OAK RIDGE NATIONAL LABORATORY

Review

Achieving a circular economy:

New section

OAK RIDGE National Laboratory

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On the Cover

ORNL environmental scientist Natalie Griffiths studies the environmental impact of bioenergy crops. Image credit: Carlos Jones, ORNL

Pursuing a circular economy

One of the critical challenges of the 21st century is to make full use of our planet's resources.

The United States throws away tens of millions of tons of plastic, aluminum, rubber and other valuable materials each year. We discard water after a single use, even as much of the country suffers through a long-term drought. Even the green technologies we've developed over the years face their own supply and recycling challenges.

The successful recycling and reuse of limited resources constitutes a "circular economy." Reaching this ideal requires advances on a variety of fronts.

For instance, materials such as plastics are mostly designed neither to decompose nor to be recycled. Solving that problem requires designing new materials that are more earth-friendly and reusable, but while we do that, we must also find ways to make the most of existing plastic waste — even though it was not designed to be reused.

ORNL researchers are applying expertise in supercomputing, neutron science and materials science to create a (nonnuclear) continuous flow reactor that will — among other benefits — speed and automate the research needed both to create the next generation of plastics and to recycle the plastics that surround us (see "Keeping materials out of landfills," page 8).

Our researchers are also involved in the effort to ameliorate the water crisis brought on by climate change and economic growth (see "Ensuring our water future," page 14), developing alternative sources of water — including seawater and the produced water associated with oil and gas drilling — and improving treatment systems.

ORNL researchers also are working to forestall shortages of lithium for high-tech batteries by developing new sources of lithium, in particular by mining it from the brines produced by geothermal plants.

Elsewhere in this issue of *ORNL Review*, we take a look at efforts by ORNL researchers to accelerate the development of effective COVID-19 treatments by interrupting specific stages of the virus' life cycle (see "DOE scientists deploy creativity, speed to disrupt COVID-19," page 38).

We also talk with talented researchers in all stages of their careers, including Nobel laureate Samuel Ting, who delivered our most recent Eugene P. Wigner Distinguished Lecture (see "Eugene Wigner Distinguished Lecturer," page 50), and five promising ORNL researchers recognized by the Early Career Research Program sponsored by the Department of Energy's Office of Science (see "A tremendous achievement in a tumultuous year," page 44).

Finally, we are introducing a new section to *ORNL Review*. Research Insights features technical articles highlighting key areas of ORNL research. We focus in this inaugural edition on materials in extreme environments — a field in which Oak Ridge has historic leadership — with applications in advanced manufacturing, nuclear energy, information technology, batteries, transportation and national security.

I hope you will find many topics of interest in this latest review of research around ORNL.

Thomas Zacharia
Laboratory Director

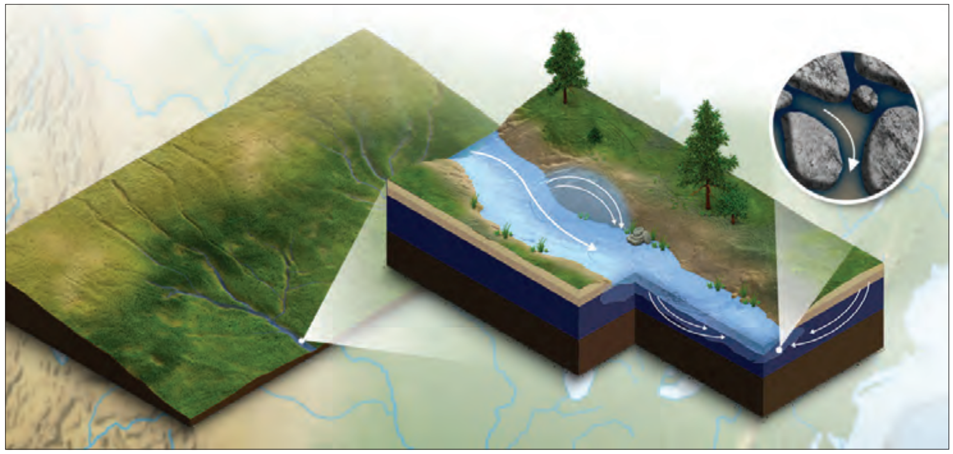
Advance in modeling improves water analysis

A new modeling capability developed at ORNL incorporates important biogeochemical processes taking place in river corridors for a clearer understanding of how water quality will be impacted by climate change, land use and population growth.

Researchers used high-performance computing and the award-winning Amanzi-ATS software to include biogeochemical reactions in microbially active zones near streams in models that track the movement of dissolved chemicals in river networks. These reactions have a major influence on the cycling of carbon, nutrients and contaminants at basin scales. The new multiscale model better tracks water quality indicators such as nitrogen and mercury levels.

"To build a next-generation modeling capability to address water quality issues, we needed a new multiscale framework that allows us to incorporate fundamental understanding of key processes and how those fine-scale processes manifest at much larger scales," ORNL's Scott Painter said.

The research team validated and demonstrated the model on several watersheds. — *Kim Askey*



An ORNL research team has incorporated important effects from microbially active hot spots near streams into models that track the movement of nutrients and contaminants in river networks. Image credit: Andy Sproles, ORNL

ORNL teams take seven R&D 100 awards

ORNL research teams and their technologies have received seven 2021 R&D 100 Awards, plus special recognition for a COVID-19–related project.

Established in 1963, the R&D 100 Awards each year recognize 100 accomplishments in research leading to significant new commercial products, technologies and materials from around the world. This year's wins bring ORNL's total R&D 100 Awards to 232 since the award's inception.

ORNL researchers and technologies named among this year's winners are listed below.

Autonomous self-healing sealant, developed by ORNL.

ORNL researchers have tackled the problem of brittle, leaky sealants by developing an adhesive material that self-heals autonomously.

ORNL's team developed the self-healing sealant by integrating a self-healing polymer, poly(BCOE), with existing commercial sealants. The novel material can autonomously self-heal cracks that arise within days at room temperature. It also adheres better to dusty surfaces than current products, eliminating the need to clean an area or apply a primer to the substrate prior to using.

Precision deicer, developed by Clinch River Computing LLC and ORNL.

Researchers developed a method to more precisely gauge the amount of deicing materials, such as salt or brine, needed to deice a particular road.

The precision deicer uses light-detection and ranging data to consider traffic, road conditions, slope and solar radiation to calculate a road vulnerability index indicating how much deicing material should be applied in a particular area.

QED: Quantum Ensured Defense of the Smart Electric Grid, developed by Los Alamos National Laboratory, ORNL and EPB of Chattanooga.

Scientists at LANL and ORNL have sought to escape the ongoing attack–defend cycle of cybersecurity breaches by developing a new method for protecting information called Quantum Ensured Defense, or QED.

The technology harnesses single particles of light, or photons, to distribute cryptographic keys that can be used to lock control signals into secret codes. This novel method brings the security assurances of quantum communication systems to long-haul distances inherent in electric grid systems.

UCC: Ultraconductive Copper–Carbon Nanotube Composite, developed by ORNL.

Copper is a key element in many electrical devices, but its resistance leads to power losses, meaning that new low-resistance conductors are needed to meet current clean energy goals.

ORNL researchers have developed an ultraconductive copper–carbon nanotube composite, or UCC, as an alternative that improves on the mechanical and electrical properties of pure copper. The product, made of carbon nanotubes integrated within a copper matrix, has high mechanical strength and excellent electrical properties.

GridDamper, developed by ORNL, the University of Tennessee, Knoxville, and the Electric Power Research Institute.

The increasing integration of renewable energy has created more severe, complex and frequent electrical oscillations in the grid. If not sufficiently controlled, they can lead to major blackouts.

GridDamper is a deployment-ready technology that allows for more renewable electricity in power grids. The technology automatically updates its parameters, sensors and actuators to guarantee power grid stability and reliability when renewable energy and electricity demand fluctuate.

MSC MillMax, developed by ORNL, MSC Industrial Supply Co. and Manufacturing Laboratories.

MSC MillMax uses measurements to eliminate wavy marks on metal that occur in milling when a tool's spindle is not stiff enough.

Metalworkers cut metal with a rotating tool, typically manually adjusting the machinery in an unscientific process that can take hours. The new computerized system measures tool characteristics, the tool holder and the machine tool, then produces a report on ideal depth and spindle speed in 15 minutes.

BIG-NET: Bis-iminoguanidine Negative Emission Technology, developed by ORNL, ReactWell and Holocene Climate Corporation.

Researchers developed a method for separating carbon dioxide from the air that has the potential to permanently remove billions of tons of the greenhouse gas out of the atmosphere. In the process, scientists use an aqueous solution containing ORNL-discovered receptors called Bis-iminoguanidine, or BIGs, to absorb carbon dioxide.

Upon absorption of carbon dioxide, BIGs turn into an insoluble crystalline salt, which can easily be removed from the liquid solution. The carbon dioxide can then be extracted from the salt under mild conditions and sent for deep underground storage, either in aquifers or former oil fields.

Domestic supply chain of filter media and face masks, a project led by ORNL, Techmer PM and DemeTECH, received the Silver Award in the Special Recognition: Battling COVID-19 category.

Researchers adapted melt-blowing capabilities at DOE's Carbon Fiber Technology Facility to enable the production of filter material for N95 masks in the fight against COVID-19. The team used polypropylene supplemented with an additive from polymer material manufacturer Techmer PM.

The resulting process had the capability to produce filter media for 9,000 masks per hour at greater than 95 percent filtration efficiency. — *Alexandra DeMarco*

For more information: https://go.usa.gov/xeZjc

ORNL scientists co-developed the 2021 R&D 100 Award-winning Quantum Ensured Defense method to bring security to the electric grid. Image credit: ORNL

UT-Battelle honored for veteran recruitment

ORNL's managing contractor, UT-Battelle LLC, has received a gold medallion award from the Department of Labor's Honoring Investments in Recruiting and Employing American Military Veterans, or HIRE Vets, program.

"Military veterans are an important part of the ORNL workforce, and we appreciate the knowledge and experience they bring to the lab each day," said ORNL Director Thomas Zacharia. "It's a significant honor for the HIRE Vets programs to recognize the commitment we have made to veterans."

The award recognizes exemplary efforts in recruiting, employing and retaining military veterans.

"By meeting the criteria required for a gold medallion award, UT-Battelle has demonstrated both patriotism and recognition of the value veterans bring to the workplace," said Randall Smith, HIRE Vets Medallion program director.

Large employers recognized with gold medallions must have at least 7 percent of new hires who are veterans, maintain a 75 percent retention rate for 12 months, and offer a veteran's resource group and leadership program. — *Karen Dunlap*

New computer code focuses on power grid

ORNL, University of Tennessee and University of Central Florida researchers have released a new high-performance computing code designed to more efficiently examine power systems and identify electrical grid disruptions, such as power outages.

The Resilient Adaptive Parallel sImulator for griD, or RAPID, relies on a novel parallel-in-time, or "parareal," algorithm that divides calculations into smaller time intervals, then completes them simultaneously on different processors to streamline traditionally time-consuming simulations.

RAPID also uses adaptive model reduction, which reduces computational demand

An open-source code developed by an ORNL-led team could provide new insights into the everyday operation of the nation's power grid. Image credit: Pixabay

by focusing only on areas near a disruption. The code is compatible with various architectures and could eventually help predict grid dynamics and assess algorithms for the integrated transmission and distribution network as fast as — or faster than — real time.

"The goal is to run these simulations as fast as possible and provide information to grid operators about how to address problems," said ORNL's Srdjan Simunovic. — *Elizabeth Rosenthal*

Researchers 3D-print new high-tech alloy

ORNL researchers have additively manufactured a lightweight aluminum alloy and demonstrated its ability to resist creep, or deformation, at 300 degrees Celsius.

Materials that can perform in high-pressure, high-temperature environments are needed for automotive, aerospace, defense and space applications. The alloy, which combines aluminum with cerium and other metals, was printed using a laser powder bed system that deposits one thin layer of material at a time for precise results. Researchers printed pistons made of the alloy for deployment inside a full-scale engine.

"Using powder-bed 3D printing allowed the alloy to rapidly solidify into fine, stable strengthening particles in the microstructure, resulting in the remarkable high-temp creep resistance we measured," ORNL's Ryan Dehoff said. "We expected notable improvements but were surprised by how strong and stable these alloys proved to be."

The pistons will undergo additional testing inside of a four-cylinder, turbocharged engine. — *Jennifer Burke*

Nanostructures promote stretchier alloys

ORNL researchers have developed a method for adding nanostructures to high-entropy metal alloys, or HEAs, that enhance both strength and ductility, which is the ability to deform or stretch under tensile stress without failing.

The results, published in *Science*, open a promising pathway for tailoring HEA properties using small gradient structures to produce improved high-performance metals for a wide range of applications.

Conventional metallic materials, including HEAs, become less ductile or more brittle as their strength increases. HEAs are composed of five or more elements.

The scientists used neutron diffraction methods at ORNL's Spallation Neutron Source to confirm that tiny defect features, called stacking faults, form easily in an HEA compared to conventional fine-grained alloys.

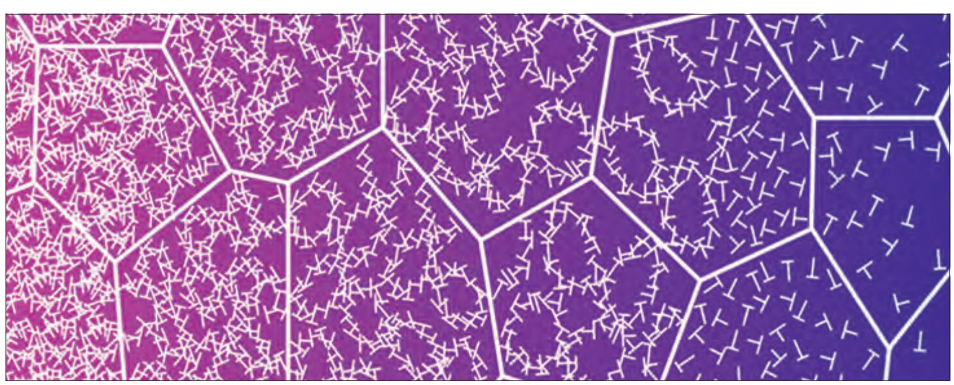
"The stacking faults enhanced the test alloy's plasticity while also contributing to increased strength and hardening," said ORNL's Ke An. "Industries that could greatly benefit include automotive, power distribution and aerospace." — *Paul Boisvert*

Data to aid models for Colorado River Basin

New data hosted through the Atmospheric Radiation Measurement Data Center at ORNL will help improve models that predict climate change effects on the water supply in the Colorado River Basin.

Mountains are natural water towers that collect the snowpack, which becomes drinking water for millions of people. ARM's goal is to collect data needed to advance understanding of complex land–water–atmosphere interactions in these regions and improve model predictions of future climate and water availability.

More than four dozen instruments measure atmospheric factors affecting the water cycle and climate near Crested Butte, Colorado, as part of ARM's SAIL project. This data will be integrated with other measurements taken at and below



ORNL researchers used the lab's Spallation Neutron Source to analyze modified high-entropy metal alloys with enhanced strength and ductility. Image credit: Rui Feng, ORNL

Instruments gather atmospheric data at the Colorado site as part of the Atmospheric Radiation Measurement User Facility's SAIL project. Image credit: DOE ARM User Facility

the surface to provide a clearer picture of key processes.

"The ARM data services team is making terabytes of data accessible to facilitate the multi-institutional effort investigating the hydrologic processes that influence climate and the availability of critical water resources," said ORNL's Giri Prakash. — *Kim Askey*

Gene helps switchgrass become more adaptable

An ORNL team has successfully introduced a poplar gene into switchgrass, an important biofuel source. The gene allows switchgrass to interact with a beneficial fungus, ultimately boosting the grass' growth and viability in changing environments.

Scientists observed the ectomycorrhizal fungus *Laccaria bicolor* as it enveloped the plant's roots. This behavior, not known to occur naturally between these fungi and switchgrass, helps the plant to efficiently take up nutrients and water. This symbiotic relationship results in switchgrass that is more disease- and drought-resistant.

"We've engineered switchgrass to grow where it would typically struggle, that is, marginal land that is unsuitable for food crops," said ORNL's Jay Chen. "The fungus allows the switchgrass to absorb minerals from the soil."

In a previous study, the team identified the receptor gene that looks out for friendly fungi. Next, the team will validate the laboratory findings with a field study. — *Karen Dunlap*

New ORNL tech targets cyberattacks

ORNL researchers have created a technology that more realistically emulates user activities to improve cyber test beds and ultimately prevent cyberattacks.

Data Driven User Emulation, or D2U, uniquely uses machine learning to simulate actual users' actions in a network and then enhances cyber analysts' ability to thwart, expose and mitigate network vulnerabilities.

"Understanding and modeling individual user behaviors is critical for cybersecurity," said ORNL's Sean Oesch. "D2U can create unlimited, realistic test users of a particular network for developers of cyber tools to improve their products."

Where other user models need large numbers of testers or make assumptions about their behavior, D2U requires just a small number of users and emulates actual user behavior.

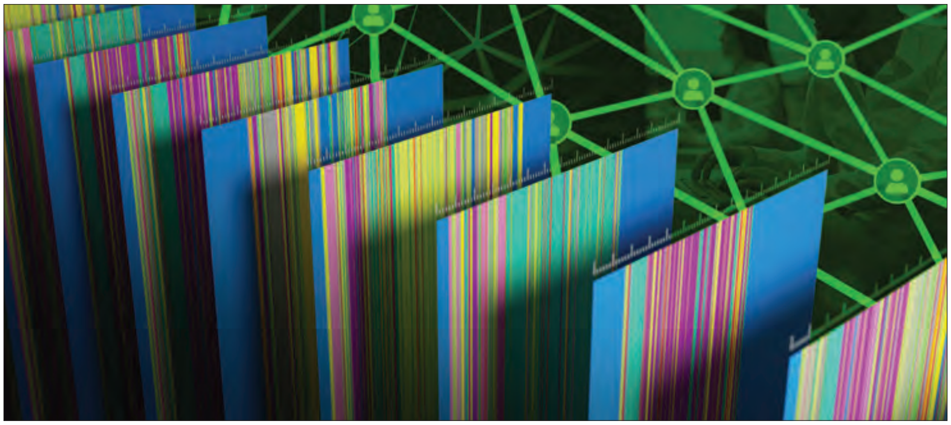
The software is currently deployed to help evaluate defensive cyber technologies but could have benefits to the broader cyber community. — *Liz Neunsinger*

Novel process creates heat-resistant composites

ORNL researchers have developed a novel process to manufacture extreme heat-resistant carbon–carbon composites. The performance of these materials was tested in a Navy rocket that NASA launched in October.

Made of graphite reinforced with carbon fiber, the composites use a pure graphite matrix instead of epoxy to bind the fibers. Researchers manufactured a nose cone and fins embedded with temperature sensors for the launch, which is designed to expose the material to the harsh environment of high-speed flight.

"This launch will allow us to collect data and characterize the temperature performance in extreme environments, which are difficult to reproduce in a laboratory at full scale," ORNL's James Klett said. "The nose cone and fins were produced using a method that significantly cut production time." — *Jennifer Burke*



The D2U model categorizes user data by capturing behavior in all open programs throughout a user's day. Image credit: Nathan Armistead, ORNL

Two ORNL researchers named APS fellows

Two ORNL scientists have been elected fellows of the American Physical Society, or APS.

APS is a nonprofit membership organization working to advance and diffuse the knowledge of physics through its research journals, scientific meetings and education, outreach, advocacy, and international activities. APS members represent academia, national laboratories and industry throughout the world. The APS Fellowship Program recognizes members who have made advances in physics through original research and publication or made significant innovative contributions in the application of physics to science and technology.

The new fellows include two ORNL scientists:

Larry Baylor

Andrew Lupini

Larry Baylor, group leader for the Blanket and Fuel Cycle Group in the Fusion Energy Division, was honored for "experimental investigations involving the physics of fueling magnetic fusion plasmas with hydrogenic pellets and development and demonstration of pellet injection for use in the mitigation of edge-localized modes and disruptions in fusion plasmas."

Baylor's research focuses on the deposition of cryogenic pellet fuel in fusion plasmas utilizing the ORNL pellet injector on the DIII-D tokamak at General Atomics in San Diego, California. Other current projects include development of pellet fueling systems for the ITER fusion reactor in France and the W7-X stellarator in Germany, as well as a pellet-based disruption mitigation system for ITER.

Andrew Lupini, a scientist in the Scanning Transmission Electron Microscopy Group in the Center for Nanophase Materials Sciences, was honored for "groundbreaking contributions to the fields of electron microscopy and aberration-correction in scanning transmission electron microscopy, and for development of new image and spectroscopy capabilities, higher-resolution, and better sensitivity to atomic-resolution imaging and spectroscopy."

Lupini's current research interests include various forms of atomic-resolution aberration-corrected electron microscopy, nanoscale monochromated electron spectroscopy, and the application of these techniques to novel quantum materials. He has worked in several different areas with publications on imaging, analyzing and controlling single atoms. — *Karen Dunlap*

Scientists honored as highly cited researchers

Ten ORNL scientists are among the world's most highly cited researchers, according to a bibliometric analysis conducted by the scientific publication analytics firm Clarivate.

The annual list identifies researchers who demonstrated significant influence in their field through the publication of multiple highly cited papers during the last decade. These researchers authored publications that rank in the top 1 percent by citations for field and publication year in the Web of Science citation index.

"Researchers at ORNL are leading the advancement of scientific knowledge in multiple fields," said ORNL Director Thomas Zacharia. "This recognition demonstrates that the laboratory and our scientists are engaged in cutting-edge research and development to solve some of the world's biggest challenges."

The ORNL scientists listed are:

- **Miaofang Chi**, Center for Nanophase Materials Sciences
- **Sheng Dai**, Chemical Sciences Division
- **Easo George**, UT-ORNL Governor's Chair for Advanced Alloy Theory and Development, Materials Science and Technology Division
- **Colleen Iversen**, Environmental Sciences Division
- **Michael McGuire**, Materials Science and Technology Division
- **Karren More**, Center for Nanophase Materials Sciences
- **Richard Norby**, retired, Environmental Sciences Division
- **Art Ragauskas**, UT-ORNL Governor's Chair for Biorefining, Biosciences Division
- **Anthony Walker**, Environmental Sciences Division
- **Jiaqiang Yan**, Materials Science and Technology Division

David Mandrus of the University of Tennessee, Knoxville, is named on the list with ORNL as his second affiliation. Michael Naguib, also listed as affiliated with ORNL, was an ORNL Wigner Fellow from 2014 to 2017 and is now an assistant professor at Tulane University in New Orleans, Louisiana.

The methodology by which Clarivate determined its list of the world's most highly cited researchers draws on the data and analysis performed by bibliometric experts and data scientists at the Institute for Scientific Information at Clarivate. It also uses the tallies to identify the countries and research institutions where these citation elites are based. — *Karen Dunlap*

New EV controls yield up to 30 percent savings

ORNL researchers have developed and demonstrated algorithm-based controls for a hybrid electric bus that yielded up to 30 percent energy savings in testing compared with existing controls.

The Integrated Eco-Drive technology used a combination of powertrain control techniques, advanced machine learning

Researchers from ORNL's Vehicle and Autonomy Research Group created a control strategy for a hybrid electric bus that demonstrated up to 30 percent energy savings. Image credit: University of California, Riverside

and multiple sensors to determine an optimal driving speed that conserves the most energy. The technology, developed in collaboration with the University of California, Riverside, and US Hybrid Corporation, offers significant energy savings for medium- and heavy-duty vehicles operated on defined bus and delivery truck routes. The system was subsequently licensed by US Hybrid.

"Co-optimizing the combustion engine output, electric motor output and battery state of charge — and taking into account the repeated route — helps us ensure the best performance," said ORNL's Zhiming Gao.

"We can apply this same strategy to light-duty cars and trucks, especially networks of connected vehicles, and realize significant energy savings," said ORNL's Tim LaClair. — *Stephanie Seay*

Three ORNL researchers named Corporate Fellows

ORNL has named three researchers Corporate Fellows for their significant career accomplishments and continued leadership in their scientific fields.

Mitchel Doktycz, Yutai Kato and Burak Ozpineci represent ORNL's strengths in electrical engineering, materials research, and analytical and imaging technologies, respectively. The Corporate Fellow designation recognizes standing in the scientific community as an exceptional and influential researcher and as a role model and mentor among peers and early-career researchers.

"Oak Ridge National Laboratory must be a place known for equipping scientists to reach the pinnacle of their fields and rewarding them when they do," ORNL Director Thomas Zacharia said. "Our Corporate Fellows represent the very best of our research staff. Congratulations to Mitch, Yutai and Burak. We will continue to benefit greatly from their scientific contributions and leadership."

Mitchel Doktycz

Mitchel Doktycz is the Bioimaging and Analytics section head in ORNL's Biosciences Division. He also has appointments at the University of Tennessee, Knoxville, in the UT–ORNL Bredesen Center for Interdisciplinary Research and Graduate Education and the UT Genome Science and Technology Program.

His research interests focus on the intersection of natural and synthetic systems. Doktycz's laboratory is involved in the development of analytical technologies for postgenomics studies with specific emphases on molecular and cellular imaging techniques and the use of nanomaterials to study and mimic biological systems.

Yutai Kato

Yutai Kato, professionally known as Katoh, leads the Materials in Extremes section in ORNL's Materials Science and Technology Division and manages the laboratory's fusion materials program.

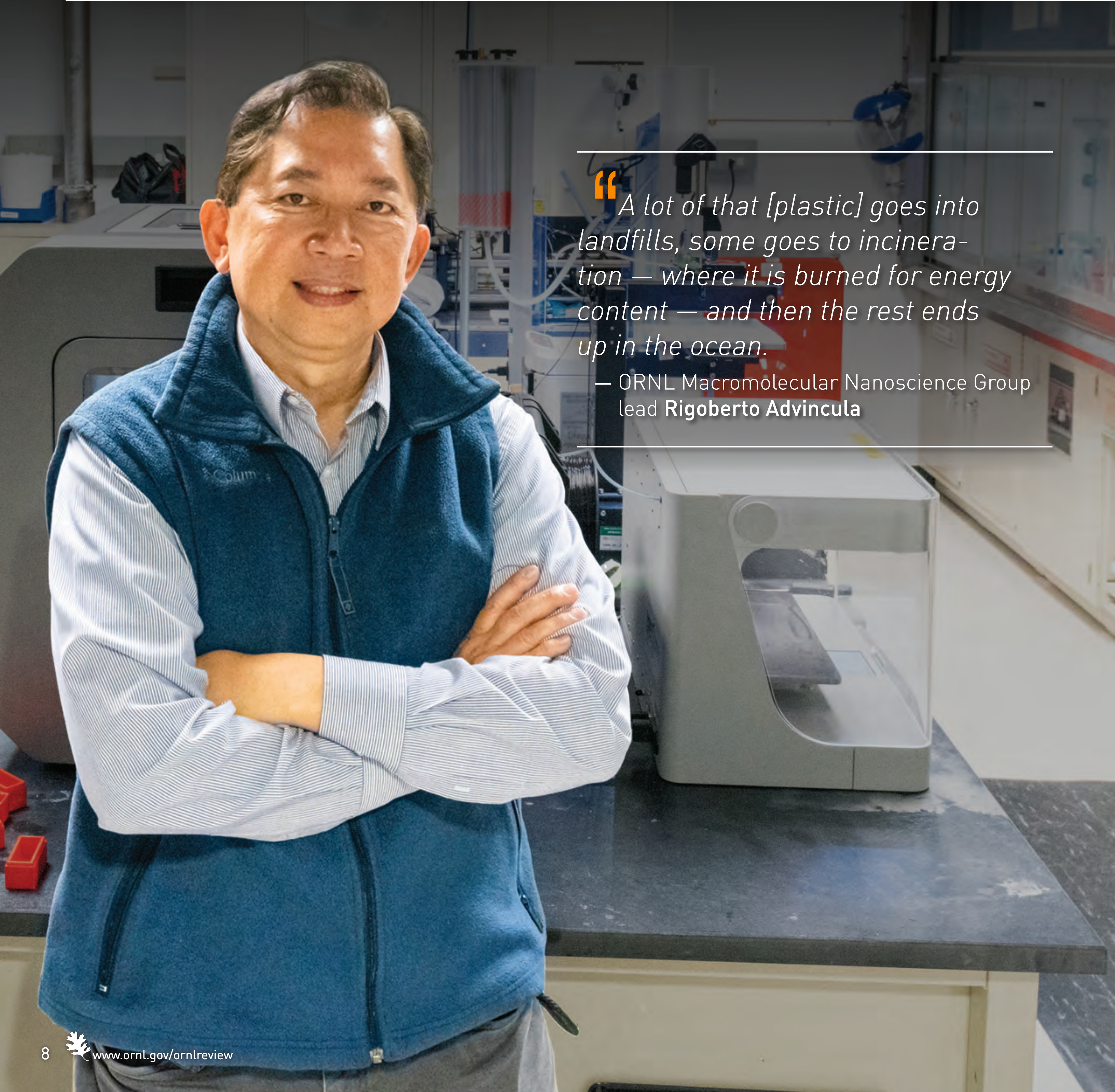
Kato's research interests involve the development and characterization of ceramics and composites, graphite and other advanced materials for severe-environment applications including nuclear fusion and fission energy. He also studies the effects of neutron and high-energy particle irradiation in metals, alloys and ceramics, with emphases on irradiation effects on properties and microstructures of silicon carbide and influences of helium on irradiation effects in materials.

Burak Ozpineci

Burak Ozpineci is head of the Vehicle and Mobility Systems Research section in ORNL's Buildings and Transportation Science Division. He also serves as a joint faculty with the UT–ORNL Bredesen Center.

Ozpineci focuses on transportation electrification and wireless charging of electric vehicles. His team achieved the world's first 20-kilowatt wireless charging system for passenger cars and also demonstrated a 120-kW benchtop wireless charging system both through a 6-inch gap and above 95 percent efficiency. — *Bill Cabage*

Keeping materials



> “A lot of that [plastic] goes into landfills, some goes to incineration — where it is burned for energy content — and then the rest ends up in the ocean.
>
> — ORNL Macromolecular Nanoscience Group lead **Rigoberto Advincula**

out of landfills

by Leo Williams
williamsjl2@ornl.gov

The U.S. economy went through nearly 36 million tons of plastic in 2018, the last year for which we have data. Of that amount, 9 percent was recycled, 16 percent was burned for energy, and the remainder — 30 million tons, or fully three-quarters of the total — ended up in landfills or in the ocean, where it is destined to stay in its current form essentially forever.

Plastics may be our most troubling example of a linear economy, one in which natural resources — in this case, petroleum, for the most part — are used once and then discarded.

But they are not the only example. The Environmental Protection Agency reports that in that same year, two-thirds of cans and other aluminum, 61 percent of bottles and other glass, and 54 percent of discarded tires, shoes and other rubber and leather items also found their way into landfills.

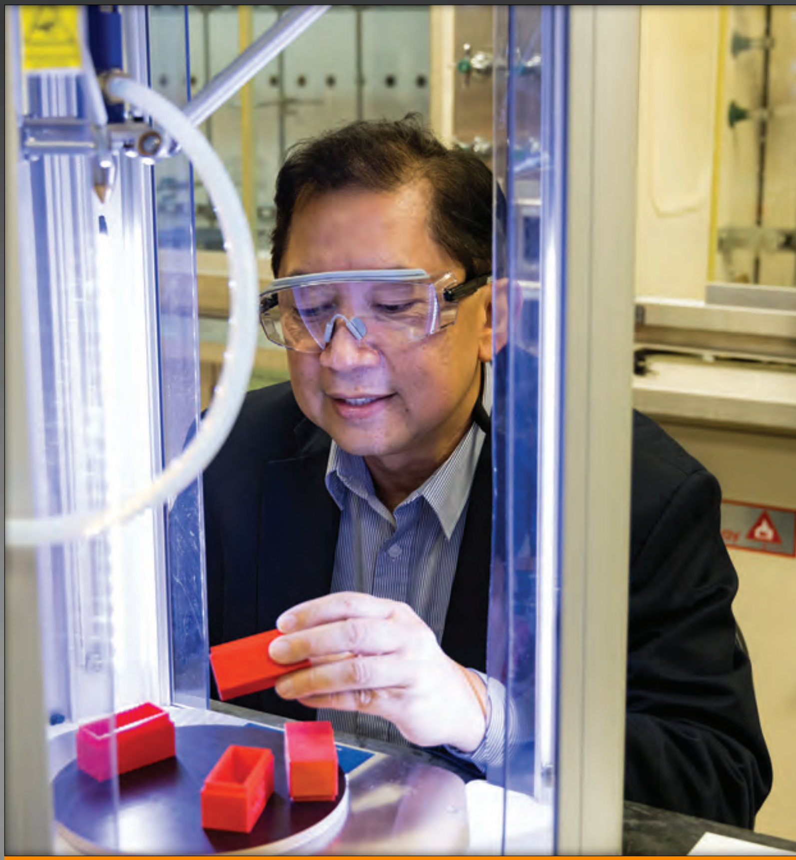
This level of waste is unsustainable, both in terms of the resources being lost and the pollution being created. In order to achieve a sustainable economy, we must be able to take our leftover products and appliances — even our water — and put them to good use again. This is known as a circular economy.

