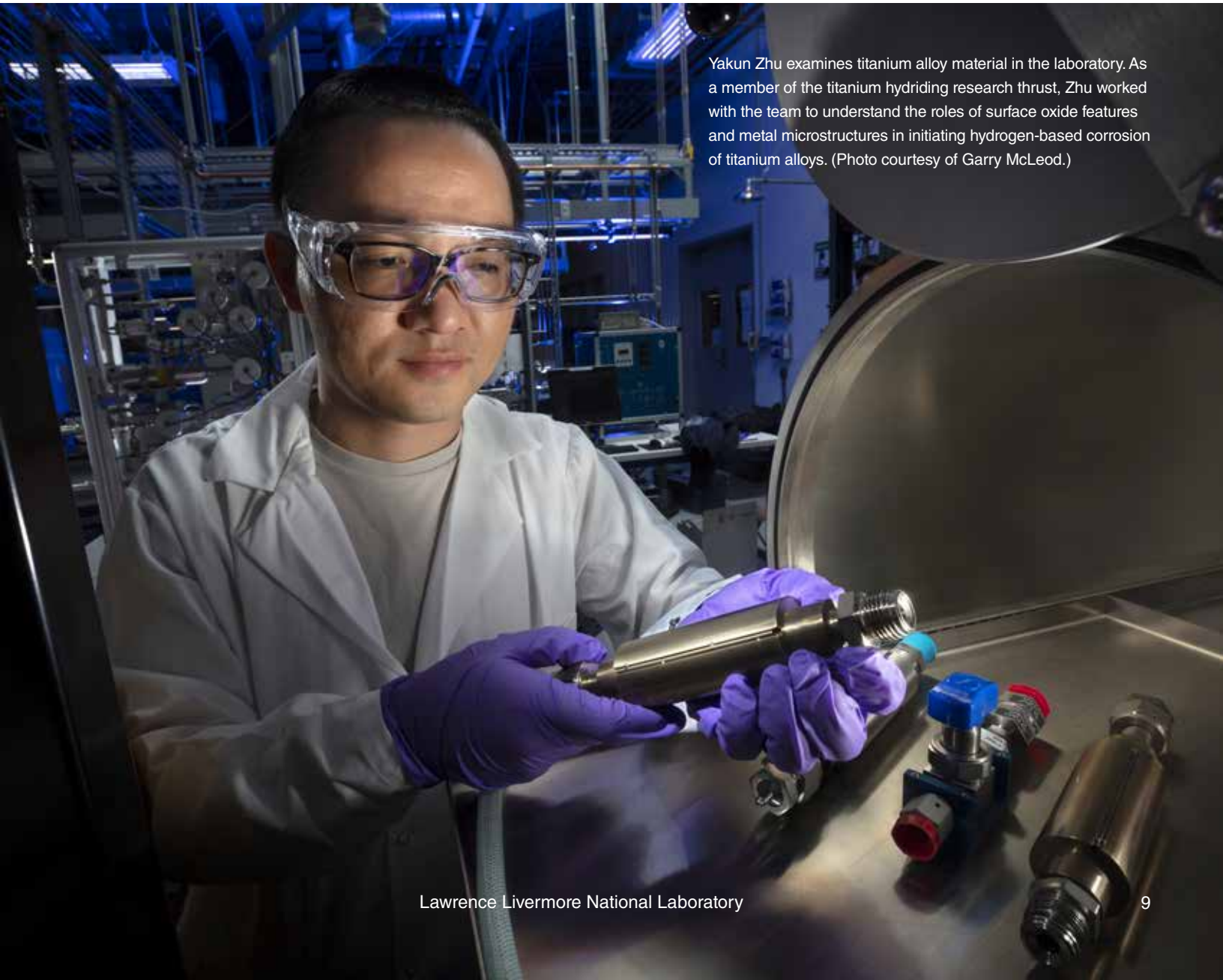
Sometimes hydriding happened very swiftly, while other times it took much longer. After the hydrogen permeated the oxide, the fracture and cracking of the metal itself could also be random, depending on the surface condition and internal microstructure of the metal. Despite this complexity, the team discovered certain patterns related to the local atomic arrangements. For example, the behavior of hydrogen within the surface titanium oxide is highly sensitive to local oxygen coordination geometries within the atomically disordered regions.