ORNL researchers are deeply involved in applying the principles of a circular economy, focusing, for instance, on plastics and polymers, water (see "Ensuring our water future," page 14) and critical materials (see "Lithium recovery: A critical challenge for battery tech," page 18).

Plastics are forever

One challenge we face in creating a circular economy for plastics is that new plastics are cheaper than their recycled counterparts. Another is that traditional plastics are not designed to decompose.

"Here's the problem: Most of the plastic that has been produced is still around," said Rigoberto Advincula, who leads the Macromolecular Nanoscience Group at ORNL's Center for Nanophase Materials Sciences and serves as Governor's Chair of Advanced and Nanostructured Materials at ORNL and the University of Tennessee.



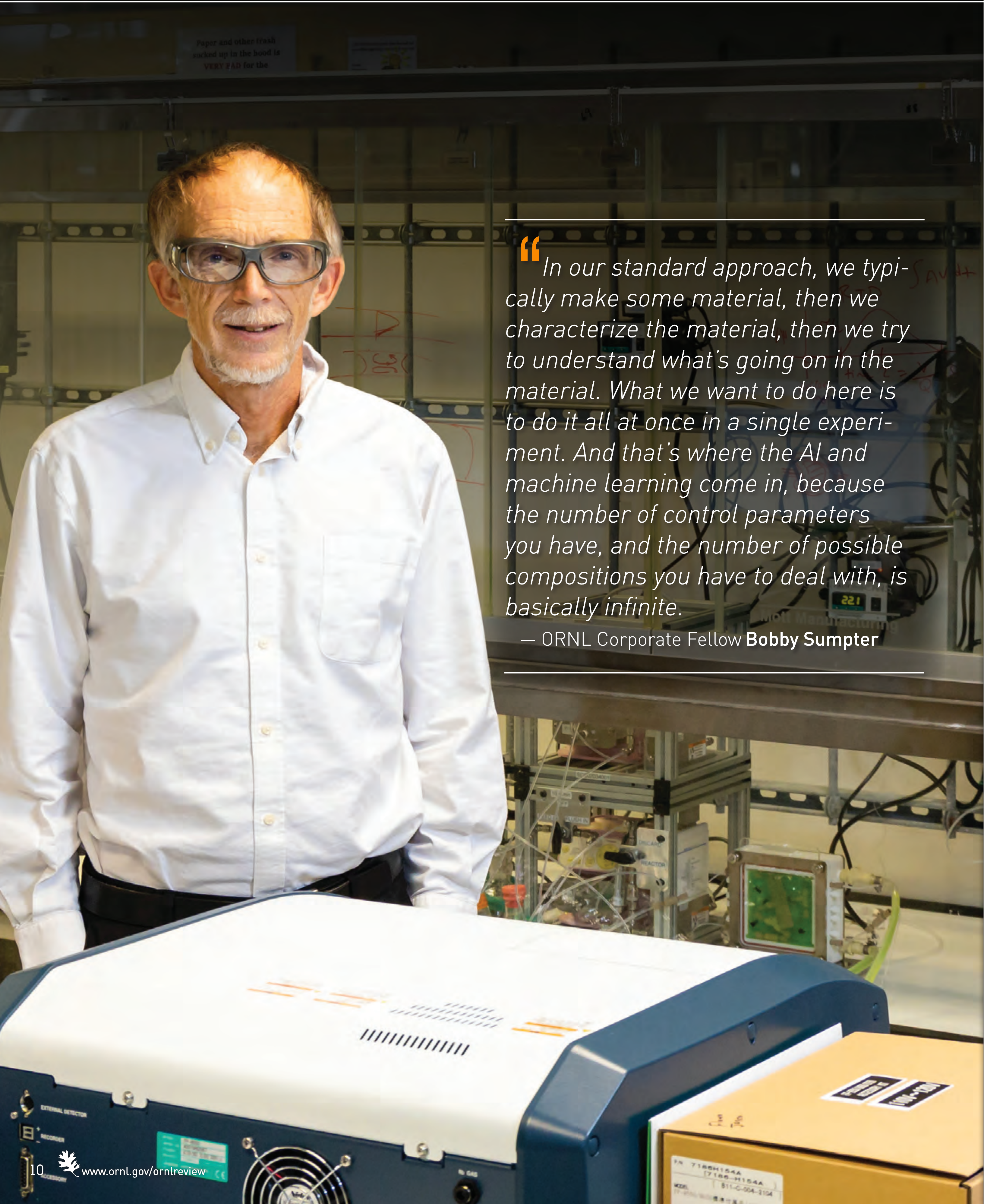
ORNL Macromolecular Nanoscience Group lead Rigoberto Advincula examines 3D-printed PLA plastic sample holders. Image credit: Carlos Jones, ORNL

"A lot of that goes into landfills, some goes to incineration — where it is burned for energy content — and then the rest ends up in the ocean," Advincula explained.

The challenge, then, is twofold: first, to find a way to recycle existing plastics and polymers and keep them out of landfills and, second, to create new plastics and polymers that are designed to be easily recycled and reused.

One big challenge to plastics recycling is that plastic waste doesn't refer to just one material. There are a variety of plastics, each with unique properties. To create valuable products from recycled plastic, then, we must handle the diversity of materials

See KEEPING MATERIALS OUT OF LANDFILLS, page 11



> *In our standard approach, we typically make some material, then we characterize the material, then we try to understand what's going on in the material. What we want to do here is to do it all at once in a single experiment. And that's where the AI and machine learning come in, because the number of control parameters you have, and the number of possible compositions you have to deal with, is basically infinite.*
>
> — ORNL Corporate Fellow **Bobby Sumpter**

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going into the process. This involves breaking them down into their component molecules.

"We have a term called construction–deconstruction chemistry," Advincula said. "We take these existing polymers, which are large molecules, chop them and start connecting them back.

"Deconstruction–construction means that we need to discover new types of catalysts or reaction mechanisms that allow us to deconstruct them properly and to reconstruct them and then to process them in the melt."

Putting those component parts back together into economically viable products is a monumental scientific challenge. For Advincula, the best way to make the process successful is to create products that are more valuable than the original plastics. This approach is called upcycling.

"It could be a more high-performance polymer or plastic product," he said, "or it could be an intermediate for another chemical reaction. It has to have an added value for people to buy and use it."

Enabling autonomous materials research

Both challenges, then — designing more recyclable materials and recycling those we already have — require a massive amount of experimentation. One approach being taken at ORNL to accelerate the process is the creation of a reconfigurable continuous flow reactor, which is essentially a (nonnuclear reactor) device to automate large-scale chemistry experiments.

The reactor — a three-year investment by ORNL — takes advantage of the lab's strengths in supercomputing, neutron science and materials science. Planned for the lab's Center for Nanophase Materials Sciences, the reactor will combine analytical tools such as nuclear magnetic resonance, various forms of spectroscopy and chromatography, X-ray analysis and neutron analysis with artificial intelligence and machine learning to automatically conduct, analyze and rework experiments to recycle existing materials and create new ones.

"In our standard approach, we typically make some material, then we characterize the material, then we try to understand what's going on in the material," said ORNL Corporate Fellow Bobby Sumpter, who serves as CNMS's Theory and Computation section head. "What we want to do here is to do it all at once in a single experiment. And that's where the AI and machine learning come in, because the number of control parameters you have, and the number of possible compositions you have to deal with, is basically infinite."

By automating the "make–measure–model" approach of traditional chemistry and using AI to provide feedback to allow autonomous decisions, the reactor can greatly accelerate the discovery process. And while it will be used on a wide variety of important scientific problems, two of these will be the recycling of existing mixed plastics and the creation of smarter future plastics.

"We have focused efforts to use AI to mimic a real chemist or materials scientist in making decisions on which compositions or which catalysts or which reactor parameters are required to deliver a particular material property or a recyclability possibility," Sumpter said. "Oak Ridge is putting forth a pretty significant investment to build capabilities to not just automate materials synthesis, but to make it autonomous."

ORNL Corporate Fellow Bobby Sumpter in ORNL's Center for Nanophase Materials Sciences. Image credit: Carlos Jones, ORNL

High-tech materials

The challenge of plastics doesn't just apply to consumer products such as water bottles and grocery bags. It also extends to the high-tech composite materials that go into high-performance plastic products such as electric vehicles, aircraft and wind turbine blades.

By combining plastics with carbon or glass fibers, these composites combine the light weight and strength needed in these 21st century products. Yet, once the cars or windmill blades reach the ends of their useful lifetimes — typically 20 years for a wind turbine blade — the problem of the linear versus circular economy remains. On top of that, high-tech composite materials have a

See KEEPING MATERIALS OUT OF LANDFILLS, page 13

> *"Oak Ridge is a science laboratory. We have an interdisciplinary team of chemists, materials scientists, product design engineers, computational experts and others who can support all of the diverse, complex and necessary aspects of the technology development.*
>
> — ORNL materials scientist **Soydan Ozcan**

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significantly larger carbon footprint than lower-tech plastics, and demand for these composites is expected to grow about 7 to 10 percent each year for the next decade.

According to ORNL materials scientist Soydan Ozcan, who also leads the Institute for Advanced Manufacturing Composite Innovation's composite recycling effort, the challenge of composites, like that of conventional plastics, requires both short- and long-term approaches.

"We cannot design everything in the next five years to switch to a new world," Ozcan said. "We'll have this problem for at least the next 30 years. It's going to take time to switch to more sustainable material and product designs. In the meantime, we've got to develop advanced recycling technologies that will work with current materials."

Ozcan suggested a variety of uses for these materials. For example, windmill turbine blades can find a second lifetime as structural reinforcements in bridges, buildings and even power poles. The materials can also be broken down and used in advanced 3D-printing applications, a process being demonstrated at ORNL's Manufacturing Demonstration Facility.

One advantage to recycling in the composites industry is that its waste streams aren't as contaminated as commodity plastics. However, it is still critically important to minimize contamination in recycled composites to ensure they can be used in the highest-value applications. As such, the material must be tracked throughout its life cycle with techniques such as radio-frequency identification, or RFID, and cloud-based data management.

"We need to capture value throughout the digital supply chain," Ozcan said. "Where are these wind turbine blades? Where are these cars? Or where are these composite materials? How many times have they been used? How many years have they been used? What type of thermosets or thermoplastics were used? Where are the closest recycling centers or facilities?"

The goal is to keep composite materials out of landfills, take advantage of the energy and cost that has gone into them, and maximize their useful lifetimes.

For example, Ozcan said, "There are many steps in the production of a blade. Raw materials are mined, polymer is then synthesized, fiber is made, and the composite is then manufactured. Each step involves transportation costs — capital, energy and CO_2 — before you get the final product and the utility. In 20 years when you are done, you don't need to redo every step. The structure is still fine and, if designed appropriately, can potentially be used for other purposes."

Efforts to recycle existing materials are necessarily a stopgap effort as researchers design more inherently recyclable materials, he noted. After all, the materials themselves were not created to be recycled.

"We design for performance, mechanical strength, stiffness, rigidity, longevity and so on," Ozcan said. "This is typically what I do as a materials engineer. While we were creating these materials, we didn't talk about what was going to be happening to them at the end of life.

"Composite materials are extremely complex. It's not easy to unzip and reuse the resin system. So, the starting point should be how we can develop and implement inherently recyclable resin systems."

Soydan Ozcan. Image credit: Carlos Jones, ORNL

Composites may also lend themselves to bio-based materials, he said, allowing manufacturers to forgo petroleum-based materials altogether.

"Instead of starting with a petroleum base, what if we start with biologically sourced materials? When you make a resin or fiber out of wood, your starting material already has a negative carbon footprint because trees and plants process CO_2 during their lifetime."

For Ozcan, ORNL is an ideal place to answer these questions.

"Oak Ridge is a science laboratory. We have an interdisciplinary team of chemists, materials scientists, product design engineers, computational experts and others who can support all of the diverse, complex and necessary aspects of the technology development."

Ensuring our water future

by Leo Williams
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The United States — and indeed the world — is in the midst of a water crisis.

The situation in the American West is especially critical, qualifying as a "megadrought" because it has lasted for decades. Nineteen percent of the country is experiencing "extreme" drought, according to the National Integrated Drought Information System. This includes nearly 90 percent of California and Utah and roughly two-thirds of Nevada, Montana, Idaho and Oregon.

And while the situation in the West may seem the most dire, the rest of the country is not out of the woods.

"We're beginning to run into a situation in many parts of the country where the sources of water that we traditionally use are now becoming less and less available," said ORNL Energy Systems Integration Section Head Yarom Polsky. "Everybody is familiar with the issues that plague California right now, but you're also running into situations in cities like Atlanta, for example.

"Atlanta does not have a very extensive watershed. Sure, it receives an abundance of rain; they have fairly good surface water catchments and reserves. But it has a very large population, and they're running into a situation where those traditional sources of water are becoming less available."

Any discussion of the circular economy and sustainability needs to include our use — and reuse — of water. Growing populations and changing climate mean we will need to be creative in meeting our water needs.

Conservation, of course, needs to be part of the solution, but it is only a part. Our approach to water must also include the development of nontraditional water sources and more intelligent treatment and reuse of the water that goes down our drains.

Nontraditional sources are found in a variety of places. The category includes seawater and less-salty brackish water, which can be found in aquifers or where rivers meet the ocean. In addition, oil and gas drilling also bring up water, known as "produced water." And our approach must also include reused wastewater from throughout the economy, including industrial, agricultural, mining and municipal sources.

A national effort

DOE responded to the water crisis in 2018, creating an Energy-Water Desalination Hub focused on early research and development into desalination and the promotion of nontraditional water sources. In response, a consortium of three national labs (Berkeley Lab, the National Renewable Energy Laboratory and ORNL), universities and industrial partners formed the National Alliance for Water Innovation in 2020.

Its goal is to make alternative sources of water available at essentially the same cost as traditional sources such as rivers, lakes and aquifers.

"The goal of the consortium is to substantially reduce the energy intensity and cost of water treatment, and in particular to make nontraditional sources of water available for use," said Polsky, who serves as NAWI's lead for process innovation and intensification R&D. "That can be for human consumption, but it can be for other applications as well.

"Achieving this goal centers around a concept that DOE developed a few years ago called pipe parity. The basic objective is to treat water at a cost that's comparable to traditional sources in that region."

"We're beginning to run into a situation in many parts of the country where the sources of water that we traditionally use are now becoming less and less available. Everybody is familiar with the issues that plague California right now, but you're also running into situations in cities like Atlanta, for example.

— ORNL Energy Systems Integration Section Head **Yarom Polsky**

NAWI's approach is outlined by challenge areas denoted by the acronym A-PRIME, which stands for

- "Autonomous operations," especially in water treatment and the development of advanced sensors for water quality monitoring
- "Precision separations," focused on removing pollutants in industrial wastewater
- "Resilient treatment and transport," for instance, that adapts to varying water quality
- "Intensified brine management," focused on managing ultrasalty brines
- "Modular systems" using improved materials and manufacturing processes
- "Electrified treatment systems," including the development of electrocatalytic processes and treatment systems that integrate with the electrical grid

These challenge areas guide research projects across the alliance, including at ORNL, Polsky said.

"All of our research projects are basically defined by the A-PRIME topic areas. We have projects in the autonomous water challenge area, the intensified brine management challenge area and the resilience challenge area. And then we have projects that focus on electrified treatment as well."

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ENSURING OUR WATER FUTURE, page 15

Modernizing water treatment

The NAWI approach acknowledges that water treatment systems need to be modernized.

"Many conventional water treatment approaches are very old — some of them over 100 years old," Polsky said. "The treatment approaches require an application of sequential treatment trains: You use one process to remove one constituent, then you use another process to remove another and so on."

The approach relies on the composition of input water not changing drastically, he explained. When water composition changes, treatment needs can also change, and existing systems can become inefficient or ineffective.

"And so one of the goals of the research hub is to break that paradigm of linearity so that the treatment trains work more efficiently together and can handle a much larger variety of input water types. In the future, we may need to be more flexible with respect to where we get our water from."

Keeping stream water clean

Bioenergy, while critical to a circular economy, can also create challenges for water quality. For one, there is the danger that efforts to grow bioenergy crops quickly — in particular with the use of fertilizers and herbicides — may lead to stream pollution.

These risks were the focus of an ORNL-led project that studied the environmental effects of producing loblolly pine, which may be used for heating, transportation fuels and electricity generation.

The experiment was conducted on three adjacent watersheds at DOE's Savannah River Site in South Carolina, said ORNL environmental scientist Natalie Griffiths. The watersheds emptied into separate streams, allowing researchers to test the impact on water quality at each site.

Because the trees are intended for bioenergy, researchers wanted them to grow more quickly than is needed for traditional forestry, so the team applied the chemicals multiple times during early tree growth.

"If we're growing trees for bioenergy, we want to make sure we're not impacting the environment and water quality," Griffiths explained. "In this case, it's possible that the fertilizers and herbicides that are applied could run off into the streams or enter groundwater."

The team left one of the watersheds as they found it, letting it act as the experiment's control site. With the other two, it cut down half the trees in the watersheds and planted loblolly pines, treating them with fertilizer and herbicide.

The researchers monitored the area for a total of eight years, including two years before they planted the new trees. The most important measurements were focused on tracking where the applied fertilizer ended up.

"Most importantly, we were looking at the nitrogen content of the water, specifically nitrate," Griffiths said. "Nitrate is a form of nitrogen that is readily available for microbes and algae to take up. It can cause water quality issues if it's at a high level because it can cause algal blooms."

She noted that there are also drinking water limits for nitrate because they can be harmful, particularly to infants.

Griffiths found that nitrate levels were elevated in groundwater under the planted pine trees, but the levels had gone back down by the time the water reached the streams.

"Not all of the applied fertilizer was taken up by the trees, and some entered the groundwater. But by the time the groundwater reached the stream, the nitrate concentration was reduced," she said. "We did not see any effects in the stream, likely because biological processes occurring along the pathway to the stream removed the nitrate."

Griffiths noted that the experiment focused on the pines' early years, running for six years after the trees were planted, even though they are typically grown 10 to 15 years before they are harvested for bioenergy. She said the chemicals would affect the environment primarily during these early years, when the trees were still small.

"We expected effects mostly to happen initially, when the trees were still small and growing quickly," she said. "The trees were likely too small to take up all the fertilizer. And as they get bigger and bigger, they're shading out other vegetation, so you don't need to apply herbicides."

She said the team also collaborated with a computational researcher at Oregon State University who developed models using data from the project. This step allowed them to extrapolate their results to larger areas and longer time periods.

"As experimentalists, we can't grow the trees for 10 years, cut them all down, grow more trees for another 10 years, cut them down and keep doing it for 50 years. We need the models to estimate what's going to happen in the future and understand potential regional impacts."

"If we're growing trees for bioenergy, we want to make sure we're not impacting the environment and water quality. In this case, it's possible that the fertilizers and herbicides that are applied could run off into the streams or enter groundwater.

— ORNL environmental scientist
Natalie Griffiths

Lithium recovery:

A critical challenge for battery tech

by Jim Pearce
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DOE's *National Blueprint for Lithium Batteries 2021–2030* makes it clear that lithium production is a national priority. The report notes that the worldwide lithium battery market is expected to grow by a factor of 5 to 10 in the next decade and warns: "The U.S. industrial base must be positioned to respond to this vast increase in market demand that otherwise will likely benefit well-resourced and supported competitors in Asia and Europe."

Taking advantage of this impending increase in demand for lithium will be particularly challenging for the United States, which currently produces very little of the critically important mineral.

"Less than 2 percent of our lithium comes from the U.S. and Canada," said ORNL Corporate Fellow Parans Paranthaman, who has spent years investigating alternative sources of lithium. "Forty percent comes from Australia. We get about 35 percent from South America — Argentina, Bolivia, Chile — and the rest comes from China.

"Because we are using more lithium batteries in electric cars and many other devices, to alleviate supply chain shortages we have identified alternative sources of lithium. The most promising of these is recovering lithium from brine generated by geothermal power plants or from mine tailings."

Mineral-rich brine

Geothermal plants generate power by drilling into reservoirs of pressurized, superheated water deep underground and pumping it to the surface. Depressurized, the water turns to steam and spins turbines that power generators to produce electricity. The leftover, mineral-laden water, known as brine, contains high concentrations of several minerals and a much lower concentration of lithium.

"We see 300 to 400 parts per million of lithium chloride," Paranthaman said. "Compare that to 50,000 parts per million of sodium chloride. In the brine, we have sodium chloride, potassium chloride, calcium chloride and manganese at very high concentrations, whereas the concentration of lithium is low. So the challenge is to extract the lithium efficiently and with a high level of purity.

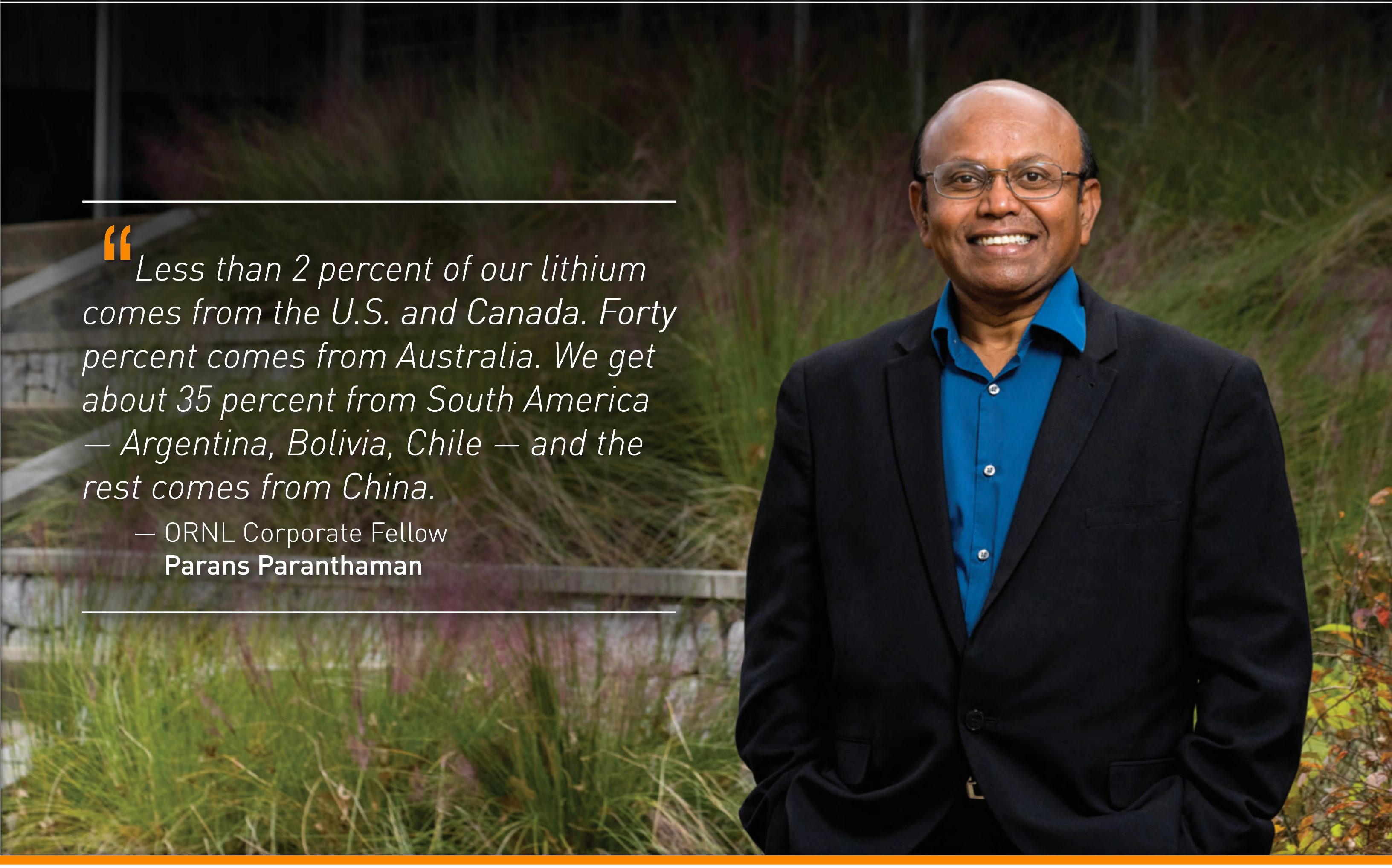
Though the concentration of lithium is relatively low in geothermal brines compared to other sources, brines require no mining, and no wells have to be drilled because they are already being exploited for power production.

Normally, geothermal power plants pump their cooled brine back underground. However, Paranthaman is working with scientists at ORNL, DOE's Critical Materials Institute and industry partner All-American Lithium to devise methods of first recovering the lithium from the brine. The key to this recovery is the development of a sorbent material that will selectively adsorb, or chemically remove, lithium chloride from the brine. So far, the material that has shown the most promise is pure or iron-doped lithium-aluminum-layered double hydroxide chloride, or LDH.

"We designed the sorbent to exclusively adsorb lithium chloride," Paranthaman said. "LDH has the advantage of being relatively low cost and highly selective for lithium — meaning that it not only adsorbs a large percentage of the available lithium, but it doesn't recover other minerals in the process."

In tests, simulated brine was pumped through a column containing layers of LDH separated by water molecules and hydroxide ions that preferentially admit lithium chloride ions and block sodium and potassium ions. This process removed more than 90 percent of the lithium from the simulated brine.

Paranthaman and his colleagues are also investigating using a membrane that will concentrate the lithium chloride solution before



it is exposed to the sorbent. This is expected to increase the efficiency of the process. "Using the membrane, we can go from roughly a 3-percent lithium chloride solution to a 22-percent solution. We hope to be able to go all the way to 40 percent. When we concentrate the lithium chloride, the sodium chloride and potassium chloride — which have lower solubility — precipitate out, so they can be removed by filtering. This results in a pure lithium chloride solution that can then be converted to lithium hydroxide or lithium carbonate. These are the starting materials for lithium battery production."

A good situation to be in

If this technology can be scaled up and employed on an industrial level, it is estimated that a 50-megawatt geothermal plant could recover 15,000 tons of lithium carbonate per year, and there are more than 20 geothermal power plants just in the vicinity of California's Salton Sea. Currently, the entire world's production of lithium carbonate is only around 160,000 tons. So, if the lithium recovery capacity of these geothermal plants were to be fully utilized, it would provide more than enough lithium to meet domestic demands.

"Then, we could be an exporter of lithium carbonate," Paranthaman said. "That would be a good situation to be in."

Critical leftovers

Paranthaman and his colleagues are also teaming up with the Critical Materials Institute as well as several small companies and university partners to develop conceptually similar methods for recovering lithium from mine tailings left over from boron mining operations.

"As part of CMI's Critical Materials Project, we are working with Rio Tinto Borates, among others, which has been mining boron in California for almost 150 years," Paranthaman said. "Boron tailings contain lithium sulfate. So we're in the process of developing a prepilot demonstration of lithium recovery from these tailings right now. We expect that we will be ready for a full-scale demonstration within a year."

Recovering lithium from mine tailings, naturally, uses different methods and processes than recovering lithium from geothermal brine.

"Chemistry-wise, geothermal recovery is a chloride stream; mine tailings are a sulfate stream, so they require different processes," Paranthaman said. "However, the idea is the same, and the product resulting from both processes will be the same."

Taking it to the next level

Over the longer term, Paranthaman and his colleagues envision mounting a comprehensive effort to address the challenges associated with lithium-ion batteries. For example, in addition to lithium, there is a critical need for nickel, cobalt and graphite in the production of lithium-ion batteries.

Welcome to Neutrino Alley:

Q&A with ORNL's Marcel Demarteau

by Dawn Levy
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Marcel Demarteau, director of ORNL's Physics Division, shapes a research agenda exploring topics from nuclear structure to astrophysics. One of his challenges is advancing knowledge of neutrinos — electrically neutral particles that interact only weakly with matter, making their detection difficult.

ORNL plays key roles in four major neutrino collaborations, including the COHERENT experiment at the Spallation Neutron Source, a 1.4-megawatt pulsed neutron source at ORNL. Because neutrinos are a byproduct of neutron production, COHERENT makes the most of SNS's neutrino factory with five detectors sited along a 164-foot-long hallway that has come to be called Neutrino Alley. Here, Demarteau explains its successes and possibilities.

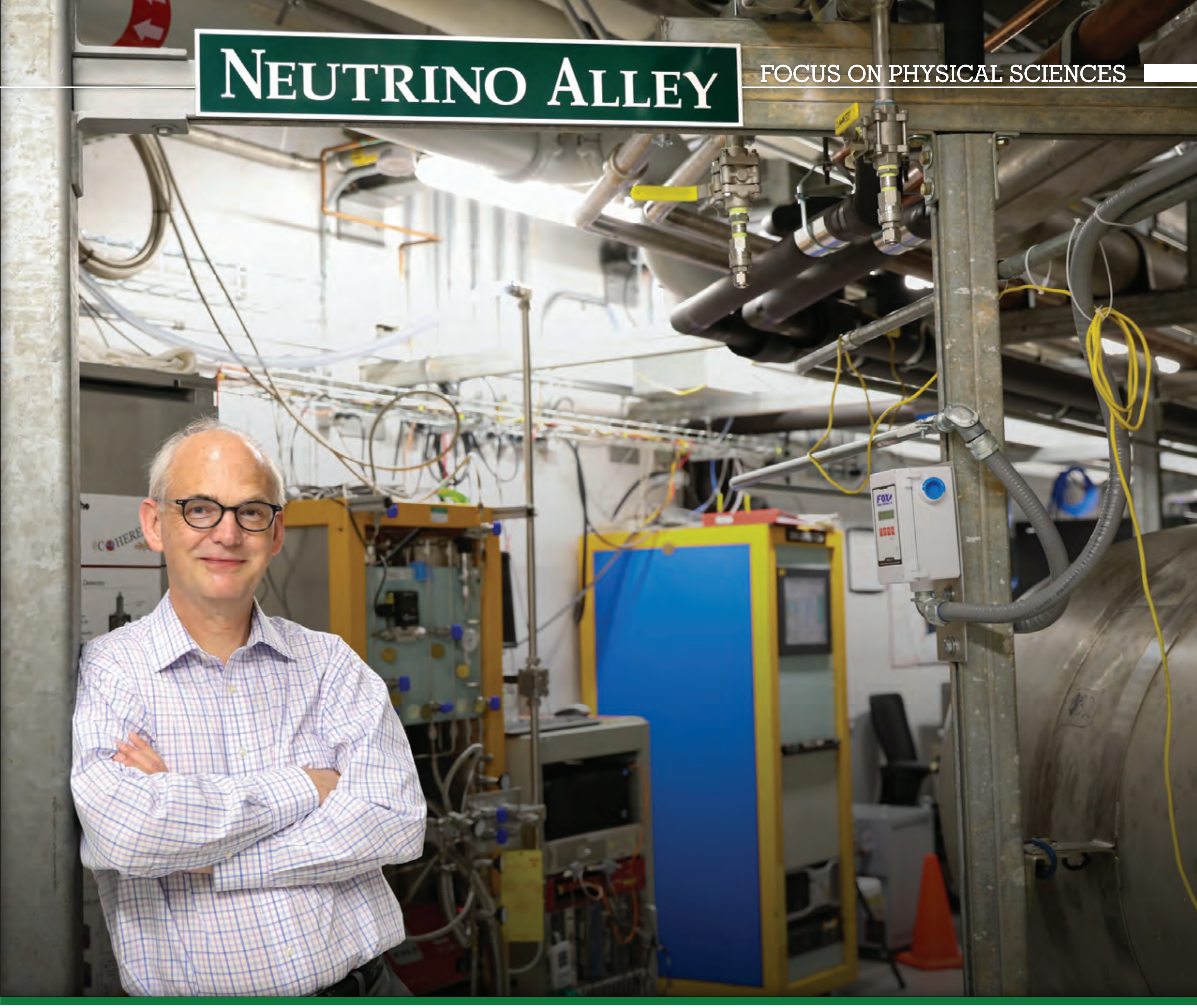
Q: What is Neutrino Alley, and how did it come to be?

A: Neutrino Alley is a service corridor at the Spallation Neutron Source that is ideally suited for neutrino experiments. As SNS's name says, it is a facility to create neutrons, but in the process, a lot of other particles are created, especially pions. Pions are stopped very quickly in the liquid mercury target and decay at rest to give us three different neutrinos: promptly emitted muon neutrinos with a precise energy, and delayed electron and antimuon neutrinos.

Q: What experiments are going on there now?

A: The COHERENT experiment measures neutrino interaction processes including coherent elastic neutrino–nucleus scattering, or CEvNS, which is pronounced "sevens." This is a collective process in which a neutrino interacts with the nucleus as a whole, rather than with individual components of that nucleus. Eleven neutrino experiments at spallation and reactor sources worldwide are looking for this interaction.

Scientists predicted this process about 50 years ago. However, it has been very difficult to observe because the interaction probability is small and the energy to be detected is tiny. A frequent analogy is a mosquito bouncing off an elephant and measuring the movement of the elephant. We designed COHERENT to look for this process, and nearly three years ago we were the first to observe it. The COHERENT collaboration, comprising 20 institutions from four countries, conducts the experiment at the SNS. Jason Newby is the enthusiastic principal investigator at ORNL, which itself has nearly a dozen participants.



ORNL's Marcel Demarteau stands under the Neutrino Alley arch at the Spallation Neutron Source, which makes neutrinos as a byproduct. Image credit: Genevieve Martin, ORNL

The first target that we used to measure and discover the CEvNS process was a cesium iodide crystal. We have recently also measured this process on argon nuclei; that detector uses liquid argon as the detection medium. Moreover, we have other experiments in preparation — one with a detector of sodium iodide crystals and the other with a detector of germanium crystals. Measuring the interaction rate for different nuclei provides us with insight into the fundamental physics processes occurring in these target materials.

Q: What questions do you hope to answer with these detectors?

A: Currently, the Standard Model of Particle Physics tells us what matter is made of — quarks and leptons interacting through the electromagnetic, weak nuclear, strong nuclear and gravitational forces. The model was completed in 2012 with the discovery of the Higgs boson.

This model has been extremely successful in enabling us to calculate a lot of the phenomena that we see in nature. However, we know that this model is incomplete. One salient new discovery that demonstrates that is the fact that neutrinos have mass. Because they have mass, they can oscillate. They also can change identity between the three known types of neutrinos, and that does not fit in our current description of the Standard Model.

The high flux of neutrinos at the SNS also enables us to look for deviations from theoretical predictions, which could point to the existence of a completely new form of matter, such as sterile neutrinos that do not interact via any of the fundamental interactions of the Standard Model. That would inform our understanding of the origin of dark matter, which would be absolutely transformational. Furthermore, we believe that neutrinos can provide insight into matter–antimatter asymmetry in the universe. Neutrinos provide a unique window that will help us probe and uncover the new physics.

For more information: https://go.usa.gov/xHsfF

Compelling evidence of neutrino process

opens physics possibilities

by Dawn Levy
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The COHERENT particle physics experiment at ORNL has firmly established the existence of a new kind of neutrino interaction. Because neutrinos are electrically neutral and interact only weakly with matter, the quest to observe this interaction drove advances in detector technology and has added new information to theories aiming to explain mysteries of the cosmos.

"The neutrino is thought to be at the heart of many open questions about the nature of the universe," said Indiana University physics professor Rex Tayloe. He led the installation, operation and data analysis of a cryogenic liquid argon detector for neutrinos at ORNL's Spallation Neutron Source, or SNS.

The study observed that low-energy neutrinos interact with an argon nucleus through the weak nuclear force in a process called coherent elastic neutrino-nucleus scattering, or CEvNS. Like a ping-pong ball bombarding a softball, a neutrino hitting a nucleus transfers only a small amount of energy to the much larger nucleus, which recoils almost imperceptibly in response to the tiny assault.

Laying the groundwork for the discovery made with the argon nucleus was a 2017 study in which COHERENT collaborators used the world's smallest neutrino detector to provide the first evidence of the CEvNS process as neutrinos interacted with larger and heavier cesium and iodine nuclei. Their recoils were even tinier, like bowling balls reacting to ping-pong balls.

"The Standard Model of Particle Physics predicts coherent elastic scattering of neutrinos off nuclei," said Duke University physicist Kate Scholberg, organizer of science and technology goals for the collaboration, which has 80 participants from 19 institutions and four countries. "Seeing the neutrino interaction with argon, the lightest nucleus for which it has been measured, confirms the earlier observation from heavier nuclei. Measuring the process precisely estab-

Jacob Zettlemoyer, Indiana University Bloomington, led data analysis and worked with ORNL's Mike Febbraro on coatings, shown under blue light, to shift argon light to visible wavelengths to boost detection. Image credit: Rex Tayloe, Indiana University

Indiana University physics undergraduate Maria del Valle Coello views the CENNS-10 detector installed in SNS's Neutrino Alley. Image credit: Rex Tayloe, Indiana University

lishes constraints on alternative theoretical models."

Yuri Efremenko, a physicist at the University of Tennessee, Knoxville, and ORNL who led development of more sensitive photodetectors, said, "Argon provides a 'door' of sorts. The CEvNS process is like a building that we know should exist. The first measurement on cesium and iodine was one door that let us in to explore the building. We've now opened this other argon door." The argon data is consistent with the Standard Model within error bars. However, increased precision enabled by bigger detectors may let scientists see something new. "Seeing something unexpected would be like opening the door and seeing fantastic treasures," Efremenko added.

"We're looking for ways to break the Standard Model. We love the Standard Model; it's been really successful. But there are things it just doesn't explain," said physicist Jason Newby, ORNL's lead for COHERENT. "We suspect that in these small places where the model might break down, answers to big questions about the nature of the universe, antimatter and dark matter, for instance, could lie in wait."

The team uses the world's brightest pulsed neutron source to help find those answers. The same process for producing neutrons at the SNS for research also creates neutrinos as a byproduct. A service corridor beneath the SNS mercury target has been converted into a dedicated neutrino laboratory, dubbed Neutrino Alley. A 53-pound detector called CENNS-10 sits 90 feet from a low-energy neutrino source that optimizes opportunities to spot interactions that are coherent. This means approaching neutrinos see the weak force of the nucleus as a whole.

The CENNS-10 detector was originally built at Fermilab by COHERENT collaborator Jonghee Yoo. He and Tayloe brought it to IU and reworked it there before it was installed at SNS in 2016.

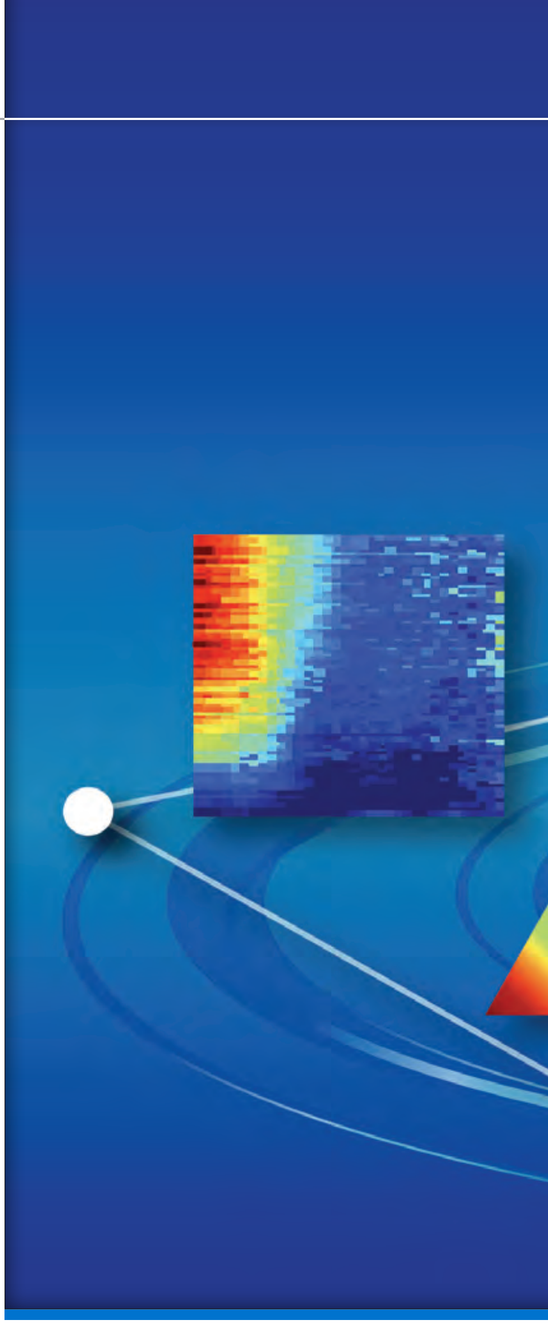
Wavelength-shifting coatings were applied to the photodetectors and inner reflectors that significantly improved light collection.

Analysis of 18 months of data collected from CENNS-10 revealed 159 CEvNS events, consistent with the Standard Model prediction. COHERENT's data will help researchers worldwide interpret their neutrino measurements and test their theories of possible new physics.

The findings have practical applications, too. "This is a way to measure the distribution of neutrons inside nuclei and the density of neutron stars," Efremenko said. "It's a contribution to nuclear physics and astrophysics because the processes are very similar."

For more information: https://www.ornl.gov/news/compelling-evidence-neutrino-process-opens-physics-possibilities

The Spallation Neutron Source also produces neutrinos in large quantities. Image credit: Carlos Jones, ORNL



Automated chemistry

sets new pace for materials discovery

by Ashley Huff
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Steps to automate the process of materials discovery are key to speeding the search for new perovskite materials to advance solar energy technologies.

Metal halide perovskites, or MHPs, are thin, lightweight, flexible materials with outstanding properties for harnessing light. Their high efficiency and low fabrication costs make them attractive for potential applications in solar cells, energy-efficient lighting and sensors.

Through the Science Alliance, a Tennessee Center of Excellence, researchers at ORNL and the University of Tennessee, Knoxville, are teaming up to find the best MHP candidates for device integration using a new workflow that combines robotic chemistry and machine learning.

"Our approach speeds exploration of perovskite materials, making it exponentially faster to synthesize and characterize many material compositions at once and identify areas of interest," said ORNL's Sergei Kalinin.

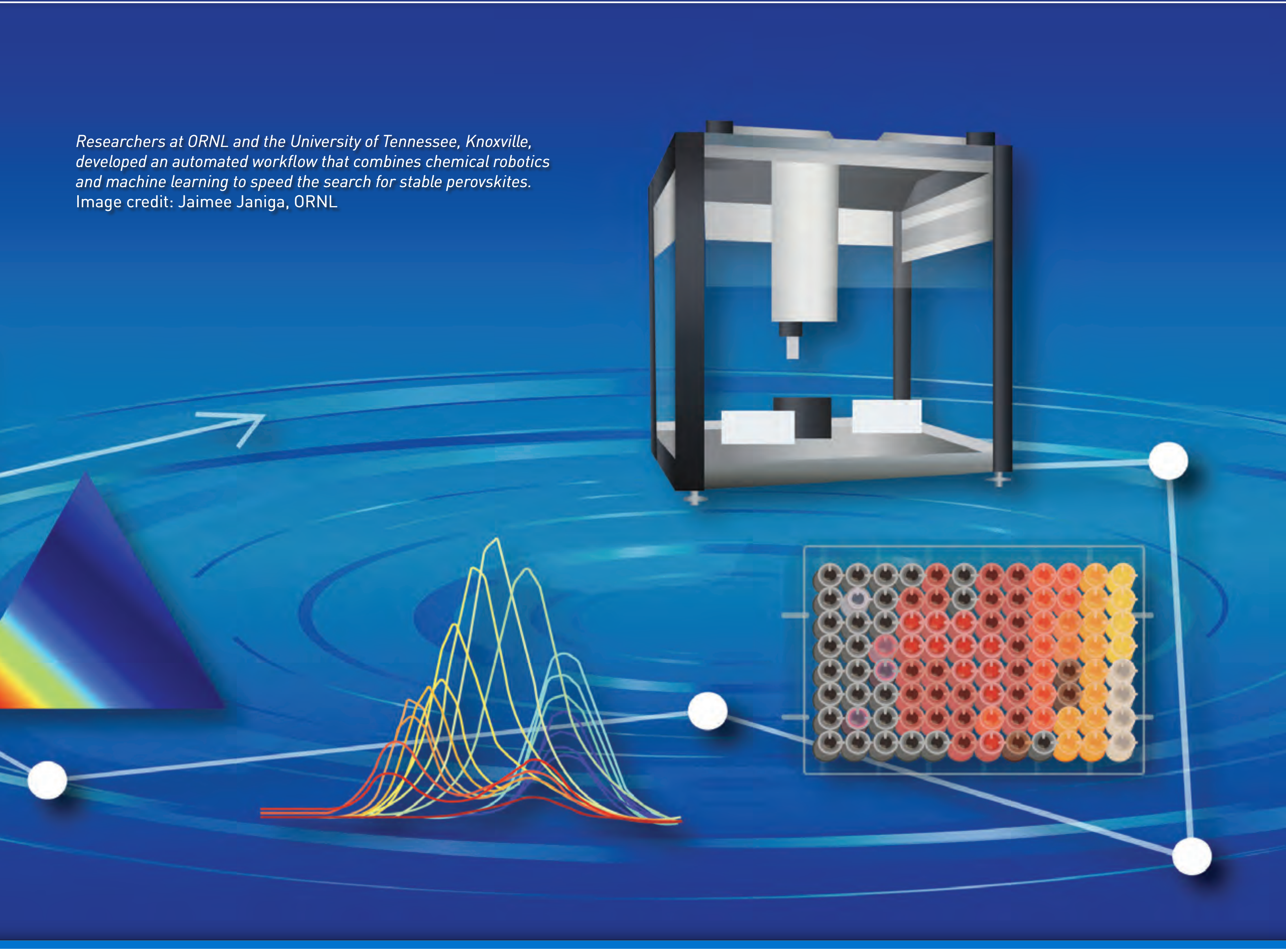
The study aims to identify MHPs with highly stable photoluminescent properties.

"Automated experimentation can help us carve an efficient path forward in exploring what is an immense pool of potential material compositions," said UT Knoxville's Mahshid Ahmadi.

While perovskites open cost-effective avenues for commercializing solar energy technologies, their sensitivity to the environment has been a bottleneck. They tend to degrade too quickly in real-world conditions — such as light, humidity or heat — to be practical.

Scientists face a vast design space in their efforts to develop more robust models. More than a thousand MHPs have been predicted, and each of these can be chemically modified to generate a near-limitless library of possible compositions. This enormous potential for new candidates presents an inherent obstacle for materials discovery.

"It is difficult to overcome this challenge with conventional methods of synthesizing and characterizing samples



Researchers at ORNL and the University of Tennessee, Knoxville, developed an automated workflow that combines chemical robotics and machine learning to speed the search for stable perovskites. Image credit: Jaimee Janiga, ORNL

one at a time," Ahmadi said. "Our approach allows us to screen up to 96 samples at a time to accelerate materials discovery and optimization."

The team selected four model MHP systems — yielding 380 compositions total — to demonstrate the new workflow for solution-processable materials, compositions that begin as wet mixtures but dry to solid forms.

The synthesis step employed a programmable pipetting robot designed to work with standard 96-well microplates. The machine saves time over manually dispensing many different compositions, and it minimizes error in replicating a tedious process that needs to be performed in exactly the same ambient conditions, a variable that is difficult to control over extended periods.

Next, researchers exposed samples to air and measured their photoluminescent properties using a standard optical plate reader.

"It's a simple measurement but is the de facto standard for characterizing stability in MHPs," Kalinin said. "The key is that conventional approaches would be labor intensive, whereas we were able to measure the photoluminescent properties of 96 samples in about five minutes."

Repeating the process over several hours captured complex phase diagrams in which wavelengths of light vary across compositions and evolve over time.

The team developed a machine learning algorithm to analyze the data and home in on regions with high stability.

"Machine learning enables us to get more information out of sparse data by predicting properties between measured points," said ORNL's Maxim Ziatdinov, who led the algorithm's development. "The results guide materials characterization by showing us where to look next."

While the study focuses on materials discovery to identify the most stable compositions, the workflow could also be used to optimize material properties for specific optoelectronic applications.

The automated process can be applied to any solution-processable material for time and cost savings over traditional synthesis methods.

A simple salt:

Making batteries faster and safer

by Paul Boisvert
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One of the biggest factors affecting consumer adoption of electric vehicles is the amount of time required to recharge the vehicles, which are usually powered by lithium-ion batteries.

It can take up to a few hours or even overnight to fully recharge EVs, depending on the charging method and amount of charge remaining in the battery. This can force drivers to either limit travel away from their home chargers or locate and wait at public charging stations during longer trips.

Why does it take so long to fully charge batteries, even those used to power smaller devices, such as mobile phones and laptops? The primary reason is that battery-powered devices and their chargers are designed to charge only at slower, controlled rates. This is a safety feature to help prevent fires and explosions due to rigid tree-like structures called dendrites, which can grow inside a lithium battery during fast charging and induce short-circuits.

To address the need for a safer and faster-charging lithium-ion battery, ORNL scientists and researchers from the University of California at San Diego focused on a new material — lithium vanadium oxide — a "disordered rock salt" similar to table salt but with some randomness in the arrangement of its atoms. Working together at the VULCAN instrument at the Spallation Neutron Source, the team placed samples of the material in a powerful neutron beam to observe the activity of ions inside the material after a voltage was applied.

"The two most common materials used to make lithium-ion battery anodes are graphite, which can deliver high energy density but has caused fires in some situations, and lithium titanate, which can charge rapidly and is much less likely to cause fires, but has lower energy storage capacity," said Haodong Liu, a research scientist at UC San Diego. "The disordered rock salt material we developed combines the desired properties of both — it is safer, faster-charging and has a higher energy density."

The material demonstrated desirable qualities for many battery applications, such as EVs and power tools, including the speed with which the energy can be stored and discharged for use.

During testing, the rock salt anode material was able to discharge more than 40 percent of its energy capacity in just 20 seconds. The rapid charging and discharging appear to be possible because the rock salt material can cycle two lithium ions in and out of vacant sites within its crystal structure.

"Neutrons can easily track lithium ions and oxygen atoms inside rock salt and do so at high resolution, which helped us understand how the rock salt ions behave when we applied voltage to the material," Liu said.

The VULCAN neutron instrument is ideal for examining how materials are affected by deformations, residual stress and microstructures during manufacturing and finishing processes. Data produced by such studies can be used to improve production and minimize defects.

"VULCAN is the world's top neutron scattering instrument for studying engineered materials," said ORNL neutron scattering scientist Ke An. "Its open design permits large samples and even functioning mechanical devices, such as running combustion engines, to be tested and to observe their internal properties. Over the years, this instrument has provided critical scientific information about energy storage during battery materials synthesis and about their behavior in working batteries."

The researchers demonstrated that the rock salt anode can be cycled over 10,000 times with negligible capacity decay. Such durability would be important for consumer applications.

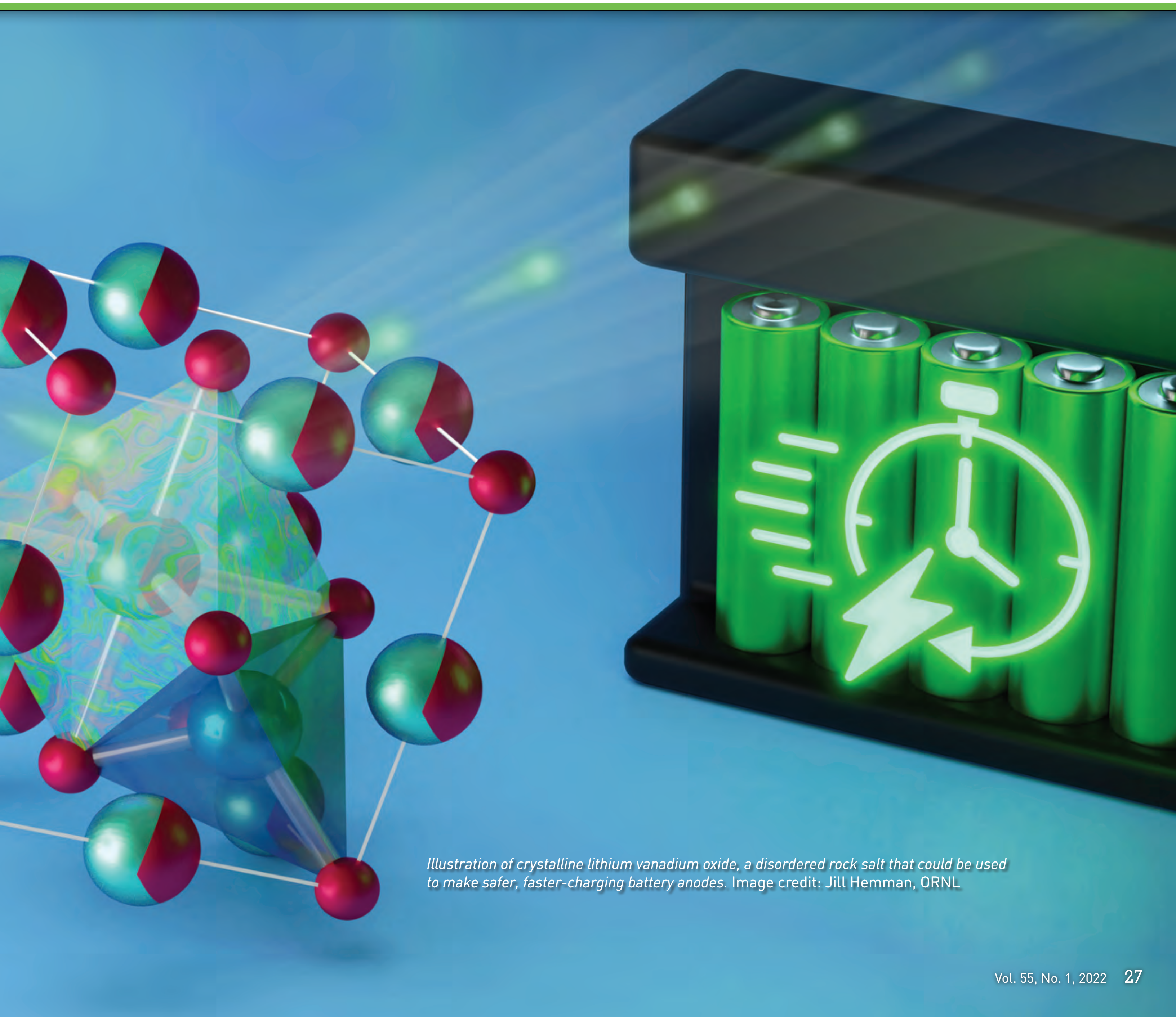

Illustration of crystalline lithium vanadium oxide, a disordered rock salt that could be used to make safer, faster-charging battery anodes. Image credit: Jill Hemman, ORNL

Twist and flex:

'Hinged' atoms improve solar power specs

by Paul Boisvert
boisvertpl@ornl.gov

Most solar power is produced by converting sunlight into electricity through the use of thin films made of semiconductor materials that absorb particles of light, called photons. These absorbed photons knock electrons loose from atoms in the thin film, and the free electrons are then channeled into an electrical current.

However, even the most widely used semiconductor materials, such as crystalline silicon, have limits on how much electrical current they can produce, because their electrons recombine quickly with atoms in the film. The materials also need to be highly stable to withstand the heat, humidity and other environmental conditions found in solar power applications.

An inorganic cesium-lead-bromide crystalline perovskite material has shown excellent stability and electron transport capabilities, even in harsh, humid environments. A better understanding of the dynamics inside this material could help scientists optimize the optical and thermal properties of a wide range of perovskite materials, some of which have demonstrated more than a 25 percent power conversion efficiency and could potentially surpass the efficiency of silicon-based materials.

Researchers recently conducted neutron scattering experiments at ORNL's Spallation Neutron Source and reported the most direct observations to date of the atomic motions inside cesium-lead-bromide crystals. "Our experiments reveal the high power conversion efficiency of cesium-lead-bromide is due in large part to its bromine atoms, which act as hinges that enable the rest of the atomic structure to flex and twist," said Olivier Delaire, associate professor at Duke University. "This twisting motion is thought to inhibit some free electrons from recombining with the semiconductor atoms, leaving more electrons available to produce an electrical current."

The researchers started by carefully growing a large, centimeter-scale, single crystal of the perovskite. Despite having the simplest perovskite structure, cesium-lead-bromide crystals are notoriously difficult to grow to such a size, which is one reason previous studies of the material's atomic dynamics were not able to achieve the same level of detail.

Another key to the research was using the cold neutron chopper spectrometer and wide angular-range chopper spectrometer instruments at SNS. Their high-intensity neutron beams and detectors provided the high-resolution data needed to fully illuminate the atomic vibrations characteristic of perovskite materials.

"Neutron spectrometry at the SNS allowed us to determine that the data

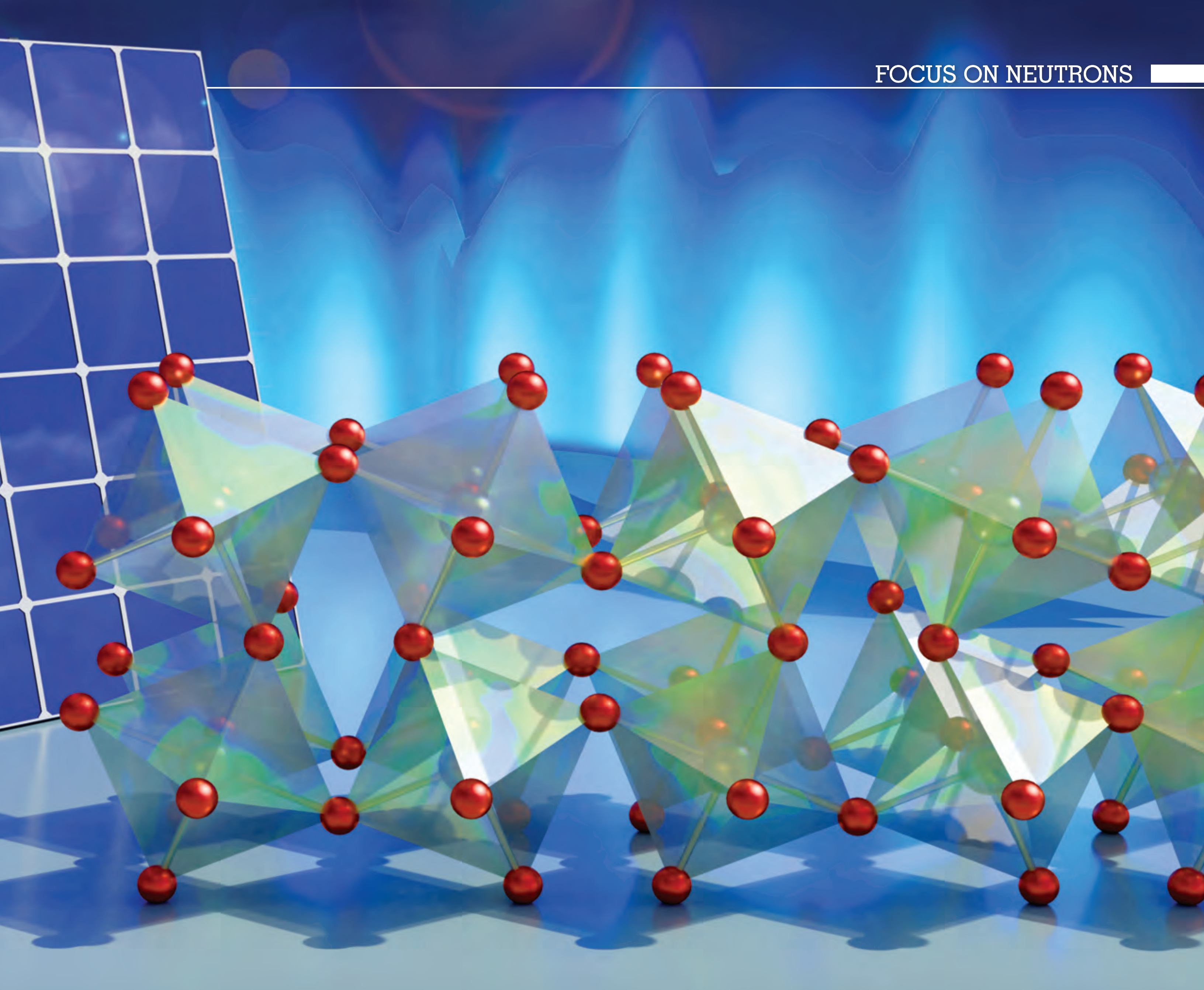

Illustration of the hinged atomic structure of an inorganic perovskite material. The flexible atomic arrangement could help scientists optimize other materials' solar power storage and delivery properties.
Image credit: Jill Hemman, ORNL

was indeed recording the flexing and twisting of octahedral groupings of atoms," Delaire said.

After comparing the neutron and X-ray data with computer simulations, the researchers confirmed just how active the perovskite's crystalline structure is. Each eight-sided octahedral group of atoms — imagine two pyramids stuck together back-to-back — is connected to its neighbors by a bromine atom hinge. This hinge-like arrangement allows the atomic structure to bend back and forth in a fluid manner.

Scientists have known about the pivot points and that they are essential to a perovskite's properties, yet the structural dynamics had not been clearly observed.

The fluidity or flexing of the perovskite's atomic structure is thought to slow down and disrupt movement of the free electrons, similar to how running in a straight line across a trampoline is more difficult than running across a hard surface. The free electrons can't get back very quickly to the vacancies created when they were knocked loose by photons, so the electrons are easier to assemble into an electrical current.

The perovskite's relatively weak atomic bonds also result in a softer metal semiconductor material that is easier to make into thin films.

According to Delaire, "Our findings very likely extend to much more complicated perovskites, which many scientists throughout the world are currently researching. As they screen enormous computational databases, the atomic dynamics we've uncovered could help them decide which perovskites to pursue."

After 20 years,

physicists find a way to keep track of lost accelerator particles

by Jeremy Rumsey
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A high-intensity accelerator beam is formed of trillions of particles that race at lightning speeds down a system of powerful magnets and high-energy superconductors. Calculating the physics of the beam is so complex that not even the fastest supercomputers can keep up.

> "The technique is actually quite simple. We take a block of material with a number of slits that we use to cut out small samples of the beam. That provides us with a beamlet containing a smaller, more manageable number of particles that we can measure, and we can move that block around to measure other sections of the beam.
> — ORNL accelerator physicist **Alexander Aleksandrov**

However, a milestone achievement by ORNL accelerator physicists has enabled beam characterizations to be studied in extraordinary new detail. They used a newly developed measurement technique to better understand beam loss — stray particles that travel outside the confinement fields of the accelerator. Mitigating beam loss is paramount to realizing more powerful accelerators at smaller scales and lower costs.

"It's a problem that's been haunting us for more than 20 years," said ORNL accelerator physicist Alexander Aleksandrov. "Beam loss is probably the biggest issue for high-intensity accelerators, like the Large Hadron Collider at CERN and the Spallation Neutron Source here at Oak Ridge."

Operating at 1.4 megawatts, the linear accelerator at SNS propels protons at nearly the speed of light down more than 300 yards of accelerating systems and smashes them into a metal vessel filled with swirling mercury. The collision creates "spalls" of neutrons that are sent to instruments used to study materials at the atomic scale.

"Ideally, we want all the particles in the beam to be concentrated into a single, very compact cloud," Aleksandrov said. "When particles stray away, they form low-density clouds, called a beam halo. If the halo gets too big and touches the walls of the accelerator, that results in beam loss and can create radiation effects and other problems."

The team made the measurement using a replica of the SNS linac at ORNL's Beam Test Facility. The advanced measurement technique is based on the

same approach the researchers used in 2018 to make the first particle accelerator beam measurement in six dimensions. Whereas 3D space includes points on the x, y and z axes to measure position, 6D space has three additional coordinates to measure a particle's angle, or trajectory.