Certain arrangements of these local environments create "superhighways" for hydrogen to rapidly penetrate through the oxide into the metal, eventually leading to embrittlement and failure. The formation of the superhighways depends both on the ratio of titanium to oxygen atoms near the surface and to the microstructure of the surface oxide. This understanding implies that both the level of hydrogen incorporation and its rate of permeation through the surface oxide can be controlled by compositional and process modification, providing possible engineering guidance for improving durability of titanium and its alloys in hydrogen environments.

Strengthened Steel

Stainless steel, one of the most commonly used and most widely studied metals in the world, can be found in nearly every facet of people's lives. While very strong, stainless steel can still corrode. However, advances in additive manufacturing offer new ways to prevent corrosion and slow its onslaught.

In the stainless steel corrosion thrust, Livermore researchers studied corrosion of stainless steel 316L (316L SS) that was additively manufactured using a technique called laser powder bed fusion (L-PBF). L-PBF applies a high-power laser to a bed of powdered metal, and the extreme heat from the laser melts the powdered metal into a thin layer of material. Layer after layer of material is melted on top of previous layers until the item being manufactured is completed. Not only does this method open up the possibilities for additive manufacturing of complex shapes, it also can change the way that atoms within the material are organized. Thomas Voisin, staff scientist, says, "Because the laser beam is only about 100 microns in



Yakun Zhu examines titanium alloy material in the laboratory. As a member of the titanium hydriding research thrust, Zhu worked with the team to understand the roles of surface oxide features and metal microstructures in initiating hydrogen-based corrosion of titanium alloys. (Photo courtesy of Garry McLeod.)

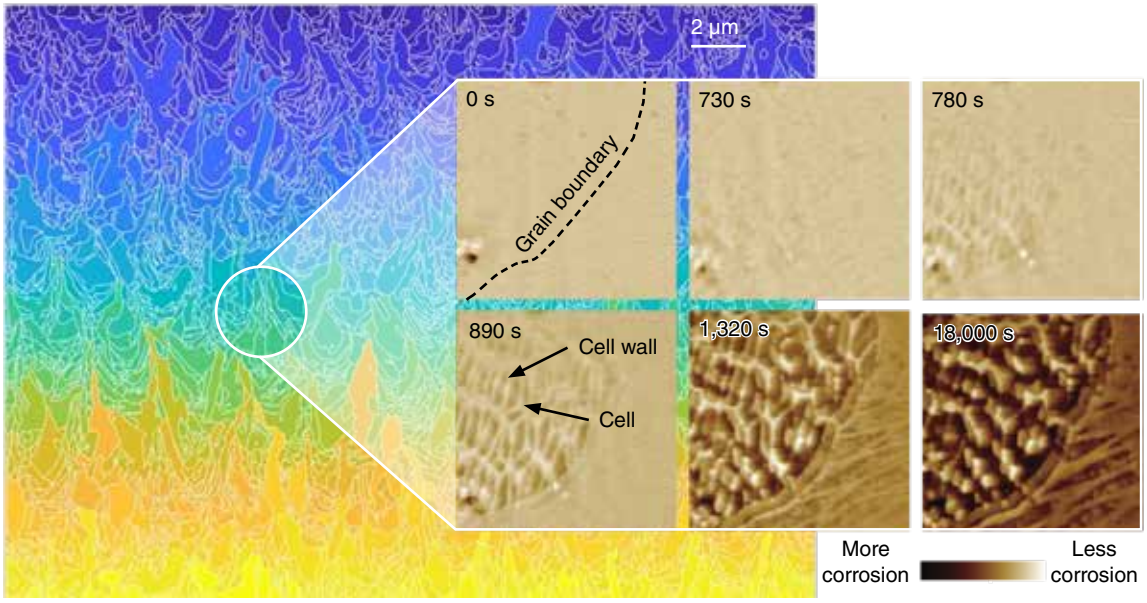
diameter, all melting is very local and very concentrated. Once the material has melted, it then cools much more rapidly than conventionally manufactured material. As a result, different atomic structures that form in the steel are maintained as they adapt to rapid solidification. These structures have significantly different properties than normal stainless steel." Among those properties is material strength two to three times greater than conventionally manufactured stainless steel with similarly improved resistance to corrosion.