"The technique is actually quite simple. We take a block of material with a number of slits that we use to cut out small samples of the beam. That provides us with a beamlet containing a smaller, more manageable number of particles that we can measure, and we can move that block around to measure other sections of the beam," said Aleksandrov.

"But, instead of cutting out 6D phase space, this time we only cut out samples in two-dimensional phase space," he said. "Basically, if you can measure in six dimensions with reasonable resolution, then you can measure in lower dimensions with much higher resolution."

The 2D measurement unlocked a radically improved level of resolution of 1 part per million, which is significant to modern accelerators for two reasons, according to Aleksandrov: It is the maximum allowable density at which beam halo is manageable, and it is the level of resolution, or dynamic range, necessary to validate and build more accurate computer modeling simulations of the beam halo effect.

"Although we could make 100 megawatt-class accelerators now, it's just not practical," said physicist Sarah Cousineau, the science and technology section head in ORNL's Research Accelerator Division. "Improving the resolution of the measurement to higher levels not only allows us to make progress in understanding and simulating beam halo, but it also advances our understanding of how to make accelerators more powerful, at smaller scales and at much more reasonable costs."

From left to right: Alexander Zhukov, Alexander Aleksandrov, Kiersten Ruisard and Sarah Cousineau. Image credit: Carlos Jones, ORNL

The team's research results are published in the scientific journal *Nuclear Instruments & Methods in Physics Research*. In addition to Aleksandrov and Cousineau, the paper's authors include ORNL's Kiersten Ruisard and Alexander Zhukov.

Labwide effort

may accelerate cancer treatment approvals

by Kristi Nelson Bumpus
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Normally, meeting U.S. Food and Drug Administration manufacturing requirements for a new active pharmaceutical agent is a multiyear process.

But for actinium-225 nitrate, used in crucial cancer treatments and clinical trials, time was of the essence. Thanks to labwide cooperation and support, ORNL implemented the requirements for its onsite Ac-225 production in just 13 months.

The result: As of January, ORNL's Ac-225 has a drug master file on record with the FDA, so that pharmaceutical companies can reference it to support applications for their own Ac-225–based drugs without disclosing proprietary information.

The FDA requires an active pharmaceutical ingredient to have an active drug master file before it will approve products containing that ingredient. This file contains information about Ac-225 derived from thorium-229 at ORNL, materials used in its preparation, and the current FDA Good Manufacturing Practice processes involved in its production.

Ac-225, a decay product of thorium-229, is used for targeted alpha therapy treatment for certain types of prostate, brain and neuroendocrine cancers, delivering high-energy radiation to individual cells or small cell clusters with minimal damage to surrounding cells. In recent years, radiation therapy with alphas has seen a renaissance as new clinical studies report dramatically improved treatment outcomes.

> *"Team members know some of these shipments are going directly to patients all over the world. It's exciting when you realize what we do matters and has a direct impact on people's lives. It can make a difference, when you can give people hope and the tools to fight cancer.*
>
> — ORNL researcher **Paul Benny**

"The promise of targeted alpha therapy is so great, demand for the isotope already outweighs the amount produced," said Laura Harvey, a scientist in the Isotope Science and Engineering Directorate's Radioisotope Science and Technology Division.

Harvey said ORNL made a significant commitment to Ac-225 production, providing dedicated hot cell and glovebox space, storage space where materials can be secured, and new equipment. The team — technicians, custodians, managers and others — received specialized training for the process.

"Everybody at the lab worked so hard to make sure the Ac-225 program had what it needed to move forward," Harvey said.

That's because they realize the importance of the work, said ISED's Paul Benny, who, like Harvey, works on ORNL's Ac-225 production team. Ac-225 is in clinical trials in the United States, and other countries have treated hundreds of cancer patients with Ac-225 and its decay daughter, bismuth-213. To augment the supply, the Isotope Program supports the production of Ac-225 through other methods as well, including with the use of accelerators.

The science that allows separation of isotopes is the result of decades of groundbreaking radioisotope separation experiments by scientists at ORNL's High Flux Isotope Reactor and Radiochemical Engineering Development Center — many now retired, Benny said.

Several years ago, a patient from another country who had benefited from treatments with ORNL-produced Ac-225 contacted an ORNL scientist involved in earlier Ac-225 production, to thank her and let her know how his life had improved.

"Team members know some of these shipments are going directly to patients all over the world," Benny said. "It's exciting when you realize what we do matters and has a direct impact on people's lives. It can make a difference when you can give people hope and the tools to fight cancer."

Harvey and Benny's team produces Ac-225 — with the support of the DOE Isotope Program — from a stockpile of thorium-229. A byproduct from past nuclear programs, the thorium material was separated and recovered to build ORNL's current inventory. Ac-225 is one of the key isotopes produced as thorium decays.

ORNL's thorium-229 stockpile is processed every few weeks to recover radium-225, which decays to the Ac-225 that is recovered and used in cancer treatments. The radium-225 that accumulates becomes a secondary source of Ac-225. Each week, the team harvests Ac-225 for further purification and packaging for shipments.

"The whole benefit to the radioactive decay is that we don't have to do anything magical to the thorium to keep it producing Ac-225," Benny said. "It is a long-lived resource that we can continually harvest."

This irradiated sample of Ac-225 at ORNL's Radiochemical Engineering Development Center glows blue because of the ionization of surrounding air by alpha particles. Earlier this year, the FDA received the drug master file for Ac-225 nitrate produced at ORNL from a thorium-229 stockpile. The isotope is in demand because it's an ingredient in targeted cancer treatments. Image credit: Jason Richards, ORNL

Better Plants Program

leads industry partners on sustainability journey

by Jennifer Burke
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As the U.S. transitions to clean energy, the country has an ambitious goal: reduce carbon dioxide emissions by 50 percent by the year 2030, if not before. One of the strategies for meeting this goal is found at ORNL, embedded within the Better Plants Program.

For the past decade, DOE has operated Better Plants as part of the Better Buildings Initiative. This initiative aims to improve lives by partnering with the public and private sectors to make homes, commercial buildings and industrial plants more energy efficient.

The industry component of the initiative, coordinated by ORNL, works with manufacturers and water and wastewater utilities to set long-term goals to achieve energy improvements. Researchers Sachin Nimbalkar, technical support lead, and Thomas Wenning, program manager for industrial energy efficiency, have worked with one simple guideline.

"We like to say we meet industry wherever they are on their sustainability journey," Wenning said. "It doesn't matter how efficient they are at the beginning

Thomas Wenning is program manager for industrial energy efficiency at DOE's Better Plants Program.
Image credit: ORNL

> *"As people develop transformative technologies in industry, they're trying to figure out how they're going to make significant improvements in carbon intensity. With Better Plants, we're giving them immediate solutions so that rather than just waiting for step changes, they can actually begin implementation. By implementing energy efficiency technologies, you can start reducing carbon intensities now."*
>
> — DOE Better Plants Program technical support lead **Sachin Nimbalkar**

of their work with us. It matters that the conversation has started. Ultimately, when their energy efficiency improves, we see that costs decrease and productivity increases."

Small changes, big impact

Nearly 250 companies have become Better Plants Program partners, representing more than 3,500 facilities across all 50 states. Cumulatively, these partners have achieved $9.3 billion in savings and amassed 1.9 QBTU — or quadrillion British thermal energy units — in energy savings since the start of the program.

"The fact of the matter is you can make major impacts with just a few facilities," Wenning said. "Slight modifications of a process or facility have resulted in savings that are equivalent to taking thousands of homes and buildings off the grid."

The Better Plants Program has worked with both well-known national industry names and locally owned and operated businesses, including cement plants, steel mills, food processors and automobile manufacturers.

"It all starts with the industry reaching out to us and setting a voluntary goal to reduce their energy intensity," Wenning said. "We work with them to assess their progress, help them establish baselines and tracking methodologies, identify areas to improve internal energy management and sustainability programs, and then oftentimes deliver training or perform an energy assessment at their facilities."

Better Plants guides partners through four core categories of benefits: recognition, to communicate partner results; peer-to-peer training, to bring industry together and share best practices; technical support, to provide employee training, resources and guidance; and research and development, to connect partners to the support available at national laboratories like Oak Ridge.

Carbon focus

While Better Plants has always focused on either reducing or improving energy use, the program's priorities change every few years.

"We rolled out a water savings initiative in 2015 and that was the first foray into expanding our scope," Wenning said. "In 2019, we began the waste reduction effort. So now you see that we're starting to fill in more of the sustainability umbrella. We cover energy, water and waste, and now we're expanding to include carbon."

Completing the sustainability picture by prioritizing carbon emissions makes sense, Nimbalkar added, and is the next logical step to Better Plants realizing even greater impact.

"As people develop transformative technologies in industry, they're trying to figure out how they're going to make significant improvements in carbon intensity," he said. "With Better Plants, we're giving them immediate solutions so that rather than just waiting for step changes, they can actually begin implementation. By implementing energy efficiency technologies, you can start reducing carbon intensities now."

Single gene makes for hardier crops

by Kim Askey
askeyka@ornl.gov

An ORNL team has discovered a single gene that simultaneously boosts plant growth and tolerance for stresses such as drought and salt. The gene also addresses the root cause of climate change by enabling plants to pull more carbon dioxide from the atmosphere.

As climate change triggers more frequent and longer-lasting droughts, water scarcity concerns are escalating. Only about 3 percent of the world's water is fresh water, and much of that is frozen in ice or otherwise unavailable to use. Agriculture is the biggest freshwater consumer worldwide, creating a need for hardier plants that can withstand drier conditions and tolerate water containing higher levels of salt.

With the aim of engineering more productive and drought-tolerant bioenergy crops, ORNL scientists at the Center for Bioenergy Innovation have been studying the mechanisms that allow desert plants such as agave and kalanchoe to thrive in dry conditions.

Desert plants use a form of photosynthesis known as crassulacean acid metabolism, or CAM, to hold carbon dioxide in their cells overnight to be turned into sugars in the daylight hours. To survive extreme desert temperatures, CAM plants open only their stomata, or leaf pores, to capture carbon dioxide during the night and keep them closed during the heat of day, avoiding water loss.

An ORNL team identified the key genes for CAM photosynthesis in 2017 using the laboratory's Titan supercomputer. Building on that study, researchers homed in on a novel variant of an important enzyme and found that it triggers two pathways simultaneously — one for carbon fixation and plant growth and another that produces proline, a key amino acid known to increase stress tolerance.

"It is unusual to find that a single genetic modification can have multiple benefits," said ORNL's Xiaohan Yang, a plant systems and synthetic biologist who led the study. "This is different than the classic model of one gene and one protein affecting one trait."

"Anything we can do to make bioenergy crops more drought tolerant and grow quickly has positive economic value," CBI Director Jerry Tuskan said. "We are looking at dedicated energy crops that do not compete with food production. To do that, we'll need to grow these crops on marginal lands that experience drought."

One gene, multiple benefits

The research team focused on a variant gene, AaPEPC1, from the desert plant agave that they had previously found expresses an important enzyme in CAM photosynthesis. They engineered the gene into tobacco, which performs photosynthesis through a non-CAM pathway. The enzyme, phosphoenolpyruvate carboxylase, is critical for nighttime fixation of carbon dioxide. As expected, the gene allowed for greater capture of carbon dioxide, which fostered tobacco plant growth and biomass yield.

The surprise came when the team found the increased biomass yield was consistent even under drought and salt

A research team led by ORNL's Xiaohan Yang used a gene from agave to engineer higher yield, improved stress tolerance and greater carbon sequestration in tobacco plants. Image credit: Carlos Jones, ORNL

conditions. Achieving simultaneous gains in yield and stress tolerance has been a big scientific challenge. Usually, it is a trade-off, with an increase in one area triggering a loss in the other. Not this time. Results showed that the dry weight of tobacco plants engineered with AaPEPC1 increased by about 82 percent over conventional tobacco under salt conditions and by 37 percent under drought stress.

> *"Our results can set a foundation for future research targeting increases in sustainable production of biomass on marginal lands with benefits for both bioenergy and carbon sequestration.*
>
> — Plant systems and synthetic biologist **Xiaohan Yang**

"These effects are most likely not specific to tobacco, so we need to do additional testing with other species," Yang said. "Our results can set a foundation for future research targeting increases in sustainable production of biomass on marginal lands with benefits for both bioenergy and carbon sequestration."

"We haven't tested the gene in corn or soybeans," Tuskan said. "Although they're grown on high-quality agricultural land, this discovery may have applications to extend their production in drier parts of the world as well."

DOE scientists deploy creativity,

speed to disrupt COVID-19

by Sara Shoemaker
shoemakerms@ornl.gov

In early 2020, before the novel coronavirus had been named a pandemic, ORNL computational chemist Marti Head abruptly switched her focus — as did many scientists and researchers around the globe — to fight COVID-19.

The world was struggling to understand this new virus, known as severe acute respiratory syndrome coronavirus 2, or SARS-CoV-2. But Head and others already knew that defeating such a highly transmissible pathogen was going to require a multipronged approach that included vaccines as well as multiple drug therapies.

Mainstream talk of therapeutics began to drop off after the FDA approved COVID-19 vaccines for emergency use authorization, and then later approved them for the prevention of COVID-19 disease in individuals 5 years of age and older.

Yet effective drug treatments still need to be in the mix, especially in anticipation of coronavirus variants expected over time.

"There's been so much focus on vaccines that development of antibodies and antiviral drugs kind of gets overlooked," Head said. "We absolutely, positively need vaccines … (to) help give us that kind of herd immunity to protect the widest population that we can. But we also need other tools."

Development of drug treatments is complex, and it often takes years to move from scientific discovery to an approved, publicly available therapeutic. As the spread of COVID-19 ramped up in 2020, DOE launched the National Virtual Biotechnology Laboratory, or NVBL, with funding from the federal government's CARES Act, and teams from across the agency's national laboratory system began assembling.

Marti Head

One of those teams is Molecular Design for Medical Therapeutics. Led by Head, the group leverages expertise in artificial intelligence and computational screening techniques used for early-stage biomedical research.

Data gleaned from the team's more recent efforts could help shorten the drug development timeline for COVID-19 drugs. The team also performs materials characterization at X-ray, light and neutron research facilities and conducts nanoscience research to accelerate scientific discovery for therapeutics targeting SARS-CoV-2.

As many national lab scientists turned from saving energy to saving lives, they gained a new level of expertise, resulting in the development of innovative research processes likely to have longer-term impacts as they shift back to their energy missions.

Energy mission, drug discovery

Head joined ORNL in February 2018 from GlaxoSmithKline to lead the lab's Joint Institute for Biological Sciences, a collaboration with the University of Tennessee. She spent about two years developing strategies to fund biological research that would leverage the lab's powerful user facilities and managing ORNL's participation in the multinational lab consortium called Accelerating Therapeutics for Opportunities in Medicine, or ATOM.

When the nation sounded the alarm on COVID-19, she drew upon her decades of experience in computer-aided drug discovery to help DOE pull together a dream team of molecular biophysicists, computational biologists and chemists.

The NVBL molecular design team surveyed the larger biomedical research landscape. ORNL and several other national labs are using artificial intelligence and computational screening techniques — in combination with experimental validation — to identify and design drug therapies to target the SARS-CoV-2 virus. The team performed that research on ORNL's Summit system, the nation's most powerful supercomputer.

Promising approaches

Generally, SARS-CoV-2 spreads through airborne droplets from an infected person. Inside the body, the virus can quickly wreak havoc, invading healthy cells in myriad ways, making copies of itself and triggering a variety of biological responses ranging from the undetectable to the deadly. The United States has reported more than 800,000 COVID-19–related deaths, and millions have perished from this disease worldwide.

"As we've seen, the virus is mutating. That's the nature of viruses, especially out in the real world in patients," Head said. "(Viruses are) continually mutating, and the mutations that allow them to be more viable grow in importance in the world."

"The rise of the delta variant brings to light the importance of a multipronged approach, including therapeutics, to tackle COVID-19," she said. "Both in the bigger picture of having this arsenal to respond as the virus changes over time and also by recognizing that trying to kill something that's not really alive … these are very hard tasks."

Within months of launching their computational–experimental research, the molecular design team offered five promising drug therapy approaches, each focusing on a unique aspect of the virus's life cycle.

One promising therapy targets the spike protein, one of the earliest and most studied points of attack against the novel coronavirus. The spikes that protrude from the virus' outer layer form a corona, giving the virus its name. It invades the cell when the spike protein binds to the human ACE2 receptor. The molecular design team used computationally designed antibodies to prevent the spike protein from binding.

If the virus binds and then enters the cell, it can mature using two proteins — the main protease and the papain-like protease. One possible drug therapy would keep the virus from maturing by blocking this activity.

ORNL scientists contributed to this potential solution with computational data and experimentation. They also contributed to the design, synthesis and testing specific to the papain-like protease, a lesser studied but highly promising antiviral target. The team characterized the main protease through world-class crystallography and X-ray and neutron experiments by ORNL's neutron scientists and performed inhibitor synthesis experiments at ORNL's Center for Nanophase Materials Sciences.

After entering the cell, maturing and replicating, the virus begins to spread throughout the body. The team has researched small molecules with the potential to become drugs that inhibit viral spread. The results have been shared with experimentalists in controlled biocontainment labs to test the small molecules on live viruses.

An increase in viral load triggers the body's immune response, while the virus itself negatively impacts the immune response by shutting it down. The team has also targeted ways to protect the body's immune response by inhibiting the papain-like protease, a key protein associated with immune response. ORNL researchers designed new small molecules fine-tuned to keep the papain-like protease from allowing the novel coronavirus to replicate inside human cells.

In the final viral replication step, new spike proteins interact with viral RNA to make new virus copies. To inhibit this process, the team is investigating ways to prevent the new virus from escaping infected cells.

Each approach, according to Head, is designed to interrupt a specific interaction between the SARS-CoV-2 virus and human cells. To achieve maximum benefit in treating COVID-19, drug developers will likely pursue a combination therapy to attack the virus on multiple fronts and reduce viral load.

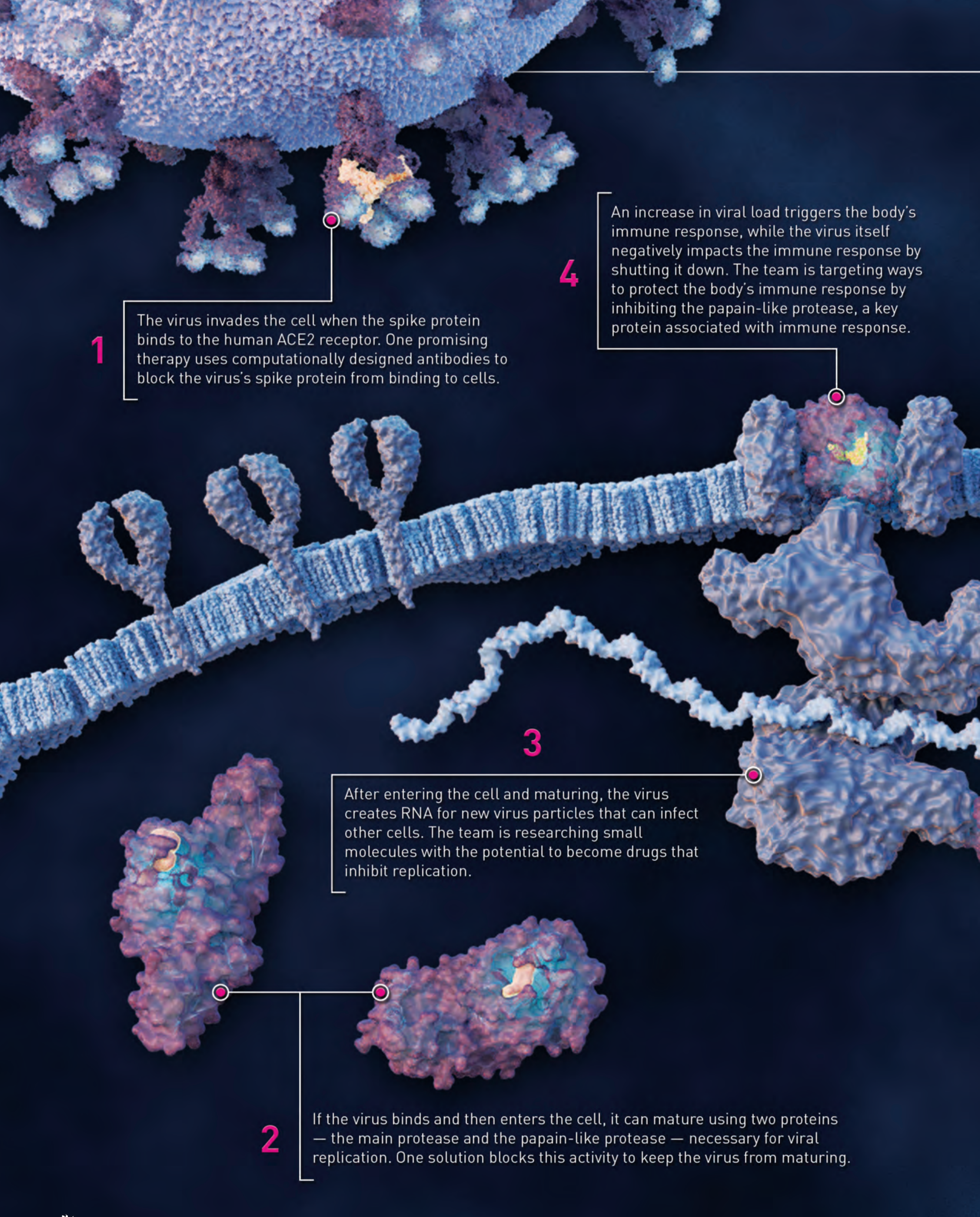
Of mice and medication

The journey from scientific discovery to an approved, marketable drug is long, and success is never guaranteed. But the NVBL molecular design team's promising early results warrant the next step: a small mouse study.

ORNL researchers determined what they think are the best candidate drug molecules from a list of papain-like protease inhibitors that will be tested in mice infected with SARS-CoV-2. In collaboration with Stanford University and SLAC National Accelerator Laboratory, the team analyzed an X-ray crystal structure of their most promising compound and found that it does bind to the protein as expected. This structure will also help guide the development of improved compounds.

Vaccines became more widely available in spring 2021. However, the molecular design team's story didn't end. Head and her colleagues continue to share their research impact and results and seek out relationships in the medical research community.

"We have relationships with several medical schools and medical centers that could potentially follow up. And we have ongoing conversations and proposals in the works with the National Institutes of Health. There does have to be this passing of the baton for someone else to take it up and move it forward," Head said.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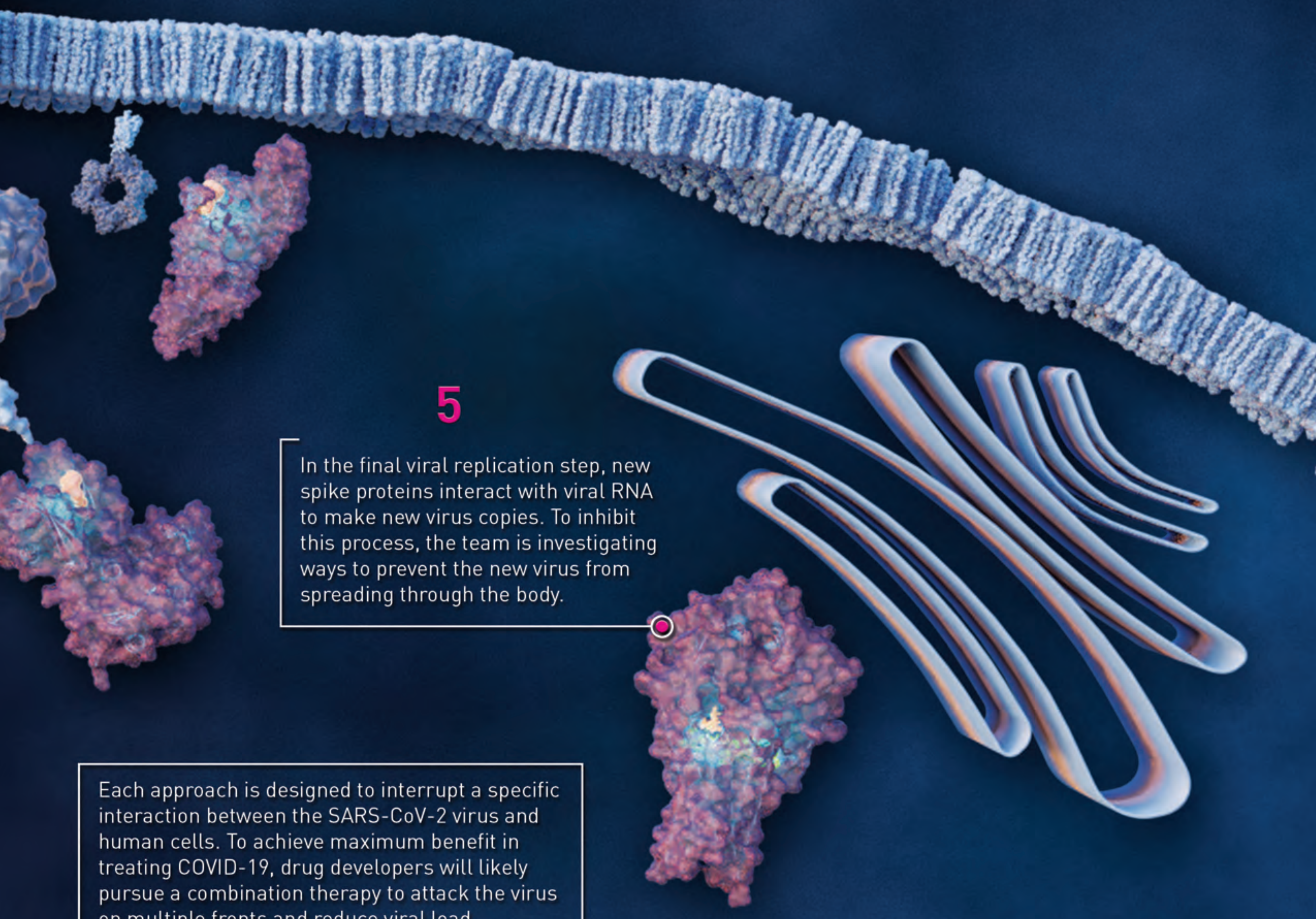
The virus invades the cell when the spike protein binds to the human ACE2 receptor. One promising therapy uses computationally designed antibodies to block the virus's spike protein from binding to cells.
2
If the virus binds and then enters the cell, it can mature using two proteins — the main protease and the papain-like protease — necessary for viral replication. One solution blocks this activity to keep the virus from maturing.
3
After entering the cell and maturing, the virus creates RNA for new virus particles that can infect other cells. The team is researching small molecules with the potential to become drugs that inhibit replication.
4
An increase in viral load triggers the body's immune response, while the virus itself negatively impacts the immune response by shutting it down. The team is targeting ways to protect the body's immune response by inhibiting the papain-like protease, a key protein associated with immune response.

Interrupting COVID-19

A collaborative research team from ORNL and other national laboratories is using artificial intelligence and computational screening techniques — in combination with experimental validation — to identify and design drug therapies to target the SARS-CoV-2 virus. Here are five promising approaches.



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This research is supported by the Department of Energy Office of Science's National Virtual Biotechnology Laboratory with funding provided by the Coronavirus CARES Act.
Image credit: Michelle Lehman

First-of-a kind superconducting magnet modules delivered to ITER site

The first of six magnet modules were delivered in September 2021 to the site of the ITER experimental fusion reactor in France, which will demonstrate industrial-scale fusion power of 500 megawatts via a self-heated plasma. The magnets, which came from General Atomics in California, make up the reactor's central solenoid and are scheduled to be installed in 2023.

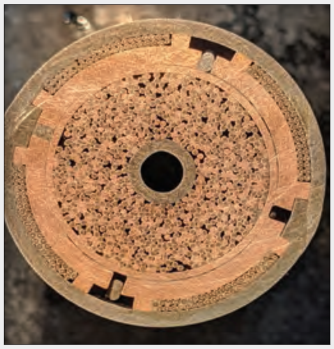
US ITER, managed by ORNL, oversees fabrication of the central solenoid. Earlier this year, the first module completed postproduction testing that simulated the ITER operational environment.

"The manufacture of the central solenoid is a great example of national laboratories and research centers coming together with industry to solve challenging engineering problems," said Kathy McCarthy, US ITER project director and ORNL's associate laboratory director for Fusion and Fission Energy and Science.

The five-story-tall, 1,000-ton magnet will initiate each plasma pulse with 15 million amperes of electrical current. The central solenoid will reach a magnetic field strength of 13 Tesla, about 280,000 times stronger than the Earth's magnetic field. Each module is 7 feet tall, 14 feet wide, and composed of 3.5 miles of superconducting cable provided by ITER Japan.

Low-resistance joints

Joints connect the module to power sources, but they can also introduce increased resistance. Three kinds of superconducting joints are required to fully power the central solenoid modules: splice joints to connect layers called pancakes at the outer turns of the module, twin box joints to connect one end of the superconducting bus bar box to a similar box from the power feeder, and coaxial joints connecting the other end of the bus bar to the module terminal. The joints were well below the resistance limit of nano-ohms.



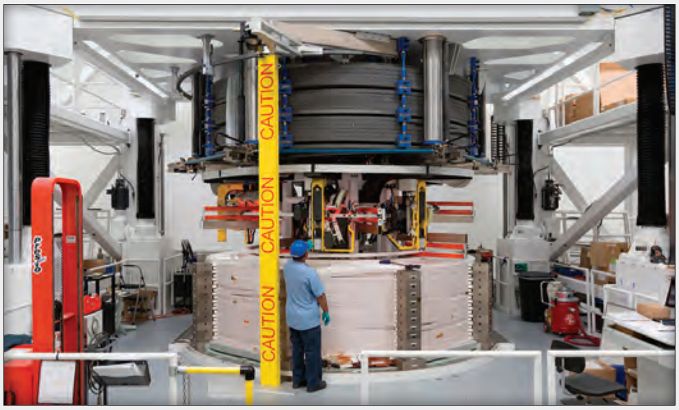
Cross-section of the redesigned, ultralow-resistance coax joint, improved with the use of Rutherford cable and smashed indium wire. Image credit: US ITER and ITER Organization

Precision winding and assembly

Module manufacturing begins with precisely wound lengths of superconducting cable surrounded by a square stainless steel outer jacket placed into the pancakes. Alignment to 1 mm must be maintained during winding. A total of 5,800 meters of conductor — about 3.6 miles — are needed for each 40-layer module.

During fabrication, pancakes are stacked, joined and, to make the assembled module superconductive, heat-treated in a large furnace. However, with this process the coils also lose the precision achieved in the winding machine. The conductor must then be uncoiled, wrapped with insulation and reassembled back to 1 millimeter precision turns.

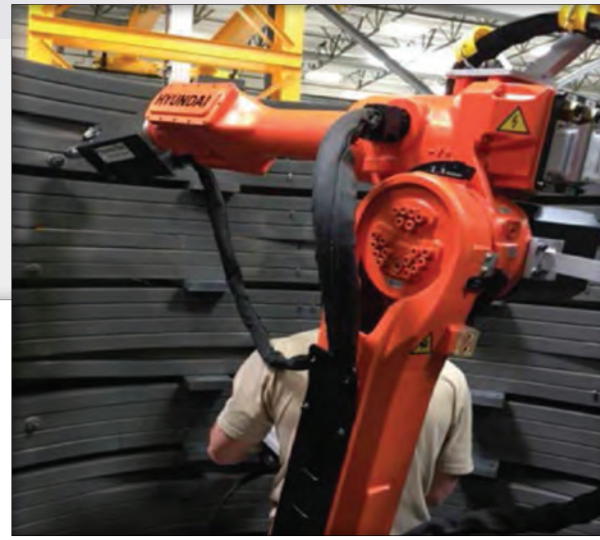
Precision winding of conductor. Image credit: General Atomics



At this stage of turn insulation, half of the module is suspended, and half is already wrapped with insulation tape. Image credit: General Atomics

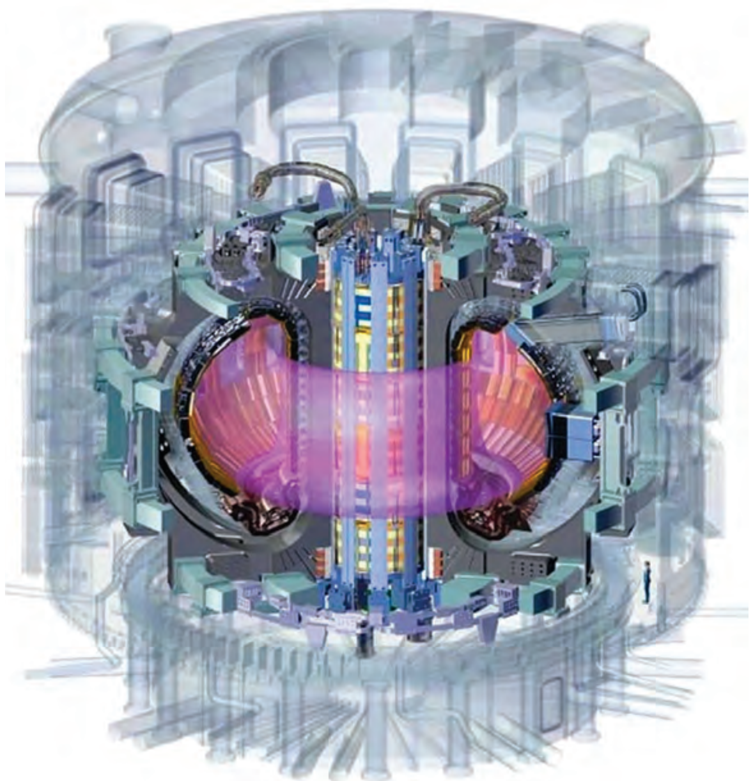
Welding challenge

A cryoplant delivers 4.2-kelvin liquid helium coolant to each module, with the coolant passing through 20 welded inlets. The helium inlets experience some of the strongest stresses within the ITER magnet system. US ITER engineering analysts determined that with robot peening at the toe of each weld, the inlets would survive more than 200,000 testing cycles — much more than the ITER design life of 60,000 cycles.



An ultrasonic peening robot strengthened critical welds in the coil. Image credit: US ITER

The heart of ITER



Six modules will be stacked to form the central solenoid of ITER. The solenoid will stand 19 meters high at the heart of the fusion device, where it will initiate and control the power-producing plasma. Image credit: US ITER

The magnet module in the final testing chamber. Image credit: General Atomics

Final test

Prior to packaging and shipment to the ITER site, the module must complete a series of tests. The module is cooled to 4.7 kelvins — about minus 452 degrees Fahrenheit — and powered to 40,000 amps, which results in internal stresses within the coil similar to what will be experienced during operation of the ITER tokamak. Central solenoid modules are the only ITER magnets tested to these extremes before assembly.

A tremendous achievement

in a tumultuous year

by Karen Dunlap
dunlapkk@ornl.gov

Five ORNL scientists have been tapped by DOE's Office of Science to receive significant research funding as part of the Early Career Research Program. They will receive grants of about $500,000 per year for five years to cover salary and research expenses.

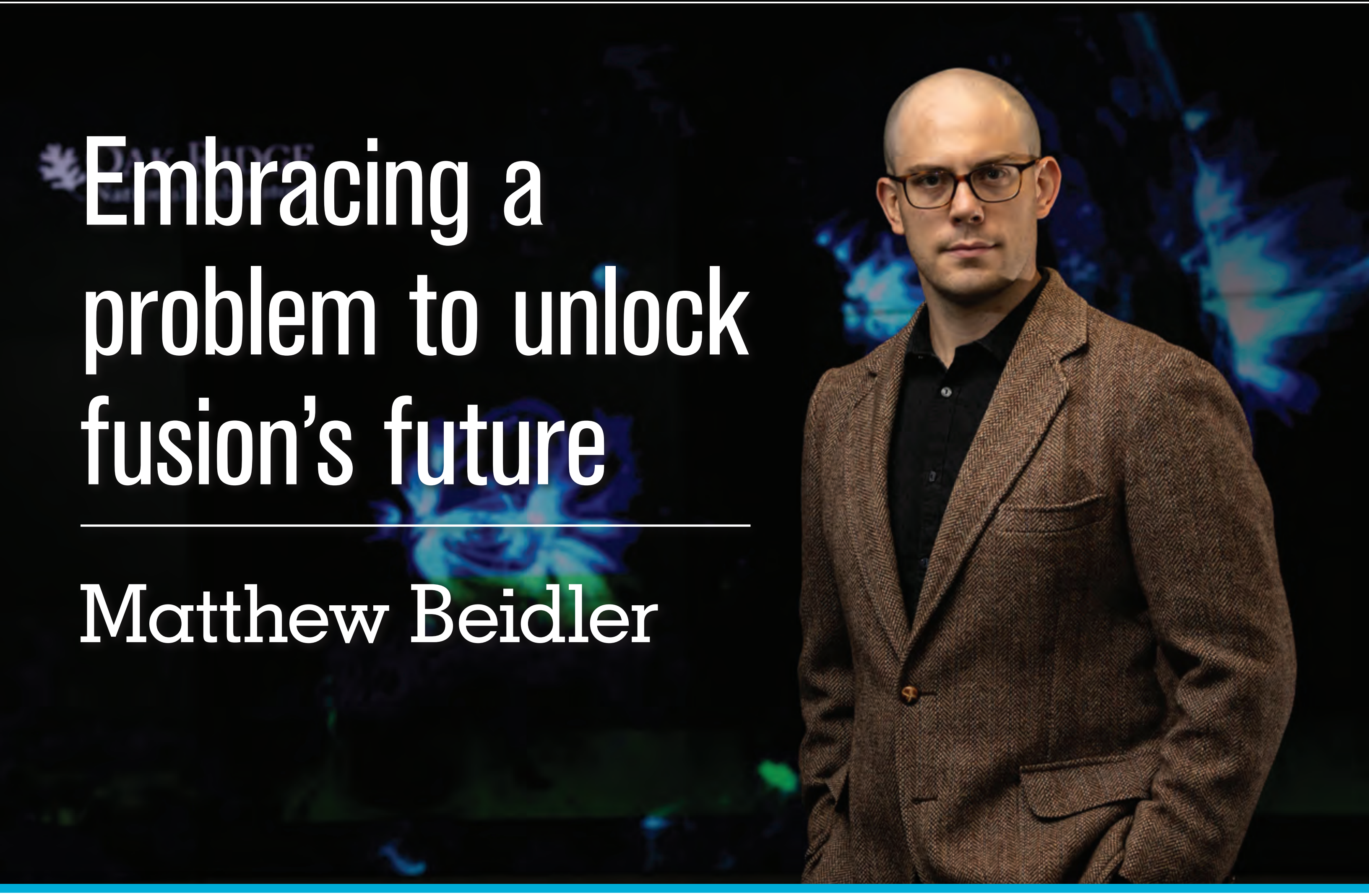
Like their peers before them, this year's winners represent a range of scientific pursuits and hold tremendous promise to make significant strides throughout their careers. Additionally, this year's winners embarked on their ambitious projects amid a world changed by the coronavirus pandemic.

Like so many other ORNL employees, they have been adapting to working mostly from home and making decisions about how to manage the merging of their family lives and careers. Over the last couple of years, they found themselves diving into their work while also baking a lot of bread, focusing on gardens and renovating homes.

> *"These early career researchers demonstrate the breadth of scientific inquiry at Oak Ridge. They are investigating complex subjects with global impact, including comprehensive climate modeling, the search for new physics and efficient fusion energy. I look forward to seeing what these talented young scientists accomplish.*
>
> — ORNL Director **Thomas Zacharia**

The ORNL winners include physicist Matthew Beidler of the Fusion Energy Division, ecologist Melissa Cregger of the Biosciences Division, neutron method development scientist Fankang Li of the Neutron Technologies Division, accelerator physicist Kiersten Ruisard of the Research Accelerator Division, and experimental plasma physicist Daisuke Shiraki of the Fusion Energy Division.

Read on to learn more about these exceptional researchers and their groundbreaking projects.



Embracing a problem to unlock fusion's future

Matthew Beidler

Matthew Beidler, a physicist in the Fusion Energy Division, started on a research path at a very young age.

"My parents like to remind me that when I was 2 or 3, I took tissues and put them on top of a lamp on the light bulb," he said. "I was always doing little experiments, seeing what would happen, and sometimes setting things on fire.

"As I got older, I was always taking apart motors of little mechanical things, splicing things together and blowing fuses — just trying to figure things out."

When the Erie, Pennsylvania, native reached his junior year of high school, he took all the available physics courses in one year. When the topic of fusion energy came up, Beidler was intrigued.

"This huge amount of energy is just waiting to be unlocked," he said. "This is an interesting problem, a hard problem.

"That's what physicists and scientists love to do, though — they find something that they don't understand and then say, 'Let's figure this out.'"

Beidler's Early Career Research Program award project aims to develop a model to predict and prevent runaway electrons in the burning plasma of the international ITER fusion reactor. If the plasma rapidly loses confinement, high-energy particles moving at nearly the speed of light can escape and damage the device.

By pairing computer codes focused on the movement of individual particles with codes focused on how the plasma as a whole is behaving and reacting, Beidler seeks to create a self-consistently coupled kinetic–fluid hybrid model that can predict and mitigate potential damage.

"In an experiment, you have many things going on, but you only have the ability to look at a limited number of these things. How do you get a full picture of a system that is changing and evolving?

"Having a sophisticated model is essentially running a virtual experiment — you can pick apart the details and see all these different aspects. In the virtual world, you can do that more readily."

Beidler said that ORNL provides the right environment to crack this problem.

"My expertise is focused on the physics, but I know that to solve this problem I'm also going to need to take advantage of ORNL's world-leading computing facilities. Now with the award resources, I'll be able to assemble and lead a team with expertise in both — something that the national lab environment really makes possible."

Harnessing microbes to boost biofuels

Melissa Cregger

A diverse group of fungi lives in symbiosis with poplar trees, sharing water and nutrients in a complex and mutually beneficial system. Understanding these interactions provides an opportunity to engineer ecosystems — maximizing soil health, mitigating adverse impacts on climate and producing resilient plants.

Because poplars grow rapidly and in many regions, they have the potential to be grown in plantations for biofuel feedstock. Melissa Cregger, an ecologist in the Biosciences Division, studies these interactions with the aim of increasing drought tolerance in poplars. For her Early Career Research Program award project, Cregger is investigating optimal poplar “holobiont,” the term used for the biological unit consisting of a tree plus all the symbiotic microorganisms interacting with its roots.

“I like to think about nutrient cycling, carbon cycling and nitrogen cycling,” she said. “I’m interested in the ways that plants and microbes interact and how can we use these interactions to alleviate climate change and increase carbon cycling in the soil. But, to do those things, we have to understand the molecular basis for how these interactions occur.”

Poplars are unique in that they can form associations with both arbuscular and ectomycorrhizal fungi. Cregger hopes to manipulate those interactions to learn more about how each operates and in which situations it might be beneficial to have more or less of one or the other.

In addition to her work at ORNL, Cregger holds a joint appointment at the University of Tennessee and is a faculty mentor in a USDA Research and Extension Experience for Undergraduates called Explore BiGG Data. The program seeks to prepare talented, diverse women for graduate programs and careers in bioinformatics, genetics and genomic sciences. Cregger draws upon her own experiences as a first-generation college student navigating graduate school and the path to finding her career focus.

“I’m passionate about this,” she said. “I want to increase the representation of women and minorities in the sciences and to mentor people like me, who didn’t know science was an option.”

Cregger also highly values the team structure and collaborative nature of working at ORNL.

“I’ve had amazing mentorship to get to this point,” she said. “A lot of people invested in me and gave me valuable feedback on my proposal.

“I think it’s important to recognize the support I’ve received. It wasn’t just me; many people have put in hard work to get me here.”

Developing state-of-the-art tools to ‘see more, imagine more’

Fankang Li

It’s Fankang Li’s job to dream up new ways to see into the dynamics at play on the subatomic level. As a neutron method development scientist in the Neutron Technologies Division, Li creates new techniques and instruments.

“Continually working toward the development of the most advanced neutron instruments allows ORNL to be a world leader in providing the best instruments for the scientific community,” he said.

Li’s Early Career Research Program award project seeks to develop a neutron probe with unprecedented resolution to obtain deeper insights into quantum materials.

This unique platform, which would boost the resolution of existing neutron scattering instruments at ORNL and across the United States, “adds a new layer to conventional neutron techniques to make the best use of neutrons, with which we could identify a very tiny change in a neutron’s behavior,” he said.

Fundamental research to comprehensively understand the interplay of quasiparticle dynamics and the discovery of new electronic phases is critical for explaining materials’ physical–chemical properties. Developing new instrumentation is necessary to drive quantum sciences forward.

“Science is based on ideas, but the relationship between science and instruments is an integral part of the story. Scientific instruments have been and will always be devices of power: Those who have the best ones can see and imagine the most,” he said. “When a new instrument comes along, new vistas open up.”

Li joined ORNL in 2016 as a Shull Fellow after receiving his doctorate in physics from Indiana University under the guidance of his advisor and mentor, Roger Pynn.

“The reason I like physics is because it is trying to explain how nature works. What’s fascinating is that physics is both consistent and cooperative. Once you understand the physical laws, they are always the same, no matter where you are or what subject you’re working on,” Li said.

"For human beings, a lot depends on culture; people speak differently and think differently. But physics is the language of nature. You may not understand a phenomenon, but it is always there, and you just need to find the way to understand it.”

At the Spallation Neutron Source, Li’s ability to drill down into a problem to get at its root provides the user community with techniques to investigate scientific questions.

“It’s a great feeling to provide a unique capability and help someone see something they would not have found otherwise,” he said.

Fighting beam loss in six dimensions

Kiersten Ruisard

Beam halo — particles ejected far outside a particle accelerator's core beam — limits the performance of high-intensity accelerators.

"As we accelerate protons to high energy, the beam carries a significant amount of power. Even one proton hitting the beam pipe is depositing power, which is causing radiation and is limiting the accessibility of our tunnels and the longevity of our accelerator hardware," said Kiersten Ruisard, an accelerator physicist in the Research Accelerator Division.

Ruisard's Early Career Research Program award project aims to improve the performance of high-power accelerators and support significant increases in beam power by developing more accurate models of beam distribution and halo.

Using the Spallation Neutron Source Beam Test Facility, Ruisard seeks to develop predictive capabilities that incorporate full and direct measurement of the beam distribution in six dimensions.

In the injector test stand, a replica of the first few meters of the SNS, the research team will map negative hydrogen ions in the first acceleration stage where complex physics are happening, which Ruisard said is challenging to model accurately.

"It sort of boils down to getting your initial conditions right to make the best possible predictions," she said.

"The particles live in a six-dimensional space. They can be three spatial dimensions that also have a momentum vector that's pointing in three dimensions," she said. "No one measures that directly. It's exciting to look at the beam that's been in front of our eyes all along, but going deeper into it and really looking at it in this high-dimensional view."

Ruisard rediscovered her interest in physics when trying out science courses during her first year at Rutgers University.

"I enrolled in Biology 101, and I think I dropped it in the first week. The vocabulary lists were so intimidating," she said. "I had a good physics background from high school, and I'd had an inspiring AP Physics teacher, but somehow I never thought physics was for me."

But, with the AP credit, she was able to jump into the second-year courses.

"It was a much smaller class, and no vocabulary, which sort of set the direction," she said smiling, "but it was also compelling because of the flexibility. You can learn about how things work on so many different scales — astrophysics to quantum physics and everything in between."

Fueling the future of fusion

Daisuke Shiraki

Researchers preparing for sustained fusion devices must shift from technologies that feed fuel to a fusion plasma's edge to ones, such as cryogenic pellets, that deliver fuel to the plasma's core.

Daisuke Shiraki, an experimental plasma physicist in the Fusion Energy Division, is developing pellet-fueling processes to control fusion plasmas at the international ITER fusion reactor and other future fusion devices. Shiraki will carry out his Early Career Research Program award project at the DIII-D National Fusion Facility in San Diego and will provide experimental studies and modeling of the plasma under pellet-fueled conditions.

"The different physics at work in fusion are so interconnected and coupled with each other that as you start to change one thing, it affects other parts of the plasma in complex ways," he said. "We need to understand that coupling. The big goal of this project is to better integrate the fueling aspect, in particular, with how everything else works."

Building on the strength of ORNL's pellet injection research, Shiraki is focused on expanding the technical capabilities of pellet fueling — making a system that is both more flexible and more precise — as the field gets closer to producing a sustained fusion reaction.

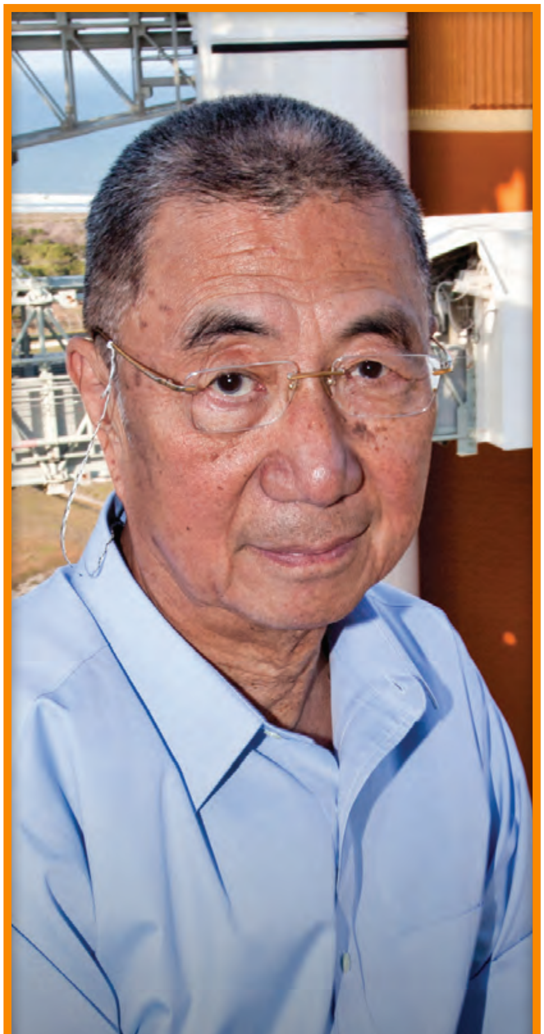
"My Early Career Research Program project is trying to take it to the next level with a more complete picture of fusion performance," he said.

Shiraki's interest in fusion began in middle school when he found an old physics textbook in his house.

"It was meant for people that are going to medical school. It explained the concepts, but without getting into the gory math," he said. "What caught my eye was the section on fusion and how it was the energy source of the sun. Fusion holds all these attractive properties and, if you could just figure out how to make it work, it would be this amazing solution."

His position as an ORNL scientist stationed in the California facility keeps him engaged and interested in his work as he continues to explore how to advance fusion to its next stage.

"DIII-D is a really fun place to work. It's one of the major fusion labs in the world but, at the same time, I'm still able to do a lot of hands-on work with the hardware for ORNL's pellet injection systems. It's a really nice mix of hands-on technical work and the theoretical and analytical side."



Samuel Ting shared the 1976 Nobel Prize in physics for the discovery of the J/psi meson, which consists of a charm quark and a charm antiquark.

More recently, he has led international collaborations in experimental physics onboard the Space Shuttle Discovery and the International Space Station, as well as at accelerators in the United States, Germany and Switzerland.

Ting is the Thomas Dudley Cabot Professor of Physics at the Massachusetts Institute of Technology. He attended the University of Michigan, earning a B.S.E. in mathematics and physics in 1959 and a doctorate in physics in 1962.

He delivered the Eugene P. Wigner Distinguished Lecture on June 17, 2021, sharing an update on the Alpha Magnetic Spectrometer Experiment, which is being conducted on the ISS.

Distinguished

Samuel Ting

1. What is the Alpha Magnetic Spectrometer, and what do we hope to discover from it?

The Alpha Magnetic Spectrometer is a physics spectrometer used in large accelerators, like in Fermilab or CERN, but this time using space. It measures the momentum, the energy and other properties of cosmic particles and nuclei.

In the past 100 years or so, we have studied cosmic rays, but those studies were done with balloons and small satellites. This is the first time a precision detector normally used in accelerators was put into space to understand the properties of all the cosmic rays.

It's like if you look at an object with your eye or with the telescope, you'll see very different things. We have been in space for 10 years, collected about 180 billion cosmic rays, up to energies of trillions and trillions of electron volts. And so far, we have many, many results on the properties of the cosmic ray elements as well as electrons and their antiparticles — positrons — and protons and their antiparticle — antiprotons. And so, they have a distribution. The rate changes with energy. Because of the precision we have been able to collect the data, and the results have completely changed our understanding of the cosmos.

2. Why are you looking for antimatter specifically?

If you believe the universe came from a big bang, then you ask, at the very beginning, the universe is a vacuum. Right after the Big Bang, there must be equal amounts of matter and antimatter. Otherwise, it would not come from a vacuum. So, we now have cosmic rays. We have Oak Ridge lab, we have MIT, and we have you and me. Where is the other half? We know the other half — antimatter — exists in accelerators, because in accelerators you have neutrons, antineutrons, protons, antiprotons from large accelerator, nuclei and its antinuclei. That is not a question. The question is if indeed all these things came from a big bang, there must be heavy antimatter in space. In the past, people have not been able to look for antimatter, because antimatter has the opposite charge as matter. So, you need a magnet. If it's positive, the magnet makes it bend one way. If it's negative, it bends the opposite way. Putting a magnet in space is difficult, because just like a magnetic compass, it will always point to the north. We managed to solve this problem; the Alpha Magnetic Spectrometer magnet is permanent and very large — about 1 meter in diameter, 1 meter in length. It doesn't rotate in space. Actually, it's a very simple trick, but people didn't find it until 40 years later.

Lecturer

3. What has the AMS revealed in its first decade?

It has revealed the flux — the rate — of electrons from very low energy to trillions of electron volts is different from positrons, and protons are different from antiprotons.

Also, all the cosmic ray nuclei in the periodic table have a behavior that is totally unexpected. Cosmic rays have two classes: primary cosmic rays and secondary cosmic rays. Primary cosmic rays like helium, carbon and oxygen come directly from nuclear fusion and are then accelerated by supernovas. The rigidity dependence of primary cosmic rays — rigidity means momentum divided by charge — is exactly the same. Secondary cosmic rays are primary cosmic rays hitting the interstellar medium, like lithium, beryllium and boron. Unexpectedly, their rigidity dependence is also exactly the same, but different from primary cosmic rays.

None of our results are predicted by any theory. You can adjust the parameters of the theory to fit one of the measurements, but the same parameter cannot fit the other measurements. We're back to square one.

4. Why was it important for you to talk with the people at Oak Ridge National Laboratory?

When I graduated from the University of Michigan, the first thing I got was a notice from the draft board. Then I went to get a physical and classified as A-1, ready to be drafted.

That was 1959. At the same time, I saw at the University of Michigan Physics Department, there was an announcement from Oak Ridge on behalf of the Atomic Energy Commission. There was a national competition to select some students in a competitive way who were good at math and physics and biology. That's because, in those days, they were competing with the Soviets, who had just launched Sputnik. They wanted to catch up and encourage people to enter the competition.

So, I went to the competition and was selected. Once you're selected, you could go to any graduate school, and the Atomic Energy Commission, via Oak Ridge, would pay your tuition and $2,000 a year for support. Mind you, in 1959 that was more than enough to go to graduate school.

So, I wrote to Oak Ridge and said I wouldn't be able to accept this AEC fellowship because I'd been drafted. I think someone in Oak Ridge got in touch with someone in Washington and said they should not draft me.

That's why I didn't go to Vietnam.

After I got my degree, the first offer I had was from Livermore. And I remember it was $30,000 a year — at that time a very high salary. But it had one condition: I could not publish my work. Then I got a second offer, from Columbia University as an instructor. It was $7,500 a year. That's how I went to Columbia and later MIT.

The Eugene P. Wigner Distinguished Lecture Series in Science, Technology, and Policy gives scientists, business leaders and policymakers an opportunity to address the ORNL community and exchange ideas with lab researchers. The series is named after Eugene Wigner, ORNL's first research director and recipient of the 1963 Nobel Prize in Physics.

ORNL is proud of its role in fostering the next generation of scientists and engineers. We bring in talented young researchers, team them with accomplished staff members, and put them to work at the lab's one-of-a-kind facilities. The result is research that makes us proud and prepares them for distinguished careers.

We asked some of these young researchers why they chose a career in science, what they are working on at ORNL, and where they would like to go with their careers.

Luc L. Dessieux

Postdoc, Neutron Scattering Division
Ph.D., Physics, University of Tennessee, Knoxville
Hometown: Cap-Haitien, Haiti

What are you working on at ORNL?

My research involves the computational modeling of neutron transmission spectra through polycrystalline materials, based on their single-crystal components. The goal is to develop tools that enable modeling of the complex mesoscale conditions found in manufactured components.

What would you like to do in your career?

I would like to continue working with diffraction techniques in research to explore or improve techniques that characterize the physical properties of engineering materials.

Why did you choose a career in science?

I enjoy gaining a deeper understanding of nature and enjoy problem solving.

Aaleyah Lewis

Graduate student, Cyber Resilience and Intelligence Division
Ph.D. student, Computer Science and Engineering, University of Washington
Hometown: Columbia, Maryland

What are you working on at ORNL?

My work involved designing and developing an interactive tool to assist cyber analysts in evaluating anomalous behavior relating to machine activity. This tool consisted of a multiview visualization system that helped analysts prioritize the most anomalous events produced by machines.

What would you like to do in your career?

I will continue to conduct human-computer interaction research, specifically developing inclusive and accessible technology to empower and improve the quality of life for individuals with diverse ranges of ability. My goal is to build technology that inspires people to embrace their differences and feel confident while interacting with systems.

Why did you choose a career in science?

Since my dad bought me my first toolbox at a young age, I have been fascinated with STEM. It wasn't until freshman year of undergrad that I was introduced to computer science. The interdisciplinary facet of CS captivated me and enabled me to combine my interests of computing, engineering and psychology.

Phil Lotshaw

Postdoc, Computational Sciences and Engineering Division
Ph.D., Physical Chemistry, University of Oregon
Hometown: Seattle, Washington

What are you working on at ORNL?

At ORNL I'm studying a quantum computing algorithm for solving optimization problems. Quantum computing is a new field, and everyone is hoping we may see important improvements over conventional computing methods in the near future. The algorithm I'm studying is one of several potential near-term applications.

What would you like to do in your career?

I'm interested in learning about nature and how things work. I'm not sure exactly what I'll end up doing, but there's lots of interesting opportunities out there.

Why did you choose a career in science?

I always enjoyed mathematics and saw physics and chemistry as ways to use math to understand the real world. I chose a career in science because it gives new perspectives on how to think about the world.

Peter Joseph Queturas Santiago

Graduate student, Center for Nanophase Materials Sciences
Ph.D. Student, Materials Science and Engineering, University of California, Irvine
Hometown: Honolulu, Hawaii

What are you working on at ORNL?

Catalysts play a vital role in various areas such as health care, energy and pollution. I investigate transition metal catalysts by designing synthesis procedures and probing their inherent properties at the atomic level. Findings can elucidate catalytic mechanisms and provide insight on methods for developing efficient earth-abundant catalysts.

What would you like to do in your career?

I want to continue pursuing renewable energy research and develop robust catalysts. To reach my goals, I plan on becoming a national lab staff scientist, followed by industry leadership positions to manufacture affordable clean energy devices. I will also mentor the next generation of scientists through internships and diversity events.

Why did you choose a career in science?

I can be creative! Many topics interest me, and collaborative research presents me opportunities to develop interdisciplinary solutions to global issues. As a result, I constantly learn and interact with different fields while also finding new passions to pursue. Science is exciting, and I look forward to the journey ahead.

Emily Costa

Graduate student, Computing and Computational Sciences Directorate
Ph.D. Student, Computer Engineering, Northeastern University
Hometown: Sarasota, Florida

What are you working on at ORNL?

My work analyzes the expected performance of BERT, a transformer-based machine learning technique for natural language processing pretraining, on Frontier, the soon-to-be first exascale supercomputer. This enables the CANDLE project to train deep learning models that accurately classify and analyze pathology reports on Frontier for the Exascale Computing Project in collaboration with the National Cancer Institute.

What would you like to do in your career?

Later in my career, I want to return to ORNL as a full-time staff scientist. I have always been amazed by the level of scientific progress and resources driven by ORNL. Also, every employee I interact with at the facility is incredible.

Why did you choose a career in science?

I chose a career in science because it simply felt instinctive to me. I love delving into methods and frameworks of thinking. I love the challenge of adding to humanity's knowledge and exploration.

Xingang Zhao

Postdoc, Nuclear Energy and Fuel Cycle Division
Ph.D., Nuclear Science and Engineering, Massachusetts Institute of Technology
Hometown: Nanjing, China

What are you working on at ORNL?

I study ways to make nuclear energy safer, more cost-competitive and better prepared for a larger role in decarbonizing the U.S. energy system. My current research seeks to develop and demonstrate interpretable artificial reasoning frameworks that advance health management capabilities to help reduce operation and maintenance costs of a nuclear power plant.

What would you like to do in your career?

I would like to be a part of a long-term campaign to continue improving the competitiveness of nuclear energy in a carbon-constrained world. I want to leverage my domain knowledge and develop expertise in artificial intelligence for nuclear applications. I also hope to be a good mentor and educator in the future.

Why did you choose a career in science?

Growing up in China, I was passionate about how science and technology could revolutionize the world. Then, as I moved to France for college, I zeroed in on low-carbon energy systems and became captivated by the multidimensional, multiphysics nature of nuclear reactors. That was the science I wanted to dedicate my career to.

COVID-19 mRNA vaccines have Oak Ridge roots

by Jim Pearce
pearcejw@ornl.gov

The COVID-19 pandemic has added a lot of new terms to daily conversation. Phrases like "mask mandate" and "social distancing" will probably fall into disuse when COVID-19 passes from the scene. However, the term "mRNA vaccine" is likely to have more staying power.

Messenger RNA — mRNA — vaccines, such as the highly effective COVID-19 jabs developed by Pfizer and Moderna, are the first inoculations of their kind to be approved by the FDA for use against any disease, and they have had a profound effect in curtailing infections.

mRNA is a specialized type of RNA — a molecule that's similar to its cousin, DNA, the molecule that carries genetic information in all known forms of life.

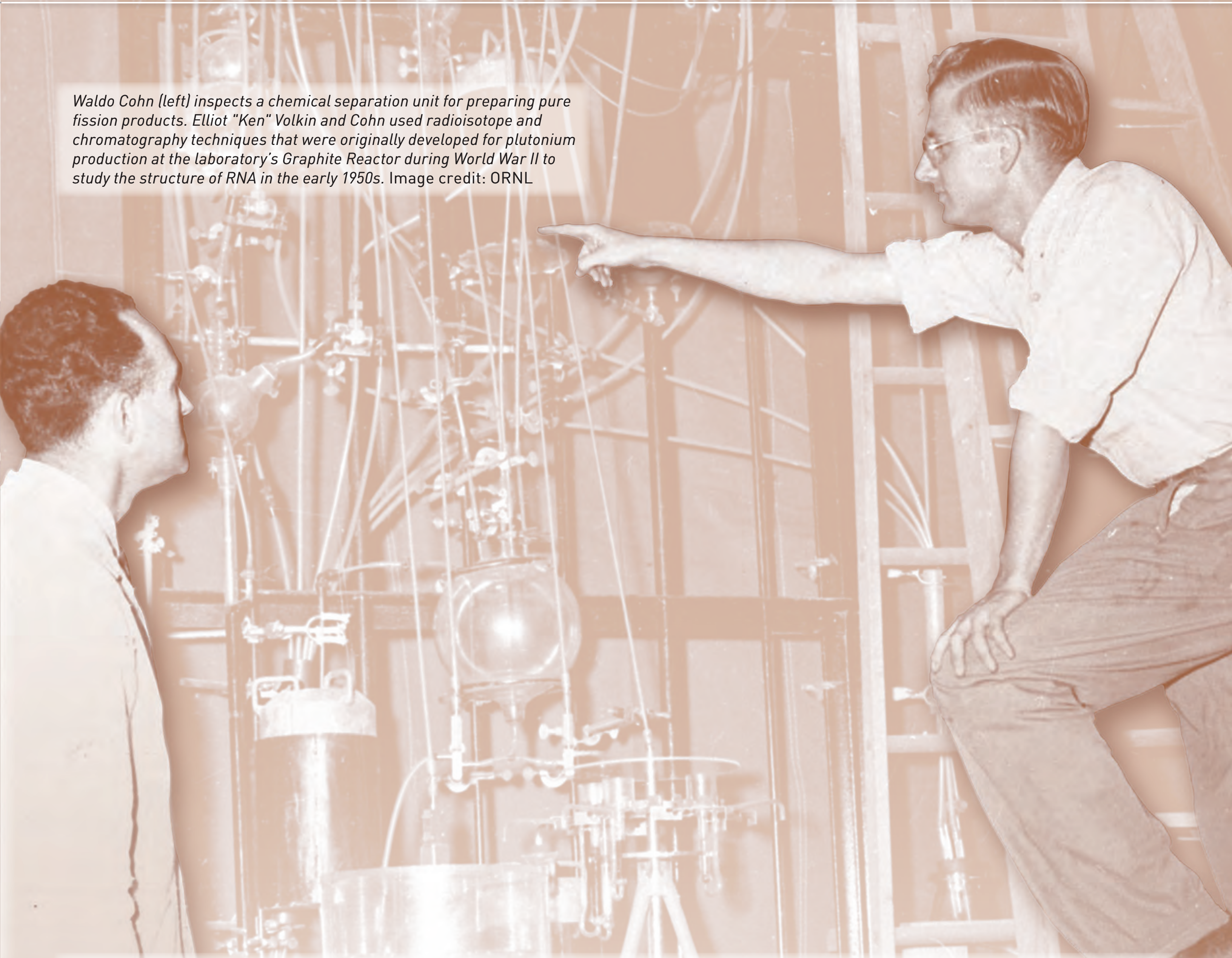
Early studies

Studies on the structure of RNA were done at ORNL in the early 1950s by biologist Elliot "Ken" Volkin and biochemist Waldo Cohn. They used radioisotope and chromatography techniques that were originally developed for plutonium production at the laboratory's Graphite Reactor during World War II.