In their work to understand corrosion of additively manufactured stainless steel, the team focused specifically on how the new surface oxide that forms under these extreme processing conditions can shield the material so well against degradation in saline water. They recreated a solution with the salinity of sea water in the laboratory, submerged the steel in the solution, and applied an electric current. Not only did the team recreate corrosion, they accelerated it, achieving years' worth of corrosion in just a few hours. Corrosion of steel in seawater takes the form of pitting, the formation of microscale craters in the material. This form of corrosion is difficult to predict and control. Although additively manufactured steel was certainly more resistant to pitting, the phenomenon still happened eventually.

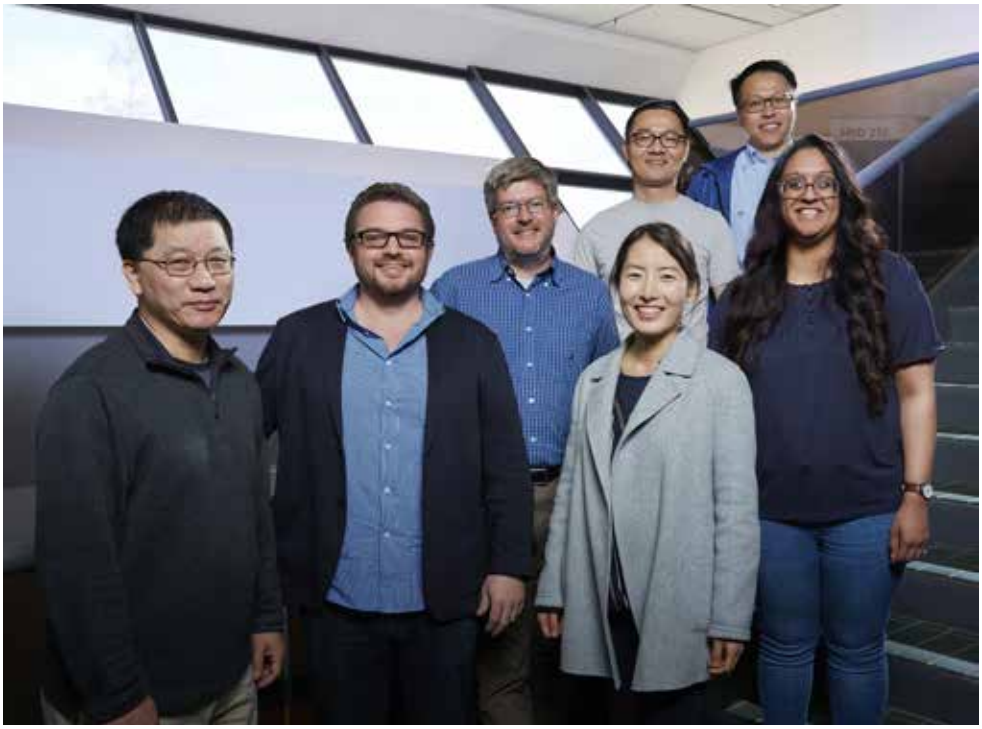
To study the corrosion effects in detail, a specialized high-speed atomic force microscopy (HS-AFM) was applied to scan the stainless steel's surface and form an image of the topographical in nanometer resolution. This technology was instrumental in helping the researchers visualize and track the evolution of corrosion's nucleation from its initialization. "The HS-AFM not only has the spatial resolution comparable to that of the conventional AFM, it also provides the temporal resolution needed for kinetics analysis. The unique combination allows us to identify the corrosion pitting site as well as the corrosion rate," says Qiu. Through the in-situ measurements, the correlation between corrosion and AM steel microstructure such as grain orientation, grain boundaries, cell wall, and cell interior can be revealed. For the ex-situ characterization, Voisin and his team conducted several TEM studies that investigated the additively manufactured steel surface structures down to the atomic scale. The chemical origin of the pitting in additively manufactured stainless steel was also identified through post-mortem characterization by TEM.