In 1956, further research by Volkin and ORNL biologist Lazarus Astrachan enabled them to observe the role that RNA plays when a virus infects a bacterium. This interaction proved to be critical to understanding the role that RNA plays in viral infections.

Paul Berg, winner of the 1980 Nobel Prize in Chemistry, said Volkin and Astrachan discovered that, when a bacteriophage virus infects a bacterium, the virus takes over the cell's protein-making machinery and instructs it to make viral proteins. The coding sequences of the virus's genes are copied from its DNA into short-lived RNAs that are transported out of the nucleus into the cytoplasm, where the proteins are assembled. Because these RNAs

Elliot "Ken" Volkin (above) and Lazarus Astrachan's observations of the role RNA plays when a virus infects a bacterium ultimately helped to pave the way for a new class of pandemic-beating mRNA vaccines. Image credit: ORNL



Waldo Cohn (left) inspects a chemical separation unit for preparing pure fission products. Elliot "Ken" Volkin and Cohn used radioisotope and chromatography techniques that were originally developed for plutonium production at the laboratory's Graphite Reactor during World War II to study the structure of RNA in the early 1950s. Image credit: ORNL

transport information from genes in the nucleus to the cytoplasm, they are called messenger RNAs.

Former ORNL director Alvin Weinberg said that Berg described these studies on mRNA as an "unsung but momentous discovery of a fundamental mechanism in genetic chemistry" and a "seminal discovery [that] has never received its proper due."

DNA-like RNA

Volkin and Astrachan called this new kind of RNA "DNA-like RNA" and spent several years investigating its behavior. Their findings, published in 1956, received a less-than-enthusiastic reception in the biology community. Volkin reportedly thought that the findings weren't widely accepted because they didn't agree with theory at the time — even though he and Astrachan repeated the studies several times with the same results.

Five years later, French scientists François Jacob and Jacques Monod published a paper that further illuminated the function of mRNA, an accomplishment for which they received the 1965 Nobel Prize in Medicine and Physiology.

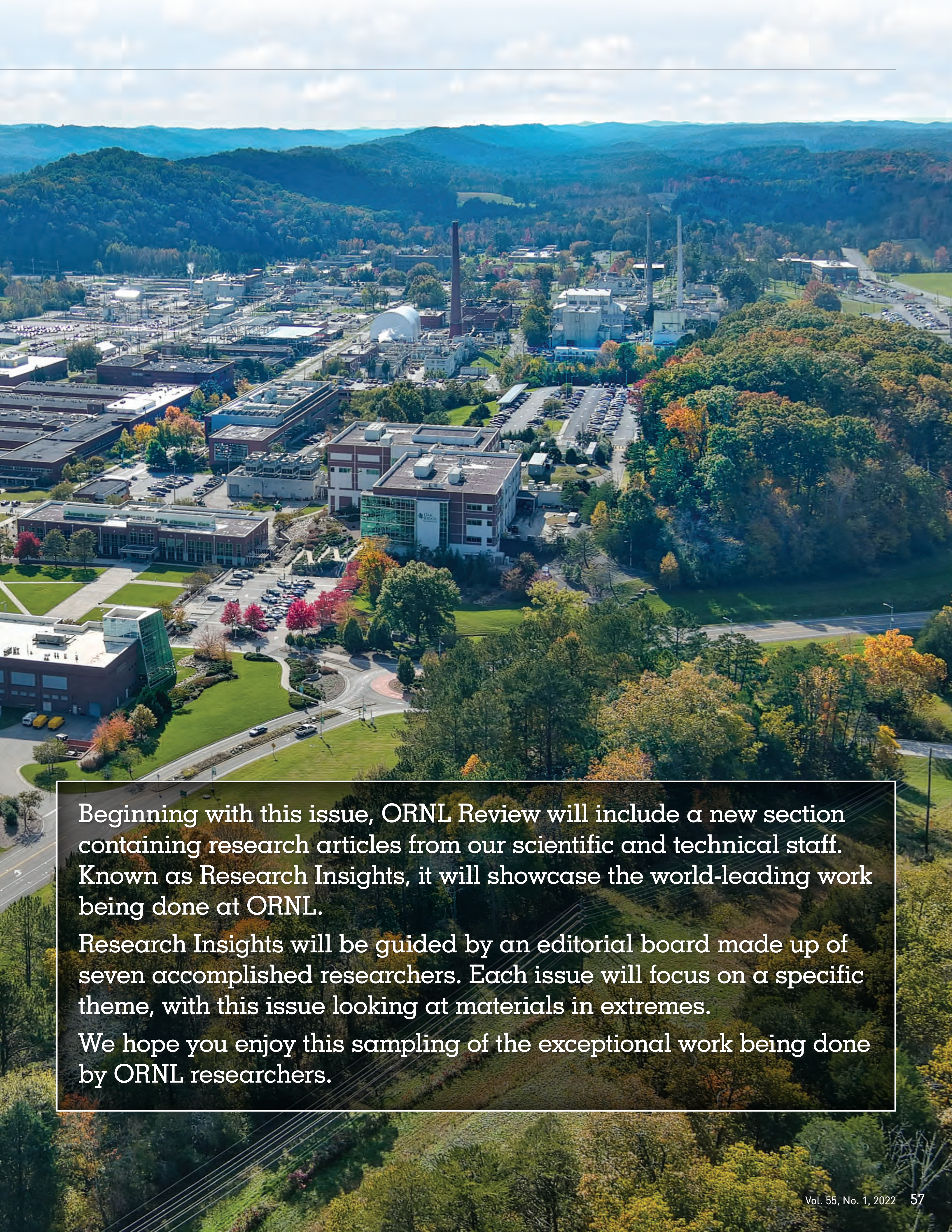
Special delivery

The mRNA vaccines developed over the last two years to combat COVID-19 take advantage of mRNA's knack for delivering instructions by telling cells to build a piece of the COVID-19 spike protein that enables the virus to attach itself to human cells.

Once this fragment of the COVID-19 protein appears on the surface of cells, the body's immune system recognizes it as a threat and starts making antibodies to eliminate it. Later, when a COVID-19 virus sporting the same spike protein appears, antibodies are already on hand to defend against it.

The success of mRNA vaccines in slowing the COVID-19 pandemic makes it likely that we will soon see efforts to apply similar technology to the task of warding off a range of infectious diseases. It also illustrates the importance of basic scientific research — like Volkin and Astrachan's findings — which, although they were dismissed at the time, ultimately helped to pave the way for a new class of pandemic-beating vaccines.

Welcome to Research Insights



Beginning with this issue, ORNL Review will include a new section containing research articles from our scientific and technical staff. Known as Research Insights, it will showcase the world-leading work being done at ORNL.

Research Insights will be guided by an editorial board made up of seven accomplished researchers. Each issue will focus on a specific theme, with this issue looking at materials in extremes.

We hope you enjoy this sampling of the exceptional work being done by ORNL researchers.

Pore-Resolved Direct Numerical Simulations of Chemical Vapor Infiltration

V. Ramanuj,[1] R. Sankaran,[1] John Turner[2]

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INTRODUCTION

Chemical vapor deposition/infiltration (CVD/CVI) [1] remains one of the fundamental material processing techniques in advancing materials fabrication for semiconductor, microelectronic, optics, nuclear, friction (brakes), and propulsion applications. Due to their ability to offer higher-temperature capability over metallic superalloys at significantly reduced weight, silicon carbide (SiC)–reinforced ceramic matrix composites (CMCs) are currently a key enabling technology to reduce fuel consumption and emissions in the gas turbine industry. CVI can be used to completely densify a preform shaped almost like the final part and, therefore, is suitable for highly engineered components such as those in the high-temperature gas path of an engine. Manufacturing CMC parts through CVI, however, has proven time-consuming and expensive because of the complexities of creating advanced composite materials.

During CVI, gaseous vapor infiltrates the porous preform component held in a high-temperature reactor chamber, undergoes chemical conversion, and is deposited in solid form to produce a component with the desired low porosity and high strength. Unless the vapor species can completely infiltrate and egress from the complex network of flow channels in the porous material, the deposition will be nonuniform and poor. Long processing times are needed to ensure uniform chemical deposition of the matrix, which increases manufacturing cost. While impressive advancements have been made using microscopy and high-resolution x-ray tomography to measure microstructural properties, challenges remain in characterizing porosity distribution and densification during the cycle. Optimization of such complex phenomena through experimentation alone is challenging due to long processing times, high processing temperatures, and lack of in situ monitoring. Physics-based modeling and simulation are essential to improve the fundamental understanding of CVI processes and to provide an alternative to expensive trial-and-error manufacturing approaches.

Modeling and simulation provide a virtual sandbox for manufacturers and industry to test design parameters and identify strategies to make CVI processes more reliable and efficient. Furnace-scale computational fluid dynamics (CFD) simulations are employed by the industry to model the temperature and composition nonuniformities within production-scale reactors and the resultant part-to-part densification differences. The CFD simulations employ effective porous media models at unresolved part scales, which are based on fundamental assumptions about microstructural properties. The effective porous media models are important for correctly determining the deposition rates as well as the transport of reagents through the media. As the pore network geometry is dependent, not only on the initial preform, but also on the topological changes that occur during the densification process, these models have been a large source of uncertainty. Direct numerical simulation (DNS) resolves the pore structure within a preform without resorting to effective media models. Further, the geometry physically evolves due to fundamental physical processes, so the microstructural states need not be assumed or modeled.

BACKGROUND

Oak Ridge National Laboratory (ORNL) is well known in the CMC community due to the far-reaching impacts of its past programs in CVI processing [2] and modeling [3]. Recent advances in DNS methods for evolving interfaces between materials [4] and the availability of high-performance computing (HPC) resources have made it possible to apply advanced simulation techniques to CVI, to gain fundamental understanding and modeling insights. The aerospace industry has seen recent increased interest in further improving CVI processing techniques to develop damage-tolerant ceramic materials that can tolerate high temperatures. The current state of the art in industry for simulating CVI relies on lower-fidelity models using their in-house computing resources. High-fidelity DNS of CVI processing and HPC simulations are currently beyond the in-house capabilities of industry and is one of the areas where industry has sought collaboration with ORNL.

DNS conducted at ORNL to study CVI densification of SiC is just one example of a broader trend across industries to utilize national laboratory HPC capabilities and expertise to improve manufacturing processes. It was the motivation behind the High Performance Computing for Manufacturing (HPC4Mfg) program [5, p. 4], initiated in 2015 by the Advanced Manufacturing Office (AMO) in the US Department of Energy's (DOE's) Office of Energy Efficiency and Renewable Energy (EERE). The program combines DOE's world-class computational facilities and scientific expertise, in collaboration with US manufacturers, to tackle major industry challenges. What started as a partnership between three national laboratories—ORNL, Lawrence Livermore National Laboratory, and Lawrence Berkeley National Laboratory—has now expanded to include most of the national laboratories. The program provides funding for national laboratory resources, with industry partners contributing at least 20% cost-share, enabling collaborators to address challenges in process optimization and design, performance, and failure prediction; conduct accelerated testing; and explore return on investment in advanced modeling and simulation. To date

HPC4Mfg has released 12 solicitations, resulting in projects that benefit many areas of the US manufacturing sector.

Rolls Royce Corporation (RRC) is a leading developer of high-temperature CMCs primarily serving the aerospace, defense, and energy markets. RRC specializes in producing structural SiC composites with SiC reinforcement for extreme environments, utilizing proprietary and patented CVI methods to produce these composites. The team from RRC, led by Dr. Chong Cha, partnered with ORNL to conduct DNS of the CVI process for various preform geometries to study the effects of process operating conditions. Quilt, a DNS solver developed at ORNL for multiphase and porous media flows, was used for performing the numerical simulations. An industry standard validation case was chosen for the preform geometry, which was composed of multiple layers of 5-harness satin (5HS) weave and for which x-ray computed tomography (XCT) images were available. The proposal was funded through the HPC4Mfg program, and HPC resources were obtained through the Oak Ridge Leadership Computing Facility (OLCF) Accelerating Competitiveness through Computational Excellence (ACCEL) industry partnerships program.

Separately, ORNL, led by J. Allen Haynes, initiated a Laboratory Directed Research and Development (LDRD) project to establish a modern research facility and computational workflow for the design and synthesis of ultrahigh-temperature structural ceramics. Under this project, additively manufactured powder-based preforms were processed through CVI at ORNL. Pore-resolved DNS of the CVI process was performed and validated against the experimental characterization, adding physics-based, high-fidelity simulation to the computational workflow.

RESULTS AND DISCUSSION

The ORNL team, composed of this paper's authors, developed a DNS solver called Quilt for interface-resolved simulations of multiphase flows in complex porous media. Quilt is a structured finite difference flow solver with immersed boundary capabilities [6], well-suited for representing complex fiber bundles, weave geometries, and packed particles without requiring time-consuming mesh generation. Furthermore, Quilt includes a level set solver [4] for evolving interfaces, which allows time-evolving topological changes to be captured on a static structured mesh without the need for expensive remeshing. It uses a distributed memory parallelism using a multiblock domain decomposition, along with on-node parallelism using Kokkos [7] and graphics processing unit–capable parallel execution patterns. Quilt has been ported to the HPC systems at the OLCF, including the former flagship supercomputer, Titan, and Summit, the nation's most powerful supercomputer. CVI in a porous medium presents a complex interplay of several physical and chemical phenomena involving species transport, temperature distribution, gas-phase and surface chemical reactions, deposition of solid on the preform, and the change in porous media topology due to the deposition. The convection of reactant gases within the CVI reactor can create a temperature and concentration profile based on the local convective and radiative effects. The simulations assume that the concentrations are uniform at a finite distance away from the preform. They also assume that the temperature is uniform across the preform thickness. The 3D simulations are performed using periodic boundary conditions in the two directions parallel to the preform. As a result, the net transport of reactants through the lateral boundaries of the preform are ignored, and only the transport normal to the preform thickness is considered. Note that the complex 3D flow channels resulting from the geometry are fully resolved. Additionally, the simulations reported here consider diffusive transport of the species through the preform without bulk advection. The former is representative of isothermal CVI, while the latter would be important in forced-flow CVI. The system is assumed to be in a pseudo-steady state, such that the time scales of the interface motion over a representative length scale, such as the tow width, is much longer than the time scales of thermal diffusion over the same length. Typical CVI processing times are on the order of days, several orders longer than diffusive time scales of gaseous reagents. Therefore, the simulation is performed using an operator-splitting strategy where the interface motion is updated alternately with the solution of the quasi-steady-state diffusion equation.

Simulations of CVI in Fiber-Woven Preforms. Initialization of a complex multilayered weave on a structured mesh to produce an implicit level set function is a computationally daunting task. We followed a multistep workflow to create such a geometric representation. An idealized representation of the weave geometry was constructed using TexGen [8] to produce a discretized stereolithography (STL) model of a warp/weft bundle composed of 50 fibers per bundle. The STL model is used to initialize the level set function on a structured mesh within Quilt. All the subsequent geometric transformations and assembly are performed on the structured mesh, thereby allowing high-resolution representations to be created efficiently (see Figure 1). The simulations were performed at two resolutions. The tow-resolved 3D model consisted of 840 cells on each dimension of the 5HS unit cell, or 592.7 million cells total. The fiber-resolved 3D model consisted of 2,400 cells on the two transverse directions and 1,800 cells in the weave normal direction, or 10.37 billion cells total. The simulations were performed for a range of the nondimensional Thiele modulus, K, which was defined as the ratio of the diffusive time scale to the chemical time scale. The Thiele modulus represents the CVI processing operating condition where the fixed pressure and isothermal temperature determine the chemical kinetic rate and reagent diffusivities. A very small value of the Thiele modulus corresponds to a slow chemistry, and a very large value of the Thiele modulus corresponds to a fast chemistry. Simulations were performed for $K = 0.001$, 0.01, and 0.1. Figure 2 shows the terminal porosity achieved as a function of the normal distance across the weave for $K = 0.001$, 0.01, and 0.1. It is seen that at the slow chemistry limit ($K = 0.001$), uniform densification occurs throughout the weave. At larger values of K, the densification at the center is poor while the outer layers have fully densified, effectively sealing the inner porosity from the chemical vapor. A parametric study was conducted by systematically varying K and selecting between overlapped, aligned, and random layering strategies. The results of the study were used to determine the influence of layer offsets on densification and to verify the modeling assumptions used in reactor-scale CFD models, as reported in [9], [10].

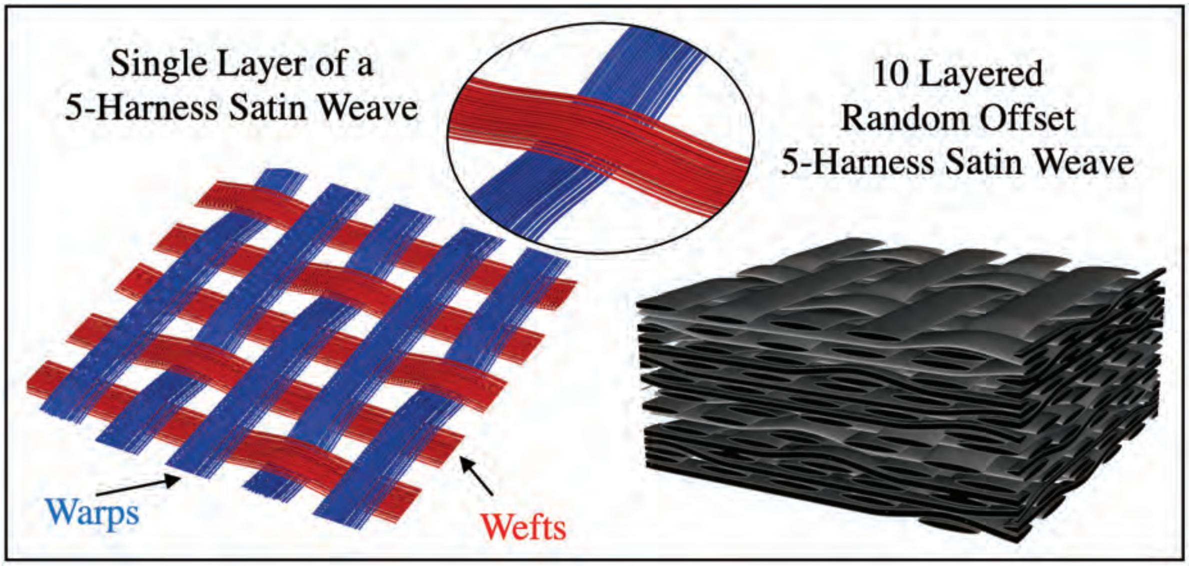

Figure 1. Geometric model used for the multilayered weave. A warp/weft is composed of a bundle of 50 fibers. A single layer of 5HS weave is created through geometric transformations on the tow and then layered with specific offset patterns. (Credit: Ramanuj et al.)

Simulations of CVI in Additively Manufactured Powder Preforms. Numerical simulations were performed to validate the DNS formulation and approach by comparing DNS results against results from additively manufactured (AM) preforms with disc and spherical geometry. The DNS of CVI was performed using finite difference on a structured Cartesian mesh. Practical geometries have curvature that impacts densification through focusing or defocusing. Convex surfaces have a focusing effect where less reagent needs to diffuse with increasing depth from the surface. On the other hand, concave surfaces are defocusing and need more reagent to diffuse with increasing length. The effect of curvature is addressed by a shape function in the DNS formulation, thereby making the results applicable to complex curved preforms. The validation against the experiments was used to solidify the shape function approach in the DNS formulation. DNS was also used to determine an effective activation energy of densification that accounts for the microstructure of the porous medium, and its evolution, thereby providing an effective media model for use in reactor-scale CFD simulations.

We used a computational workflow that generates a periodic packing of noninterfering spherical particles, matching the powder size distribution and initial density (35%), of the green AM preform. Note that, although the workflow can produce periodic packings of ellipsoidal and oblong particles, to match aspect ratio variations, the work reported here was limited to spherical particles. The experimental data collected at the ORNL CVI facility and used for DNS validation corresponded to isothermal CVI at a range of temperatures. The processing was performed for 96 h, when it was expected to have reached terminal densification, and micrographs of the final processed samples were used to determine the density as a function of depth from the surface. 3D DNS was performed using a domain with 150 million grid points, a size that corresponds to the full radial distance of the spherical preform and to a smaller distance in the two transverse directions with periodic boundary conditions. The initial preform geometry was composed of more than 100,000 particles packed to match the initial density of the AM preform, which was then translated to an implicit level set function on the structured mesh within Quilt. The chemical kinetics model for deposition of the ceramic phase from gaseous precursors assumed a single-step mechanism, with the source term described using an effective activation energy [11]. The chemical kinetics varies exponentially with temperature, while the diffusivity is weakly dependent on temperature. Therefore,

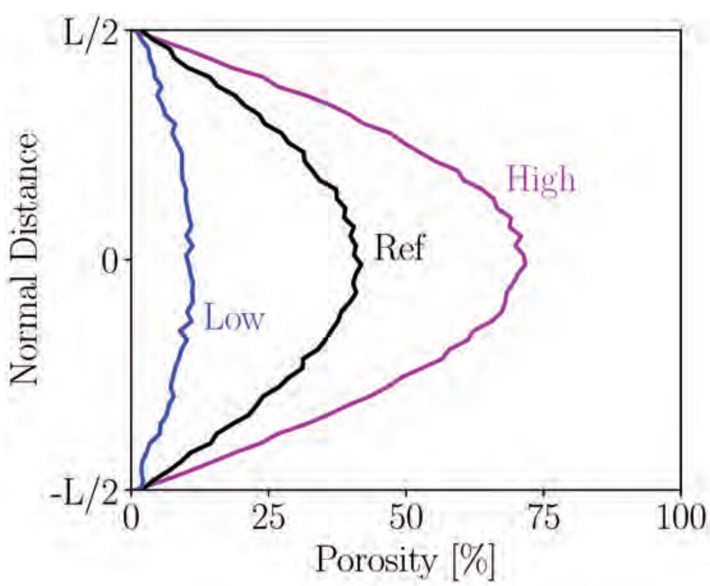

Figure 2. Illustration (not actual results and not to scale) of the expected distribution of terminal porosity after CVI processing predicted by the simulations. The terminal porosity is averaged in the two transverse directions and obtained as a function of the normal distance. The three cases illustrated correspond to various values of the Thiele modulus (K). At high values of K, the terminal porosity is high (poor densification) at the core, and vice versa for low values of K. (Credit: Ramanuj et al.)

the dimensionless Thiele modulus is a strong function of the isothermal CVI processing temperature.

DNS was performed on Summit to simulate the isothermal CVI at a range of Thiele moduli. The numerical model was validated against experimental findings based on several key criteria determining the densification behavior, namely, total density, porosity distribution, residual porosity, and time to terminal density [12]. Experimental micrographs were used to determine the radial distribution of porosity at terminal conditions and compared against DNS to derive an apparent activation energy. A comparison of the total density measured experimentally and obtained from the simulation is shown in Figure 3. A comparison of the experimental and DNS results provides a validated Thiele modulus, a temperature correlation that can be used to predict the dependence on temperature for other preform geometries and to inform process-scale models.

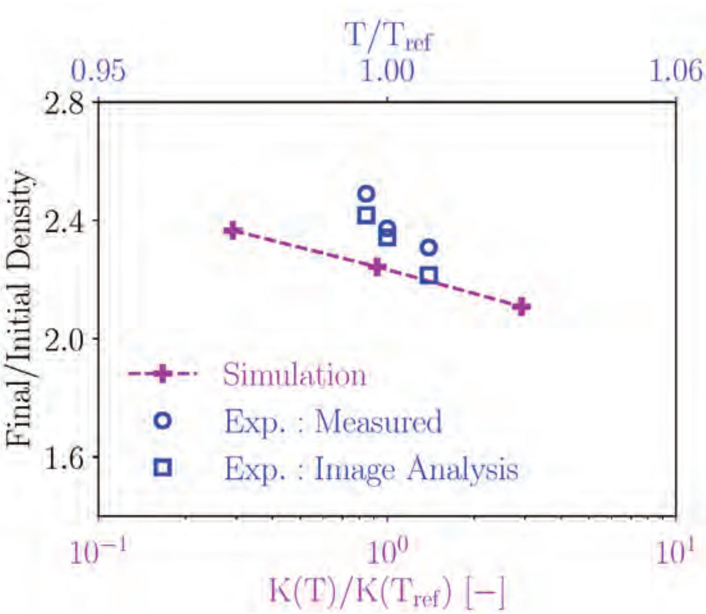

Figure 3. Comparison of the simulated and experimental total density of isothermal CVI in AM preforms. The correlation between the Thiele modulus (K) and temperature is closed by the effective activation energy of the deposition kinetics. (Credit: Ramanuj et al.)

IMPACT

Aircraft gas turbine engines are a major economic opportunity for the US manufacturing sector, but competitiveness relies on our ability to reduce specific fuel consumption (SFC). High-temperature CMCs allow for reducing turbine engine components' cooling air needs, thus increasing turbine efficiency. Improved turbine efficiency reduces the engine's SFC. The reduced weight of CMC components for the combustor and turbine also reduces SFC directly, allowing for lighter supporting structures, further reducing total SFC. In a different application, lightweight structural materials that have the capability to provide structural integrity, thermal management, and oxidation resistance at ultrahigh temperatures are critical and one of the most formidable technology barriers for sustained hypersonic flight. Lightweight extreme materials are needed for both external surfaces and the propulsion systems of air-breathing hypersonic craft. Similar materials barriers exist within the DOE mission space for next-generation turbine systems for utility power generation, transformational power generation strategies, and accident-tolerant nuclear fuels.

The manufacturing of CMCs by CVI processing is very expensive because it is slow; involves large volumes of chemicals, some of which are explosive or hazardous; and is performed at extreme operating conditions (i.e., low pressures and high temperatures). Currently, the manufacturing of CMC components by CVI can take on the order of weeks. The important advantages of CVI still motivate the pursuit of this manufacturing route despite the resulting high expense. Even a small reduction in this time will greatly reduce manufacturing costs.

SUMMARY

Materials for extreme environments pose unique challenges in manufacturing. Physics-based, high-fidelity simulations enabled by HPC can provide valuable insights to improve quality and reduce the cost of manufacturing such complex materials. The research reported here supports the advancement of CMC manufacture through CVI for aerospace and other industries. ORNL's strengths in CVI and HPC have been combined in this work to provide a validated model and workflow for the use of DNS to improve CVI processing.

ACKNOWLEDGMENTS

This research was supported by the HPC4Mfg program, managed by the AMO, within DOE's EERE. The research was funded by the ORNL LDRD program. The research used the computational resources of the OLCF and CADES (Compute and Data Environment for Science) facilities at ORNL, which are supported by the DOE Office of Science under contract no. DE-AC05-00OR22725.

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The Challenges and Opportunities for Environmental Barrier Coatings in Extreme Environments

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INTRODUCTION

Materials that can endure extreme environmental conditions such as high temperature, high pressure, steam, corrosives, and nuclear environments are in increasing demand, driven by the need for higher energy efficiencies and diversified fuel sources. Materials suitable for extreme environments must exhibit thermal or corrosion protection, as well as suitable mechanical strength, fatigue, toughness, or passivation. Coatings can provide some protection, and they can be applied using techniques such as vapor phase, powder, or slurry-based deposition. However, the kinetic and thermodynamic limitations of the coating application process are driven by the composition of the coating and the substrate, as well as the elevated temperatures required for sintering and densification.

Oak Ridge National Laboratory (ORNL) has a long history of developing thermal and environmental barrier coatings (TBCs, EBCs) for metal and ceramic systems. To answer the call for materials that can operate under even more extreme conditions, new and traditional colloid science principles must be maximized to provide the required dispersion, rheological behavior, interfacial control, and ultimate final coating architecture. ORNL's development of slurry EBC is presented herein, along with a discussion highlighting opportunities to maximize the use of new tools and approaches that have been underutilized thus far.

BACKGROUND

The slurry (dip) coating process is a familiar, viable approach for EBC production that is also reliable and affordable. Slurry coatings have been used to produce protective barriers in the housing, marine, automotive, and aerospace industries for many years. Specific examples of complex geometries requiring EBCs include turbine blades and rotors. Unlike most other coating techniques (e.g., spray coating), slurry coating is a non–line-of-sight process, meaning that the coated surface does not have to be directly visible to the coating delivery system. Thus, components with complex shapes can be dipped into a slurry (i.e., ceramic or metallic particles suspended in a solvent medium) and then dried and heat-treated at elevated temperatures to promote densification. The process is not limited to a specific material system; a variety of powders/chemistries can be applied to various substrate compositions. No unique equipment is required other than rheological behavior refinement (i.e., the design of the flow behavior of the slurry), and the process is readily transferrable to industrial production scale.

Although the overall coating process is simple once it is developed, the slurry's rheological behavior must be fine-tuned and controlled using the principles of colloidal processing. In addition, tailoring interparticle (surface) forces must be used to control the slurry's rheological behavior to ensure reproducible, quality coatings [1], [2]. In aqueous-based suspensions, the long-range attractive van der Waals forces on the particles in suspension must be balanced by repulsive forces to tailor the desired degree of suspension stability. One approach to manipulating the competing attractive and repulsive forces is to use ionizable polymeric dispersants or polyelectrolytes to modify the surfaces, thus imparting repulsive electrosteric interparticle forces [3], [4]. ORNL has demonstrated the use of slurry coatings for a variety of high-temperature coating applications, including EBCs for (1) silicon-based ceramics for advanced gas turbines and (2) chromia-based refractory materials for gasifiers.

RESULTS

Slurry development. The optimization of the slurry is critical to the successful application of slurry coatings. Several colloidal processing techniques are used to characterize and control the interparticle forces that dominate particle dispersion in a solvent system. The two main techniques are zeta potential (i.e., a measure of the surface functionality) and rheology (i.e., the study of the flow of materials). Simply described, particles have

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characteristic surface charges or forces that can be chemically or physically modified. Suspending particles into a solvent will inherently alter these forces, causing the particles to flocculate or remain discrete. In addition, the level of dispersion will determine the stability of the slurry: will the particles settle out of the suspension before the dipping process is completed, resulting in a thin, nonuniform coating, or will the particles agglomerate during the dipping process, causing the viscosity to increase and resulting in a thick, nonuniform surface? Additives such as surfactants or binders can be used to balance these forces as needed. The concentration of particles in the solvent can also be adjusted and characterized using zeta potential and rheological flow, thus enabling formation of a uniform coating thickness. Two examples of these techniques are presented below.

EBCs for Si_3N_4, SiC, and Si-based materials. Aqueous-based suspensions of mullite were evaluated as candidate EBCs. Mullite was of interest because its thermal expansion matches Si-based high-temperature material substrates. To develop the coating, a cationic polyelectrolyte, polyethyleneimine (PEI) was used as a dispersant to modify mullite powder surfaces and rheological behavior. SiC, Si_3N_4 (AS800), and silicon metal substrates were dipped into suspensions of varying rheological behavior, and when the resulting coating quality was examined (Figure 1), it was found to be relatively independent of the substrate type. It was, however, strongly dependent on the suspension's rheological behavior. A Goldilocks' effect was evident in the resulting coating behavior. The mullite suspensions with *too little* PEI resulted in thick, uneven coatings originating from a strong particle gel network. Mullite suspensions that contained *too much* PEI concentrations had a particle network that was too weak, so the coating did not maintain a uniform shape but dripped off the

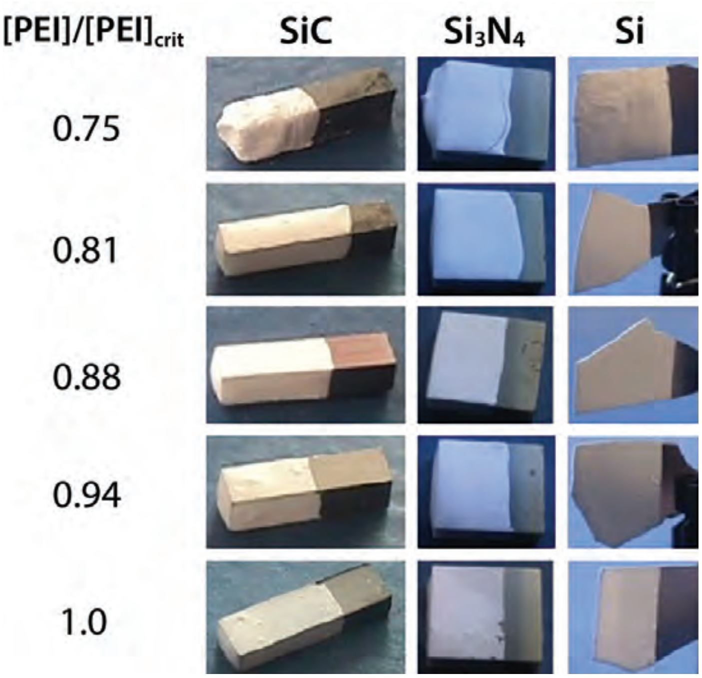

Fig. 1. Mullite coatings on SiC, Si_3N_4, and Si metal substrates. Coatings were formed by dipping into mullite suspensions of varying PEI concentration. (Credit: B. L. Armstrong)

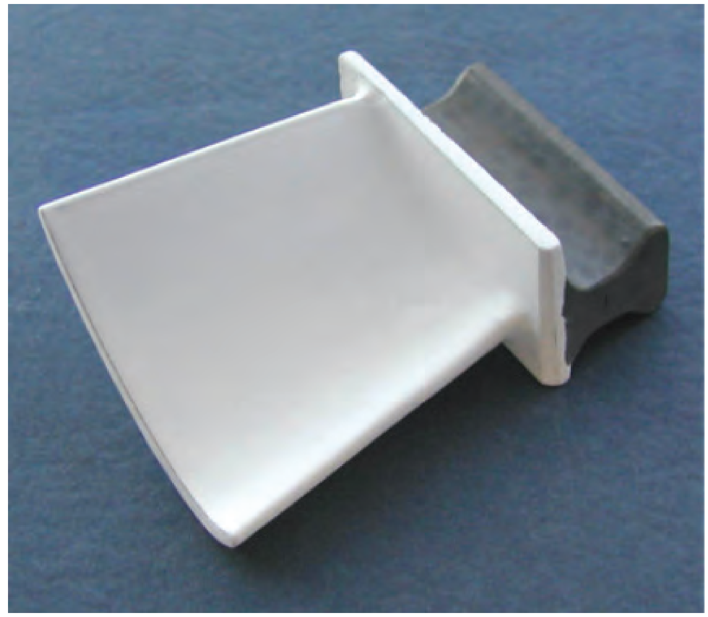

Fig. 2. Example of a rare earth–doped silicate coating on a Si_3N_4 vane. (Credit: B. L. Armstrong)

substrate before the drying process was completed. Entrained air bubbles were stabilized in these suspensions and eventually became pores in the coatings after drying. These differences in coating quality emphasize the important role of interparticle forces on the resulting properties, and they assist in identifying the best balance for additive concentration. The same approach was used to demonstrate coatings for other candidate EBC materials, including BSAS (barium strontium aluminosilicate), and yttria and ytterbium disilicates. An example of a rare earth–doped silicate coating on a Si_3N_4 vane is shown in Figure 2. This technology was further evaluated for scale-up at United Technologies Research Center and GE Aviation. A more extensive review of this effort can be found in [5].

Chromia-based refractory coatings. Another example of the use of a slurry barrier coating was in refractories. Enhancing the output and economics of fossil energy conversion and combustion systems (i.e., gasifiers) by operating at higher temperatures, higher throughputs, and variable feedstocks decreases the useful operating life of the materials used in these environments. Most high-temperature materials like ceramics are susceptible to corrosion by the molten slags, alkali metals, and gases in harsh operating environments. Therefore, to take advantage of the attractive properties of ceramics and to extend their service lifetimes, additional measures must be implemented to protect them from corrosion. Therefore, novel coatings were developed using ORNL's dip-coating process and were examined for their ability to provide additional slag resistance for Albany Research Center (ARC)–developed chromia-based refractory bricks.

Aqueous-based suspensions of chromia were characterized using the same approach that was used for the EBC development effort. Again, the powder surfaces and the rheological behaviors of these resulting suspensions were characterized in the presence of a dispersant. In this case, an anionic polyelectrolyte, PAA-PEO, was used. Dispersant and solids loadings were optimized, and flow behavior during coating was maintained. Substrates were cut from three commercial chromia-based refractory bricks and from the ARC-fabricated brick and were dipped into the optimized suspension. In addition, the coated bricks were heat-treated to improve coating density. Once the ideal slurry formulation was identified, refractory cups were coated with the optimized chromia slurry, filled with coal slag, and heated to 1,600°C for 1 h in argon. Then the reacted cups were sectioned and analyzed for slag corrosion. As shown in Figure 3, molten slag corrosion was minimized through the use of the chromia coating, with demonstrated improvement in the refractory material's corrosion resistance to the molten slag.

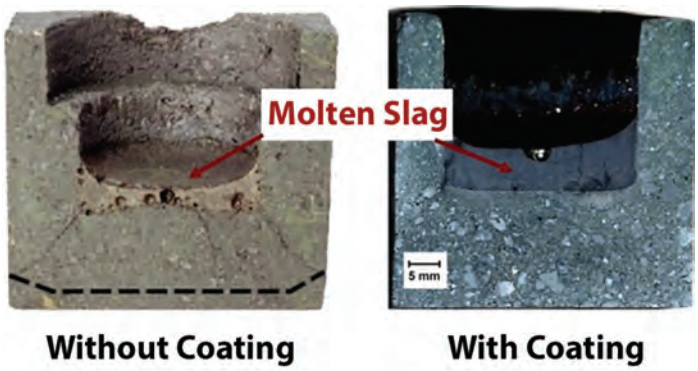

Fig. 3. Uncoated and coated refractory cups after exposure to molten slag. (Credit: B. L. Armstrong)

IMPACT

Slurry coating is a promising method for producing coatings on high-temperature materials for a variety of applications. It offers a non–line-of-sight process for uniform coatings on complex shapes, and there is no requirement for unique equipment. Furthermore, slurry coating offers process flexibility, and a variety of ceramic powders can be applied to various substrate compositions. The technology can be easily transitioned to industrial production.

CONCLUSIONS

To develop EBCs for components in extreme environments, the rheological behavior of aqueous or even nonaqueous suspensions can be optimized using the principles of colloidal processing. Dispersants can be added to concentrated suspensions to form slurries, offering a wide range of rheological properties that can be tailored to form processes such as dip coating. Suspension flow behavior, elastic modulus, and yield stress can be varied to optimize the elastic modulus of the resulting coatings, which is a key factor in the uniform distribution of material on the part's surface. The flexibility of this approach can be adapted for various coating and substrate combinations and applications.

COLLABORATE WITH ME

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Advanced Manufacturing of Refractory Metals for Extreme Environments

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INTRODUCTION

Refractory metals encompass some of the highest-performance materials in use today for extreme environments. Refractory metals are finding increasing interest for high-risk, high-reward applications such as gas turbine engines, fission, and fusion energy, in addition to the application spaces in which they have traditionally been used. The development of both refractory metals and manufacturing processing routes has been largely stymied amid the rapid developments of the space age. As a result, only simplistic geometries are fabricable by modern standards, and materials innovation has been highly impacted by limitations in manufacturing processes. With the evolution of the feasibility of advanced manufacturing processes, the technical hurdles presented by conventional processing routes have begun to shift to allow for processing of refractories into ever-complex, previously unimaginable geometries. While advanced manufacturing techniques present new technical challenges, novel ideas regarding materials processing and materials innovation are emerging.

BACKGROUND

Efficiencies associated with generating power via gas turbines and nuclear power plants are limited largely by the nickel-base (Ni-base) superalloys and steels critical to their function. The critical role played by materials innovation and manufacturing/design innovation cannot be overstated. This historical linkage is shown in Figure 1, which highlights the linkages between the evolution of operational limits of Ni-base superalloy (black line) blade alloys, the effective combustion gas temperature (red), and the influence of design and coatings technology. As a result, the current combined-cycle efficiencies (CCE) of gas turbines stand at ~62%; nuclear fission reactors CCE stands at ~37%.

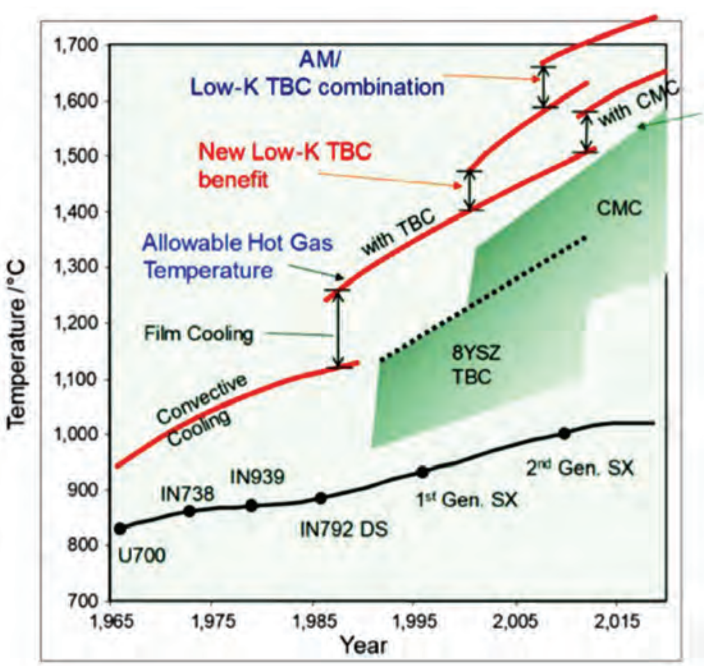

Figure 1. Evolution in Ni-base superalloy material capability and engine gas temperature with application of coatings [1].

To enable increased efficiencies in energy production systems, adoption of next-generation materials that exhibit a significant disruptive nature on the operational limits of the components is necessary. In operational terms, to increase the CCE of gas turbine engines beyond 65%, a 200°C increase in the metal's temperature is necessary. Similarly, achieving operational temperatures of 1,200°C in a fission reactor could push the theoretical CCE more than 50%. As such, the high-temperature capabilities of refractory metals such as Mo make them an excellent choice for serving in extreme environments that crosscut many energy spaces.

However, processing refractory metals and their alloys into relevant geometries is difficult and has not seen significant advancements in capabilities in decades. Conventional melting and casting is not practical due to the extreme melting points (>2,000°C) and high affinity for oxygen and other contaminants that refractory metals typically exhibit. Further, commercial practice for a wide variety of refractory metals is based on solid-state powder processing, with alloying achieved by interdiffusion of blended powder additions during either solid-state or transient liquid-state sintering reactions. As a result, refractory metals are some of the most difficult materials to alloy uniformly and process into high-density monolithic or composite net-shape components for end use. Significant interest is being given to refractory processing research through additive manufacturing (AM), with the goal of bypassing current technological limitations to produce high-density and defect-free complex refractory metal geometries [2]. However, AM processing of these materials is nontrivial and presents unique processing difficulties and challenges such as cracking and achieving high densities. Leveraging electron beam melting (EBM) powder bed AM, the ability to process pure Mo in bulk and complex geometries with high material densities and defect-free structures has been demonstrated. EBM is particularly attractive, as the local thermal history of parts can be rapidly and precisely controlled, the powder bed can be heated to temperatures higher than 1,200°C, and the process can be operated in a vacuum atmosphere that minimizes contaminants. Here, we report our successful demonstration of AM of honeycomb composite parts using EBM.

RESULTS

An example Mo core structural part used in fission thermal propulsion systems fabricated through EBM is shown in Figure 2a [3], and a representative pair of Mo airfoils for a land-based engine is shown in Figure 2b. Parallel efforts focusing on pure tungsten for fusion plasma-facing components are underway and have resulted in similar demonstration of bulk material results as Mo, which will be discussed below.

While the processing science has long been developed for demonstrating relevant geometries, one of the most interesting scientific aspects exhibited by refractory metals processed using AM is the unique anomalous crystallographic textures. EBM Mo exhibits a sharp {001}; {111}; and mixed {001} & {111} crystallographic fibers along the build direction, as illustrated in the electron backscatter diffraction (EBSD) images in Figure 3a. The selection between these build direction fibers has been found to be directly correlated (Figure 3b) to beam energy density used to melt the feedstock powders and is associated with the shape of the weld pool and local solidification velocities and thermal gradients during the liquid-to-solid phase transformation.

The resulting solidified texture is important because refractory materials are known to exhibit crystal-specific plastic anisotropy, and, hence, the mechanical behavior of the AM material can be subsequently influenced by the texture [5]. Shown in Figure 4 are room-temperature tensile curves for the different fiber textures, {001}, {111}, {001}, & {111}. From these results, it is clear that fiber texture directly influences the mechanical response, both elastically and plasticly.

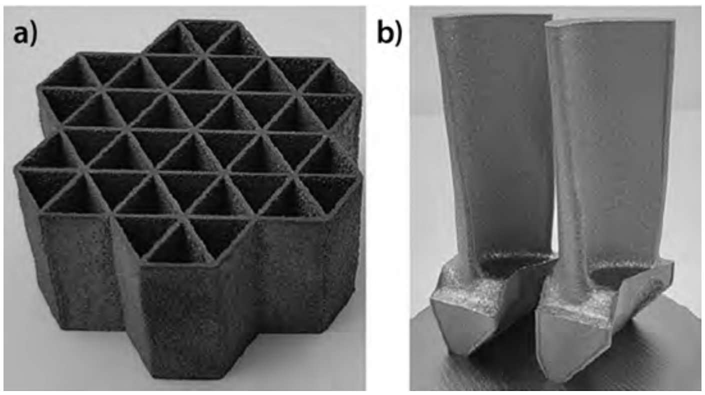

Figure 2. (a) Representative EBM Mo core structural part used in nuclear thermal propulsion system [3]. (b) Representative pair of Mo airfoils for a land-based turbine engine. (Credit: Kirka et al.)

Leveraging the understanding of the relationship between solidification texture and energy density for Mo processed via EBM, pathways exist to fabricate components with spatially controlled crystallographic texture (i.e., an engineered mesoscale composite). This is achievable through discretizing the part volume and controlling the localized energy density. We successfully demonstrated this concept in a honeycomb composite pattern (Figure 5a). Analysis of the obtained microscopy, mechanical testing, and microstructure-scale finite element simulations indicates that both the macroscale and localized microstructure behavior can be tailored. This

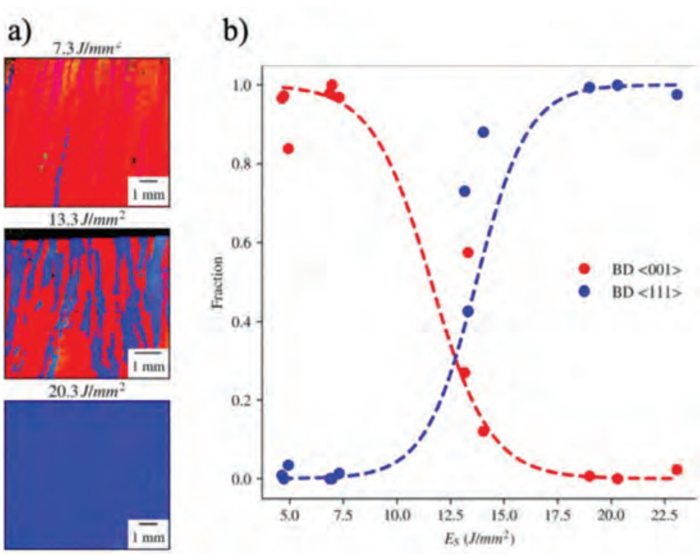

Figure 3. (a) EBSD maps of the EBM AM-fabricated material sorted by increasing E_S. Build direction (BD) is vertical in all micrographs. (b) Fraction of [001] and [111] in the BD shown as a function of energy density [4].

is evidenced by the variation of the Schmid factor within the honeycomb structure (Figure 5b). Cumulatively, this indicates that EBM can enable fabrication of complex refractory metal components with mesostructures for potential enhanced performance over a monolithic texture.

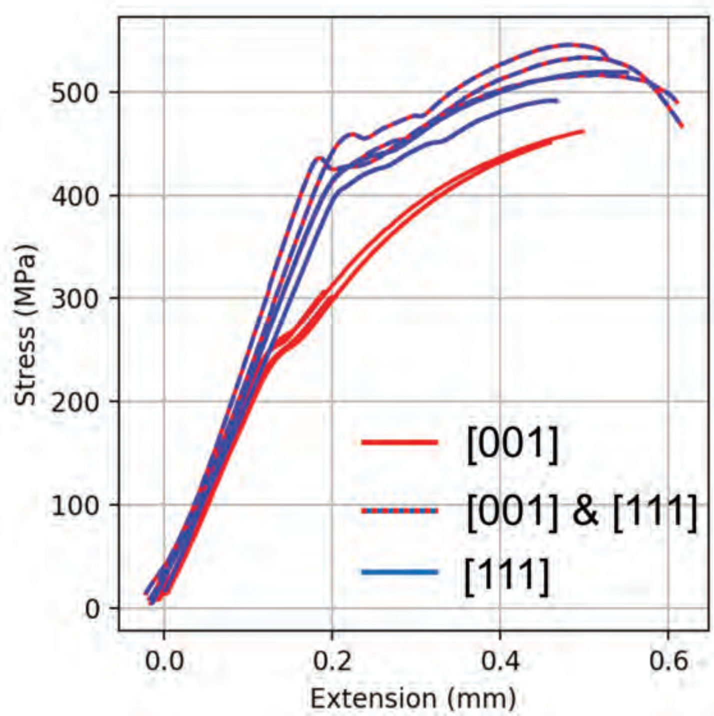

Figure 4. Room-temperature tensile behavior of EBM Mo. (Credit: Kirka et al.)

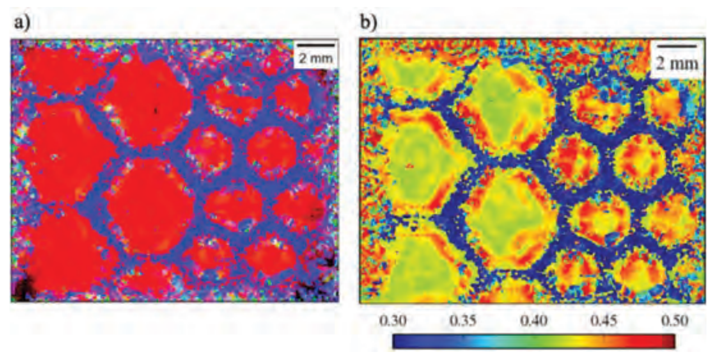

Figure 5. (a) EBSD maps for honeycomb composite mesostructures generated using circle-packing algorithm. (b) Schmid factor for honeycomb composite mesostructures. (Credit: Kirka et al.)

IMPACTS

As a result of this work, the feasibility of new design paradigms for refractory metal components for harsh environments has been demonstrated in the form of pure Mo. The ability to fabricate bulk structures with mesoscale structures embedded within the bulk presents a new avenue in refractory structures for enhancing component performance. Leveraging AM processing routes for refractory materials presents a unique opportunity to rethink the design of entire energy systems based on the promise refractory metals with enhanced operational capabilities offer over currently used materials.

CONCLUSIONS

Advanced manufacturing represents a new era in the processing of refractory materials that mitigates the limitations associated with their use when processed through conventional manufacturing routes. However, challenges remain for this emerging processing route. This work demonstrates successful processing of pure Mo into prismatic and complex geomtries with high-density and defect-free structures of relevance to various energy spaces. Further, it has been observed that the fibrous textures can be controlled on a bulk scale to give rise to unique mesostructures that have the ability to provide unique mechanical performances that could not be achieved via traditional processing routes. However, further research is needed to evaluate refractory alloys for AM processing to optimize high-temperature mechanical performance and to develop the necessary process–structure–property relationships for operaton in relevant extreme environments.

ACKNOWLEDGMENTS

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High-Throughput Operando Neutron Diffraction Study of Battery Materials under Fast Charging

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INTRODUCTION

Monitoring the structural evolution of Li-ion batteries (LIBs) during charging and discharging provides valuable insights into the structure–property relationship of electrode materials. This information plays a critical role in optimizing the performance of commercial electrode materials and could guide the discovery of new classes of cathode or anode materials for next-generation rechargeable batteries. This article highlights our recent efforts to develop a new sample environment for operando neutron diffraction characterization of LIBs at the Spallation Neutron Source's (SNS's) Nanoscale-Ordered Materials Diffractometer (NOMAD) beamline. This newly developed capability allows both high throughput and fast neutron diffraction measurements of multiple in situ cells with unprecedented time resolution (<1 min/diffraction pattern).

BACKGROUND

The quick-paced development of energy storage techniques over the past few decades has delivered great benefits to society. LIBs have attracted broad interest because of their high energy density (HED) and excellent cyclability. LIBs have been broadly used in modern portable electronics since the early 1990s [1]. More recently, increased concerns regarding pollution and global climate change have resulted in a call for drastic emissions reduction, as outlined in the Paris agreement [2]. Reducing the consumption of fossil fuel and CO_2 emissions, which has been mainly driven by the dramatic expansion of the transportation sector in the past century, will be vital to achieving the ambitious targets included in the agreement. Thus, there is an urgent need to ramp up the production of electric vehicles (EVs), the majority of which are now powered by LIBs. The market growth has approximately doubled in the past 5 years, and the projected market for the EV sector is more than $70 billion as of the 2020s (Figure 1). However, the energy density of current state-of-the-art rechargeable batteries is still inadequate to enable a driving range over 300 miles per single charge—the threshold for most of today's combustion engine–based vehicles. In addition, slow charging rates, safety, and cost of EVs also have emerged as concerns [3]. Thus, increasing the energy–power

Figure 1. (Left) Thomas Edison stands in front of an old-generation electric car powered by the Edison storage battery in 1911. (Right) Tesla Model S with falcon wings open; the EV is powered by HED Li-ion batteries (Credit: Thomas Edison National Historical Park, TESLA) [4]

density while simultaneously decreasing the cost of LIBs has inevitably become challenging.

Understanding the underlying driving forces for structural transition of electrode materials allows us to optimize performance. Conventional powder diffraction techniques have been broadly used to characterize ex situ samples scratched from cycled battery electrodes. While these studies provide useful structural information of relaxed lithiated/delithiated electrode materials, they raise concerns, as many charged/discharged samples are metastable and tend to relax and decompose rapidly even under inert atmosphere. The need to develop operando diffraction techniques to monitor structural evolution during battery cycling has attracted tremendous attention as a method to address some of these concerns. Particularly, operando x-ray diffraction has been routinely used to track the structural changes of battery materials, in large part due to the easy access, high flux, and small and easily tunable beam size. Despite these advantages, there are few drawbacks to using operando x-ray diffraction for battery characterization. These include limited sensitivity to light elements and difficulty in distinguishing neighboring 3d transition metal (TM) cations, widely used as the redox center for LIB cathode. Further, this technique often induces electrolyte dispersion, leading to reaction inhomogeneity or delay of phase transitions.

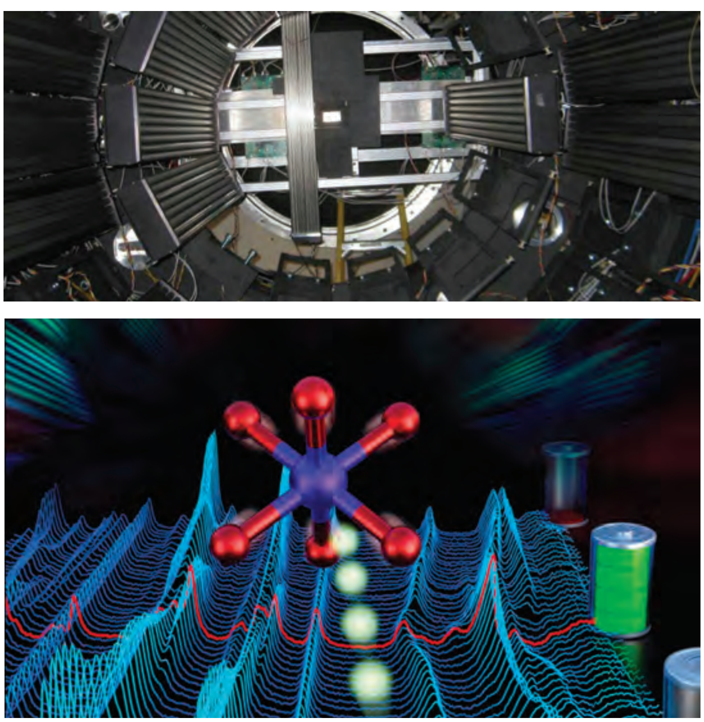

Figure 2. (Top) Detector tank of NOMAD at SNS. (Bottom) Demonstration of the operando neutron diffraction study of structural evolution of $LiNiO_2$ in the $LNiO_2$ || graphite full cell during the initial charge and discharge [5]. (Credit: Jill Hemman)

Neutron scattering is an ideal complementary technique to address the above problems. It is highly penetrating and nondestructive, making it ideal for probing structural changes in large devices such as Li-ion batteries without disturbing internal electrochemical reactions. In addition, neutron scattering lengths do not increase with atomic number. Instead, they are isotope dependent and highly sensitive to light elements (e.g., Li, C, and O), which are key elements of battery electrodes. Neutron scattering is also capable of distinguishing adjacent 3d TM cations. Many HED cathode materials contain multiple 3d TM cations, such as Ti, Mn, Fe, Co, and Ni. Neutron diffraction studies of isotope-substituted samples are very useful for revealing unambiguous cation arrangements in these complex materials. Moreover, nuclear scattering lengths do not decrease with momentum transfer, making the technique more accurate in quantitatively determining the atomic environments of light elements such as lithium and oxygen. Despite these significant advantages, neutron diffraction analysis of battery materials, especially for the operando characterization of charged and discharged electrode materials, has remained somewhat limited. The lack of widespread use can be ascribed to the relatively low neutron flux in most conventional neutron diffractometers. Larger samples (i.e., grams) or longer counting times are often required to compensate for these parameters, leading to the design of various in situ cells with much higher loadings of active materials (including commercial cells) for operando neutron diffraction. However, collecting high-quality neutron diffraction data with high time resolution (e.g., <1 min/pattern) is still very challenging even with large loadings. In addition, because neutron scattering is a relatively scarce resource, it is necessary to improve the measurement efficiency by adopting high-throughput measurements. Unfortunately, this highly sought after capability was not available previously.

The rapid increase of neutron flux for the modern spallation neutron sources has paved the way for fast data collection of small amounts of charged/discharged electrode materials (Figure 2). In particular, NOMAD is one of the fastest neutron diffractometers, thanks to the high neutron flux and extensive detector coverage (i.e., >4 str). We have recently realized in situ monitoring of both local and average structural change of the charged $Li_{0.2}Ni_xCo_yMn_zO_2$ during the thermal decomposition, using only a 100 mg sample in a gas flow tube. This study proves the possibility of conducting quantitative in situ neutron diffraction with minimal amounts of battery materials. This inspired us to develop the current high-throughput in situ neutron diffraction capability for battery studies at the NOMAD beamline.

RESULTS

In situ battery cells and sample environment at NOMAD. The newly designed in situ cell is schematically shown in

Figure 3a. A thin-walled quartz tube makes up the cell body. The cell components (i.e., cathode, separator, and a thin film of copper–graphite anode) are rolled in a configuration similar to the commercial jelly roll cell. The most significant advantage of the jelly roll configuration is the capability to cycle batteries at a very fast rate while ensuring reasonable amounts of active material within the neutron beam. The high rate enables the investigation of the structural evolution of battery materials at actual operational conditions (e.g., charge/discharge in less than 1 h). In addition, this configuration also allows rapid neutron diffraction data collection with sufficient statistics due to the illumination of large amounts of electrode materials. Multiple cells can be loaded onto the automatic sample change shifter (Figure 3b) at NOMAD. The operando experiment can be carried out in two modes. For the high-throughput mode, up to six in situ cells can be mounted on the shifter bracket, and diffraction data are collected in a sequential manner. For the high-rate mode, the neutron beam is fixed to a single cell, and data collection is carried out with very high time resolution (i.e., <1 min/pattern). The intrinsic data structure also allows event filtering, where the highest theoretical time resolution matches the time scale of a single pulse at SNS.

High-quality operando diffraction data. The unique configuration of the time-of-flight neutron diffractometer permits fast data collection without sacrificing resolution, especially with the back scattering frames (e.g., a $\Delta d/d \sim 0.3\%$ can be achieved on the back scattering bank on NOMAD). For the high-throughput measurements, we collected operando diffraction data on four different Ni-rich graphite in situ cells. A fraction of the operando diffraction data is shown in Figure 4a. The contour plot at top left highlights the change of graphite (S.G. P63mm, labeled in white) 114 reflection during lithiation and delithiation. This diffraction peak shifts to larger d-spacing upon initial lithiation ($x < 0.1$ in Li_xC_6). Further lithium insertion results in the split of this peak, and the intensity of the new Bragg reflection increases at the expense of the original 114 reflection. A new and broad diffraction peak emerges and continuously shifts toward large d spacing during further lithiation, indicating a solid solution phase instead of a line phase [2], [3]. This new phase could be fit using the lithium intercalated Stage III phase (S.G. P3 with A(Li)ABA…stacking) only when the intensity of this diffraction peak reaches its maximum ($x \sim 0.15$ in Li_xC_6). The featured 007 reflection of the Stage III phase is highlighted on the contour plot at right. When more than 0.2 Li^+/formula ($Li_{\sim 0.2}C_6$) is inserted into the graphite, a new line phase starts to emerge. The positions of corresponding diffraction peaks remain almost unchanged, as shown in Figure 4a.

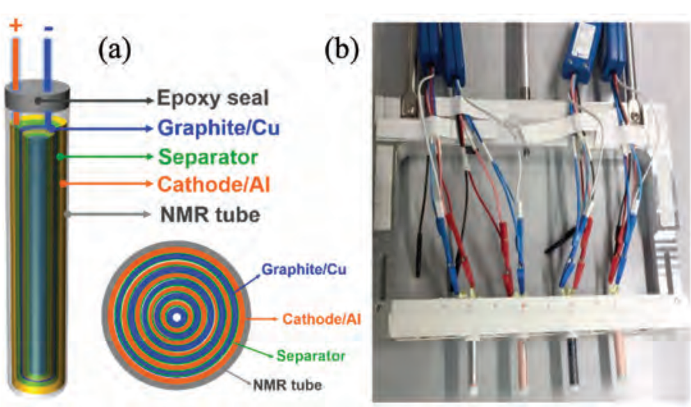

Figure 3. (a) Illustration of the in situ electrochemical cells for high-throughput operando neutron diffraction study. (b) Picture showing different Ni-rich cathodes || graphite full cells on a shift bracket for high-throughput operando neutron diffraction experiment. (Credit: Liu et al.)