As with the other thrusts, experiments were only one part of the research, and computer simulations played a large role in helping to expand the picture of corrosion. Voisin says, "Not everything can be experimentally tested. Each experiment has its own limitations, leaving gaps where computer simulations became vital to better understanding corrosion. We used simulations to uncover the mechanisms behind some of our observations. An experiment and simulation integration approach was the only way to capture the full story about corrosion of additively manufactured stainless steel in seawater." Voisin and his team used computer models to simulate changes in atomic structure inside the stainless steel resulting from corrosion, in particular the manner in which the unique structures formed during additive manufacturing affect material behavior.

This integration of simulation and experiment has enabled the team to explain the nucleation of pits on the complex as-fabricated surfaces across several length scales, from macroscopic to atomic. Voisin says, "We were able to link processing to microstructures to corrosion mechanisms



Frames from in-situ dissolution measurement on an additively manufactured 316L stainless steel disc using high-speed atomic force microscopy. The scale bar is 2 micrometers (µm). Scan rate is 10 seconds (s) per frame. The dashed line indicates grain boundary. The cell wall and cell interior are highlighted with arrows. The colorful background represents the broader surface of stainless steel and different grain regions.



The stainless steel–additive manufacturing corrosion research team (from left to right): Roger Qiu, Thomas Voisin, Shin Young Kang, Brandon Wood, Shohini Sen-Britain, Yakun Zhu, and Yuliang Zhang.

to explain the additively manufactured stainless steel properties. In the future, we're aiming to develop a simulation that will tell us where corrosion will start, how fast it will degrade the surface of steel, and when we might expect a failure."

Opportunities for the Future

HPC has long been a pillar of Lawrence Livermore's research, leaving no surprise that developing multiscale model capabilities and integrating them with state-of-the-art experimental techniques has been a game changer for understanding the evolution and kinetics of corrosion. Wood says, "The message of integration was one we championed throughout this project. One was a scale integration—we did extensive work on the experimental and computational sides to understand what happens starting at the atomistic or nanoscale and moving up to the microstructure scale. Our hypothesis was that the experimental and computational sides were implicitly connected because corrosion is a chemical process that manifests in a macroscopic way." The birth of the HPC component of the research came from previous Livermore projects focused on the energy sector that looked at the effects of temperature on highly localized conditions, so many of the foundational elements behind the computer models for corrosion were already in place. By combining the experiments and computational models, the team has created the potential to unlock new opportunities for Livermore researchers and other stakeholders in materials science. "Now we can build a more reliable model to understand corrosion science," Pham says. "We're moving into an era where high-performance computing, machine learning, and computer simulations will play a very important role in explaining corrosion and its impacts, not only for the Stockpile Stewardship Program at Livermore, but also for wider industrial and commercial purposes."

The research team has already attracted the attention of other researchers and corporations. Livermore partnered with many academic institutions to conduct different components of the work, including Texas A&M University (aqueous corrosion thrust); SUNY Polytechnic Institute (metal hydride); George Tech University (TEM microscopy on additively manufactured thrust); Monash University in Australia (characterization of additively manufactured metals); Arizona State University (data science); University of Nebraska, Lincoln (electrochemical theory); and Ohio State University (simulation theory). Early in the project, Livermore began collaborating with Raytheon to understand the impacts of high temperature corrosion and oxidation, and the team has more recently been discussing opportunities with Boeing around modeling corrosion.

Livermore is also exploring research spin-off opportunities under federal government funding. The U.S. Department of Energy (DOE) has many areas of interest that overlap with the work that Wood and his team have done on corrosion, including hydrogen and fuel cells technology, as well as the DOE Advanced Materials and Manufacturing Technologies Office. As corrosion touches on so many levels of individual, household, commercial, industrial, and national security interests, Livermore's foundational corrosion research will undoubtedly expand to develop prediction and prevention solutions.

–Sheridan Hyland

Key Words: Additive manufacturing, aqueous corrosion, confocal microscopy, dissolution kinetics, galvanic corrosion, grain boundary, high-performance computing (HPC), high-speed atomic force microscopy (HS-AFM), hydriding, Laboratory Directed Research and Development Program, Laser Powder Bed Fusion (L-PBF), machine learning (ML), nuclear magnetic resonance (NMR), nucleation, pitting, stoichiometry, transmission electron microscopy (TEM).

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