A close inspection of the diffraction peak around 1.23 Å (i.e., 110 reflection of graphite) shows a small peak splitting when 0.25–0.5 Li^+ was inserted (details not provided here), indicating the coexistence of two distinct phases within this region. The difference between these two phases is likely caused by the ab-plane lithium-vacancy arrangements because the average interlayer spacing remains almost identical. This observation is consistent with the previous observation of the diluted Stage II phase (LiC_{18} with AB(Li)BA…stacking) → Stage II phase (LiC_{12}, S.G. *P*6mm with AA(Li)AA…stacking) transition in this region. Further lithium insertion leads to phase transition from the Stage II phase → fully lithiated Stage I phase (LiC_6, S.G. *P*6mm with A(Li)A…stacking).

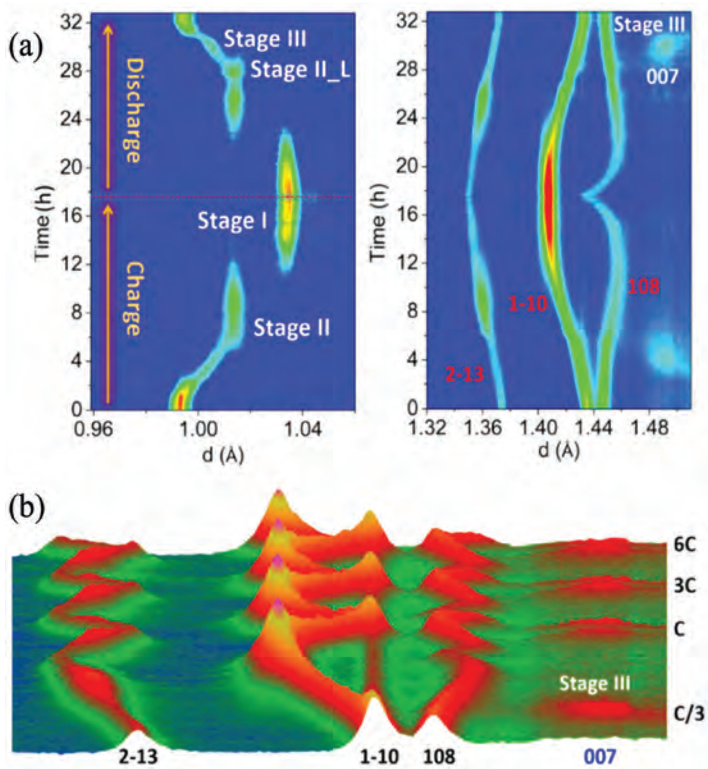

Figure 4. (a) Operando neutron diffraction data collected during the initial charge/discharge of NMC-622 at C/16 (charge/discharge battery in 16 h). The time resolution is 4 min/pattern. (b) Operando neutron diffraction data collected during battery (NMC622 cathode and graphite anode) rate testing with different charging rate (C/3, 1C, 3C, and 6C). The discharging rate is set to 1C. The time resolution is 1 min/pattern. (Credit: Liu et al.)

This in situ study also offers a detailed structural evolution of the NMC622 cathode (labeled in red in Figure 2) during its initial cycle and shows that the 110 reflection shifts continuously toward the smaller d-spacing for all four samples, indicating that the ab-plane shrinks during initial delithiation. In contrast, the 108 reflection shifts to the larger d-spacing initially but switches to the opposite direction after removing ~0.5 Li^+ per formula unit (Figure 4a), suggesting the c-lattice initially expands but starts to decrease at ~50% delithiation. Parametric Rietveld refinements were carried out for the detailed structural study, and more results can be found in recently published papers [6], [7].

We also used the high-rate mode of this newly developed in situ cell to study the structural transition dynamics in the NMC622 graphite full cell (Figure 4b). The in situ cell was cycled at different charging rates (i.e., from 1/3C to 6C), and the discharge rate was fixed to 1C). Diffraction data were collected every 1 min. The overlay of the collected diffraction data is shown in Figure 4b. Structural transitions from both NMC622 cathode and graphite anode can be clearly seen. Quantitative structural analysis using parametric Rietveld refinements was carried out, and detailed information on structural changes can be found in related references [6]. While the NMC622 cathode exhibits nearly identical structural evolution regardless of C-rates, drastic differences were observed for the Stage II → Stage I phase transition of lithiated graphite. We found that the Stage I (LiC_6) phase emerges at a much earlier stage during stepwise intercalation when the charging rate is increased. We also found that the Stage II (LiC_{12}) → Stage I (LiC_6) transition is the rate-limiting step during fast charging of the NMC622 graphite cell. Further phase transition analysis using the Johnson-Mehl-Avrami-Kolmogorov model indicates that the Stage II → Stage I transition is a diffusion-controlled [8–10], 1D phase transition with decreasing nucleation kinetics under increasing charging rates.

CONCLUSIONS

A new type of low-cost, disposable in situ cell and related electrochemical testing sample environment have been developed and commissioned at the SNS's NOMAD beamline. The sample environment allows high-throughput operando neutron diffraction study of battery materials under fast charging. This capability will help to unravel some of the most fiercely debated working mechanisms for battery electrode materials.

IMPACT

The development of this high-throughput operando neutron diffraction capability at SNS is vital for understanding the structure–property relationship of emerging battery materials during dynamic cycling, and it offers great potential for in-depth characterization of commercial LIBs. Hence, it is of great value for guiding exploration of next-generation energy storage materials.

COLLABORATE WITH ME

This sample environment will be fully open to general users in SNS's upcoming proposal call. Please contact Jue Liu if you are interested in operando neutron diffraction study of battery materials. We are currently working on developing the operando neutron total scattering/pair distribution function capability for battery research, which will be a unique tool to probe short-range structural changes.

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Levitation Techniques for the Study of Structure, Dynamics, and Thermophysical Properties at Extreme Temperatures

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INTRODUCTION

Synthesis pathways at elevated temperatures define many present-day foundational materials in areas ranging from metallurgy of superalloys to precisely controlled growth of semiconductors. However, measurement of material properties at extreme temperatures is impeded by unexpected reactions, crucible failures, and cumbersome equipment obscuring the sample.

Techniques such as levitation can enable noncontact materials processing, eliminating many complications inherent to high-temperature experiments and enabling observation of undercooled liquids and formation of nonequilibrium states. Levitation techniques use external forces (e.g., magnetic fields) to suspend samples during high-temperature processing. Although levitation techniques have existed since the early 1990s, space agencies began to develop noncontact methodologies in earnest to inform high-temperature material development and the evolution of microgravity techniques used in parabolic flights and on the International Space Station (ISS). Today, levitation processing is performed in many laboratories, providing benchmark thermophysical, structural, and dynamical data. Levitation techniques, as well as some hybrid techniques, are complementary, exhibiting varying capabilities and material compatibilities. The techniques enable experiments ranging from examinations of thermophysical properties of liquids to the kinetics of metastable phase transformations.

BACKGROUND

Levitation techniques. All noncontact levitation experiments share some common features. For instance, temperature is measured via pyrometry, and heating is accomplished via laser or radio frequency (RF) coils. The physically open nature of a levitator enables x-ray and neutron scattering techniques, as well as precise videographic measurements of density and viscosity.

Electromagnetic levitation (EML, Figure 1a) apparatuses use specially designed coils to generate an RF field, levitating samples by generating a Lorentz force. The sample must be conductive, and a resistive heating effect must be coupled to the levitation mechanism. Changes in temperature can bring shifts in sample position. EML can operate under vacuum and controlled atmospheres, and reducing gases can be used to eliminate surface oxides for optimal undercooling. Samples are typically deformed by the positioning fields. Microgravity experiments like those performed on the ISS enable analysis of fundamental properties such as calorimetry, density, viscosity, and resistivity [1].

Aerodynamic levitators or *conical nozzle levitators* (CNLs, Figure 1b) feature a special nozzle optimized to float spherical samples of solid materials of moderate density on a gas of choice. A CO_2 laser heats the floating sample from the top, heating samples up to ~3,000°C hundreds of degrees per second. Unless a secondary laser is added beneath the nozzle for bidirectional heating, levitation gas causes thermal gradients up to 1,000°C. CNLs are simple, offering rapid user training and deployment.

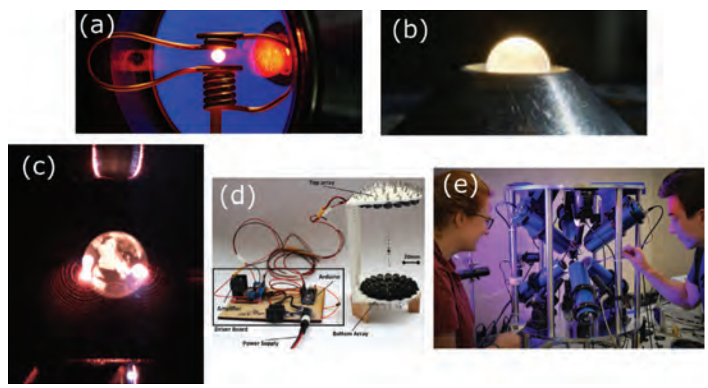

Figure 1. (a) Electromagnetic (reprinted with permission [2]), (b) aerodynamic (Credit: G. Martin), (c) electrostatic (Credit: D. G. Quirinale), (d) acoustic (reprinted with permission [3]), and (e) aero-acoustic levitators. (Credit: J. K. R. Weber)

Electrostatic levitators (ESLs, Figure 1c) rely on a complex positioning system and high-voltage electrodes to actively adjust electrostatic forces to control the position of a semiconductive (or insulating, in microgravity) material in 3D. Heating to 3,000°C is accomplished using multidirectional high-power lasers. An ultraviolet lamp recharges the sample via the photoelectric effect, limiting the speed of initial heating. ESLs are unsurpassed in positional stability, sample field of view, and uniformity of sample shape, providing excellent resolution (~.1%) for density measurements, easy viscosity measurements, and the possibility of electrical probing via inductive coupling with a pickup coil. This versatility requires experimental complexity and delicacy; an elaborate positioning system informing a high-speed feedback loop, stringent vacuum or atmospheric requirements, and the expertise required to operate ESLs have hindered their widespread use.

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Acoustic levitation (AcL, Figure 1d) uses ultrasonic transducers in the form of precisely aligned Langevin horns or transducer arrays to create standing waves in which pressure nodes can suspend small samples. AcL offers a simple setup for use with moderate temperatures and solution chemistry. The power delivered defines the maximum sample density, and the standing wave condition limits sample temperatures. AcL is commonly used below ~200°C terrestrially, and AcL temperatures can extend much higher in microgravity or when hybridized in an aero-acoustic levitation (AAL) setup (Figure 1e) [4].

Levitation at Oak Ridge National Laboratory (ORNL). This section discusses the Neutron Aerodynamic Levitator (NAL) and the Neutron Electrostatic Levitator (NESL), both operating since the mid-2000s at ORNL.

Neutron Aerodynamic Levitator. The product of a Small Business Innovative Research (SBIR) grant awarded to Materials Development Inc. (MDI), the NAL (Figure 1b) was designed specifically for the NOMAD beamline at the Spallation Neutron Source (SNS). Deployed in 2012, the NAL has been used for 15+ beamtime campaigns. A water-cooled aluminum nozzle is used for levitation; to further reduce background scattering, a ring of gadolinium is placed around the lip of the nozzle. While deep-temperature gradients occur vertically across the sample, the neutron beam is collimated into a half-moon shape just large enough to illuminate the top ~15% of the sample. The sample is heated by a 400 W CO_2 laser; the wavelength of 10.6 μm is easily absorbed by oxides, but clean metal surfaces reflect much of the power. The levitator can run in argon or oxidizing atmospheres; the current open atmosphere is best suited to the study of oxides and ceramics. An offline version of the NAL, upgraded with the capability for a controlled atmosphere and oxygen fugacity, is permanently set up and available to users for beamline preparation and pyrometric measurements. On NOMAD, the NAL is frequently used to elucidate high-temperature transformation pathways such as those in the high-entropy alloy (HEA) shown in Figure 2, and it is also used for pair-distribution function (PDF) analysis of disordered and molten materials.

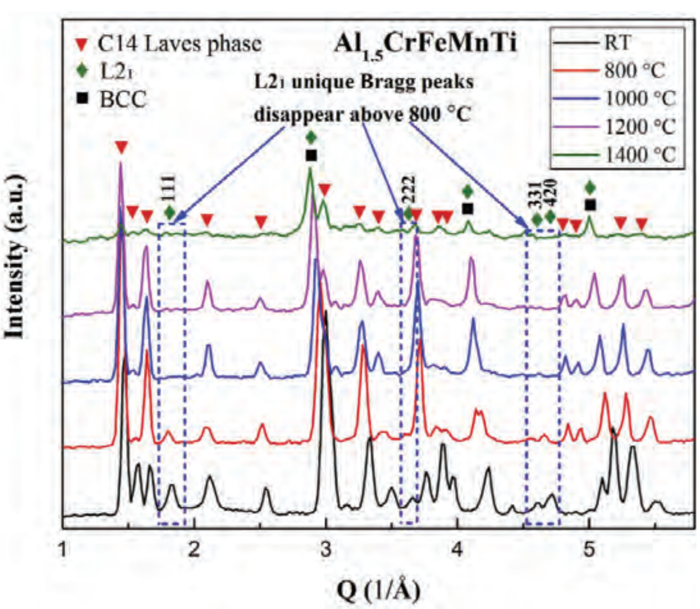

Figure 2. Phase evolution in an HEA studied with the NAL on NOMAD. Reprinted with permission [5].

Neutron Electrostatic Levitator. NESL (Figure 1c) resulted from a National Science Foundation (NSF) grant to Washington University in St. Louis and was commissioned at VULCAN at SNS in 2013. It has operated at NOMAD for PDF studies, the Angular-Range Chopper Spectrometer (ARCS) for inelastic scattering (INS), and the Cold Neutron Chopper Spectrometer (CNCS) for INS and quasi-elastic neutron scattering (QENS). Designed to fit the geometry of the vacuum detector wells at the SNS and to function as a high-vacuum chamber, NESL features a large outer tailpiece and a removable inner keystone containing the electrodes and sample space. All instrumentation, including lasers and pyrometry, access the sample via a series of internal mirrors. A sample changer above the electrode platform enables a sequence of 30 samples per load.

In addition to the NOMAD structural studies, integration into the direct geometry spectroscopy beamlines at the SNS enables users to probe the dynamics of high-temperature liquids; NESL is the only user-program levitator in the world available for this purpose. With ARCS, Ashcraft et al. [6] probed the time scale of bond breaking and forming excitations in molten Zr80Pt20. By linking this with the Maxwell relaxation time as determined by molecular dynamics simulations, a relationship between these excitations and the mechanisms of viscosity was experimentally observed. By contrast, using QENS at CNCS enables study of transport properties in molten alloys. By measuring the broadening of the elastic line, the diffusion coefficient of Ni in molten and undercooled Zr64Ni36 was determined (Figure 3).

Developing systems. ORNL's Neutron Sciences Directorate (NScD) continues to expand ultrahigh-temperature capabilities. A hybrid AAL (Figure 1e) is being acquired through an SBIR Phase II grant awarded to MDI to extend NAL capabilities by expanding the available temperature range and offering full scattering access to a levitating sample. Using six orthogonal sets of ultrasonic transducers in conjunction with a gas jet, the AAL will be able to float any type of material, eliminate the thermal gradients of the NAL system, and allow neutron illumination of 100% of the sample, similar to NESL. Early attempts are being made to develop computer vision algorithms to enable in situ density measurements on the beamline.

Additionally, through Laboratory Directed Research and Development investments, a new electrostatic levitator, the Creep ESL (CrESL) has been developed. A set of electromagnetic stators arrayed and controlled as a three-phase induction motor enables high-speed sample rotation up to 30 kHz at arbitrary angles, inducing stresses in the sample up to 100 MPa. Developed for the High Intensity Diffractometer for Residual Stress Analysis (HIDRA) at the High Flux Isotope Reactor (HFIR), when this system is deployed in FY 2022, it will offer unique contactless creep measurements via in situ neutron diffraction up to 3,000°C. Further deployment at the SNS wide-angle neutron diffractometer, WAND2, will target the kinetics of high-temperature and transient-phase transitions.

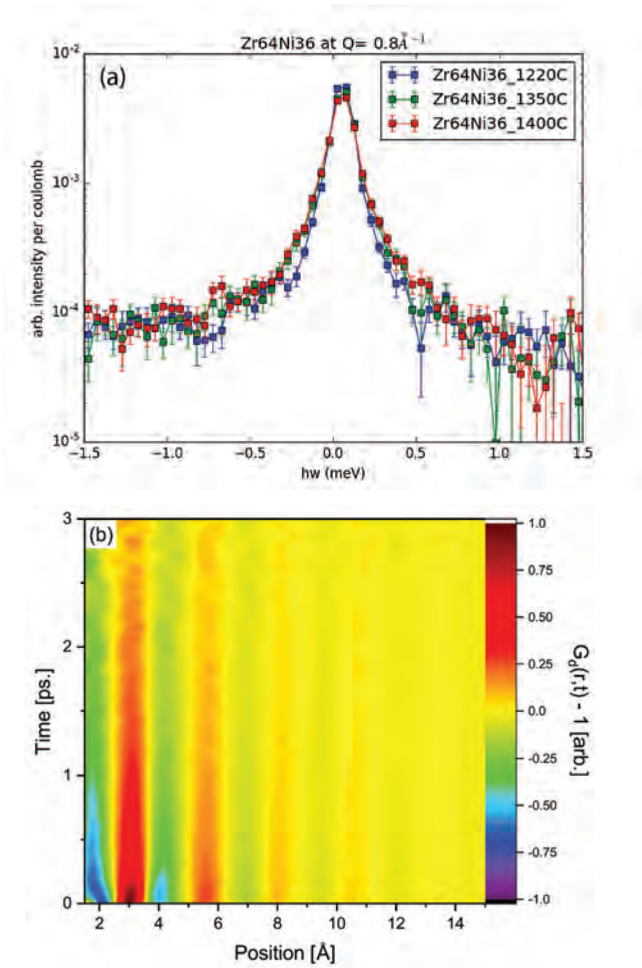

Figure 3. (a) QENS spectra of Zr64Ni36 from NESL at CNCS; (b) dynamic pair distribution function of Zr80Pt20 obtained experimentally at ARCS at 1,450°C. Reprinted with permission [6].

IMPACT

The capabilities being developed in NScD form one of the broadest technical bases for ultrahigh-temperature science globally. In addition to thermophysical property measurement, these systems can take advantage of ORNL's world-class neutron scattering capabilities. SNS and HFIR are the only user facilities offering time-of-flight INS on levitated undercooled liquids or contactless high-temperature creep measurements on the beamline as part of the general user program. As this program develops, with increased staffing and technical advancement, a comprehensive resource for ultrahigh-temperature measurements will be available.

COLLABORATE WITH ME

NAL and NESL are available to users with approved proposals. Staff can discuss experiment feasibility and help with offline thermophysical measurements and beamtime preparation. Assistance is also available with preparation of neutron proposals, execution of beamline experiments, and data analysis. As CrESL comes online and the AAL arrives for testing, NScD will begin research on the next generation of ultrahigh-temperature platforms. ORNL will soon have the world's most extensive and versatile suite of ultrahigh-temperature noncontact instrumentation, all available through the general user program. Further, the next generation of ORNL levitators will target new areas of study: containerless processing of molten salts, aqueous solutions, and ultrahigh-temperature ceramics. NScD staff are looking for input, inspiration, and collaboration on what we can do next.

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Past, Present, and Future of Materials for Extreme Environments at Oak Ridge National Laboratory

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INTRODUCTION

Materials capable of withstanding extreme environments are essential to the nation's energy, manufacturing, chemical processing, ground transportation, commercial aerospace, space exploration, and defense sectors. The history of Oak Ridge National Laboratory's (ORNL's) leadership, impact, and partnerships in development of new materials for extreme environments is very briefly reviewed, with emphasis on resistance to temperature, pressure, radiation, corrosion, wear, velocity, and heat flux. New materials have regularly been developed over the past 70 years in response to globally significant technological challenges, such as safe nuclear fission and fusion energy power, deep-space exploration, extreme vehicle velocities, structural intermetallics and ceramics development, reduction of greenhouse gases to combat climate change, improved societal products (e.g., cookstove and automobile alloys), and affordable advanced materials. Notable recent advancements include (1) effective application of modern integrated computational materials engineering (ICME) methods to guide new materials design, which captures uniquely powerful combinations of advanced materials characterization capabilities and high-performance computing resources within the national laboratory network; (2) the capability to design and tailor selected classes of new materials to achieve targeted property sets, manufacturability, and cost; and (3) reduction in the time required for materials design and development, thus reducing development costs and expanding the depth of scientific and technical understanding. Section 1 of this article briefly introduces the past and recent history of selected representative examples of alloys, intermetallics, ceramics, composites, and claddings/coatings developed or co-developed by ORNL, with many of these technologies patented and/or commercialized. Section 2 highlights, in more detail, one example of the design philosophy and strategy that is guiding ORNL's recent development of a new class of high-temperature alloys.

HISTORY OF MATERIALS DEVELOPMENT FOR EXTREME ENVIRONMENTS

The Clinton Laboratories Metallurgy Division was formed in 1946 to address the problem of neutron distortion of graphite in early reactors. This organization, and others that followed once the laboratory transitioned out of the Manhattan Project to become ORNL in 1948, focused on metallurgical and solid-state studies not related to nuclear weapons. Early research focused on thorium and zirconium metallurgy, but the research mission broadened to ceramics, composites, intermetallics, and other materials in the decades to follow, even as the various core sponsoring agencies evolved from the Atomic Energy Commission (AEC, founded by the Atomic Energy Act of 1946), to the Energy Research and Development Administration (ERDA) in 1975, and ultimately to the US Department of Energy (DOE) in 1979. Most of the undergirding mission requirements in each era demanded increased scientific understanding and/or new development of advanced materials, very often for one or more extreme environments. Table 1 provides a summary of selected examples of the classes of materials studied and developed at ORNL from the 1950s to present day and identifies key sponsoring agencies or programs, with emphasis on recent decades. Table 2 lists examples of ORNL-developed materials for extreme environments that have received national or international awards. Brief historical descriptions of a subset of these examples follow.

Zirconium alloys. Zirconium alloys (1952–1966) were among the earliest materials investigated, primarily for homogenous reactor and light-water reactor (LWR) technologies. Researchers developed the phase diagrams, as well as select alloys, within the Zr-Nb-X, Zr-Mo, Zr-Cu, and Zr-Pd systems. These early metallurgical studies motivated ORNL to pioneer development and use of vapor-pressure measurements to establish equilibrium conditions during annealing. X-ray techniques were applied to evaluate phase transformations, and the low temperature–specific heats of Zr, Ti, Hf, Zr-Ir, and Zr-Sn were measured for the study of density of states [1].

Hastelloy N alloys. Corrosion experiments in circulating molten fluoride salts in the early 1950s discovered rapid corrosion of Ni-base alloys, such as Inconel 600 alloys. Hastelloy alloys B and W exhibited good corrosion resistance but became very brittle after long-term exposure at temperatures of interest (~815°C). Consequently, ORNL developed the Hastelloy N alloys (patent issued in 1960) for improved compatibility with molten fluoride salts, largely in support of the Molten Salt Reactor Experiment (MSRE, 1965–1968). This unique application demanded a new, corrosion-resistant, high-temperature alloy that could be readily manufactured, including extrusion and welding, into complex shapes for the reactor containment vessel, piping, and heat exchangers. Ni and Mo were known to be more thermodynamically stable in fluoride compounds than Cr, but Cr was also necessary for air oxidation resistance on the external surfaces. Key design elements of the resultant Ni-Mo-Cr-Fe alloy included (1) reduced Cr (~7 wt.%), balancing the need for minimizing the corrosion rate in fluoride salts while maintaining adequate air oxidation resistance; (2) sufficient Mo (~16 wt.%) to provide effective solid solution strengthening; and

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Table 1. Examples of ORNL-developed materials for extreme environments

Materials	Era	Sponsors and key collaborators
Thorium metallurgy	1949–1956	AEC
Zirconium alloys, including Zr-Nb	1952–1966	AEC
INOR-8/Hastelloy N alloys	1952–1968	MSRE
Iridium alloys, including DOP-4, DOP-26, and DOP-40	1967–2000	AEC, ERDA, DOE, NASA
Super 9Cr-1Mo steels (Grade 91)	1970–1982	NE, FE (Combustion Engineering)
Toughened monolithic Si_3N_4 and SiC whisker–reinforced alumina and mullite	1981–1998	BES
High-reliability Si_3N_4 for heat engines	1983–1997	OTT (Norton)
Intermetallic alloys (e.g., Ni_3Al, NiAl, Fe_3Al, FeAl, Ni_3Si, Cr-Cr_2Nb)	1981–2005	Seed, BES, FE, EERE, DOD (Duraloy)
SiC/SiC ceramic matrix composites	1982–2007	FE, OIT (GE)
3Cr-3WVTa Bainitic steels	1987–2021	NE, OIT, FES
9Cr-2WVTa reduced-activation ferritic/martensitic (RAFM) steel	1984–1997	FES
Cast CF8C-Plus stainless steels	1998–2011	VTO (Caterpillar)
14YWT oxide dispersion strengthened (ODS) steel	2000–2019	LDRD, NE, FES
Alumina-forming austenitic (AFA) alloys	2006–2021	FE, Seed, EERE, DARPA, ARPA-E (Carpenter, Duraloy)
Cookstove FeCrAl/Si alloys	2007–2018	BETO (CSU, EI)
Castable nanostructured steels	2012–2021	NE, FES
Accident-tolerant fuel (ATF) FeCrAl alloys	2012–2018	NE (GE/GNF)
Cast Al-Cu-Mn-Zr alloys	2013–2017	VTO (FCA, Nemak)
Cast Al-Ce-X alloys	2013–2019	AMO
High-Cr FeCrAl alloys	2014–2019	FE
High-temperature Al alloys for 3D printing	2018–2021	AMO, VTO
CCNZ (CuCrNbZr) alloys	2018–2021	FES
Complex geometry SiC by printing + CVI	2018–2021	NE, FES
Higher-temperature piston steels	2018–2021	VTO (Cummins)

AMO = DOE Advanced Manufacturing Office, ARPA-E = Advanced Research Projects–Energy, BES = DOE Basic Energy Sciences program, BETO = DOE Bioenergy Technologies Office, DARPA =Defense Advanced Research Projects Agency, EERE= DOE Energy Efficiency and Renewable Energy programs, FE = DOE Office of Fossil Energy and Carbon Management, FES = DOE Fusion Energy Sciences program, LDRD/ Seed/ = ORNL internal Laboratory Directed Research and Development program, NASA = National Aeronautics and Space Administration, NE = DOE Office of Nuclear Energy, OIT = DOE Office of Industrial Technologies, OTT = Office of Transportation Technologies, VTO = DOE Vehicle Technologies Office

(3) tight control of Mn, Si, and Al impurities for better fabricability [2]. Over 50 tons of the new alloy (known at ORNL as INOR-8) were manufactured for the MSRE. This alloy has remained commercially available over the past 60 years under the trade names Hastelloy N and Allvac N.

Iridium alloys for space power. A series of iridium alloys capable of resisting extreme impact and heat were developed at ORNL (1967–2000) as protective fuel cladding materials for NASA's radioisotope thermoelectric generators (RTGs). In 1973 an iridium alloy containing ~0.3 wt.% W was selected for the RTGs that powered the Voyager missions, with those RTGs still operating today as Voyager 1 explores beyond the solar system. The DOP-26 alloy [3] offered further improvements, with trace additions of Th and Al to improve ductility at high strain rates. This ORNL alloy continues to be used in the manufacture of the vented shell/cladding that protects the plutonium-238 oxide fuel pellets in the RTGs powering both deep-space[1] and Mars missions.[2] The DOP-26 cladding powering the RTGs, from NASA's Cassini spacecraft through the Mars 2020 Perseverance Rover, has been manufactured by ORNL, along with the carbon-bonded carbon fiber insulation and now recently the plutonium-238 oxide fuel.

Table 2. Examples of national and international awards for ORNL materials developed for extreme environments

Year	Award	Citation	ORNL lead PI
2019	NACE*	FeCrAl Accident Tolerant Cladding	Field
2017	R&D 100	ACMZ (AlCuMnZr) Cast Al Alloys	Shyam
2017	R&D 100	ACE: Cast Al-Ce alloys	Rios
2017	R&D 100	Filler Alloys for Welding & Printing	Feng
2015	NACE*	Alumina Forming Austenitic Alloys	Brady
2012	R&D 100	NanoSHIELD: Super Hard Coatings	Peter
2012	FLC ETT**	Cookstove Alloy (Envirofit & Colorado State University)	Brady
2011	R&D 100	Stainless Tooling for High T Presses	Muralidharan
2011	R&D 100	CermaClad Coatings(w/ MesoCoat)	Blue
2009	R&D 100	Alumina-Forming Austenitic Alloys	Brady
2007	R&D 100	Cast Ni-Al for Heat-Treat Furnaces	Sikka
2007	R&D 100	Armstrong Process Ti, Alloy Powder	Blue
2006	R&D 100	TMA 6301 & TMA 4701 Alloys	Muralidharan
2003	R&D 100	CF8C-Plus: Hi. Temp. Cast St. Steel	Maziasz
2001	Energy 100	Intermetallics: Ni & Fe Aluminides	Liu
1995	R&D 100	Gel Casting of Ceramics	Janney
1995	R&D 100	3M Ceramic Composite Filter	Stinton
1990	R&D 100	HT-UPS: Lean Austenitic St. Steel	Maziasz
1990	R&D 100	Ductile Iron Aluminides	McKamey
1987	R&D 100	Fiber Reinforced CMC Fabrication	Stinton
1983	R&D 100	NiFe Aluminide	Liu
1982	R&D 100	High Performance Ceramics	Morgan
1982	R&D 100	Super 9Cr-1Mo Steel Alloys	Sikka
1979	R&D 100	DOT Structural Alloys	Liu

* NACE Materials Performance Corrosion Innovation of the Year
**Federal Laboratory Consortium, Excellence in Technology Transfer

Super 9Cr-1Mo alloys for power plants. A 1970s national task force supporting liquid metal breeder reactor technologies recommended development of improved ferritic/martensitic steels for energy applications by modification of the Grade 9 (9Cr-1Mo) class of alloys with funding from the DOE Offices of Nuclear Energy (DOE NE) and Fossil Energy and Carbon Management (DOE FE). By the early 1980s ORNL, in collaboration with Combustion Engineering, had demonstrated a new 9Cr-1Mo alloy, modified with additions of carbonitride-forming elements Nb and V, offering significantly increased high-temperature strength and creep resistance over Grade 9 in the range of 500–704°C [4]. Development of this alloy, known as Super 9Cr-1Mo or Grade 91, spawned a new class of creep strength enhanced ferritic (CSEF) steels with 7–12% Cr. After code case approvals, the unpatented alloy was widely commercialized and available

1 1977 Voyager 1 and II–Interstellar space, 1989 Galileo-Jupiter, 1990 Ulysses-Solar, 1997 Cassini-Saturn, 2006 New Horizons-Pluto

2 2011 Mars Curiosity Rover, 2020 Mars Perseverance Rover

from suppliers in the United States, Japan, Germany, and France by the 1990s. Billions of dollars in commercial impact have been generated by Grade 91 steels due to widespread adoption for applications such as superheater tubes, headers, and main steam pipes in a variety of power plant types, including ultra-supercritical. Further, a 9Cr-2WVTa RAFM steel, also designed by ORNL in the 1980s, is the alloy known to have inspired the modern European, Korean, and Chinese RAFM variants. A similar design philosophy was subsequently used to develop ORNL's higher creep strength "super" bainitic steels, Grades 33 (3Cr-3W) and 315 (3Cr-2W-1Mo), with creep properties similar to Grade 91. These 3Cr steels could replace 2¼ Cr steels limited to 550°C and potentially increase operating temperatures by 50–150°C or, perhaps more importantly, reduce wall thickness in large pressure vessels [5].

Intermetallic alloys. A scientifically rich era of intermetallic materials research and development was catalyzed by a 1981 ORNL internal Seed Money project investigating Ni_3Al. This grassroots effort rapidly grew into a multiprogram research initiative involving three DOE offices (Table 1) and the Office of Naval Research. The research strategically integrated both fundamental and applied research efforts. The overarching objective was to develop a new class of commercial high-temperature structural materials—ductile, corrosion-resistant, lighter-weight intermetallics enabled by microalloying. Intermetallics exhibit ordered long-range crystal structures over a broad temperature span, with mechanical properties between metals and ceramics due to the potential for both metallic and covalent bonds. Properties can be significantly altered with small variations in composition. It was discovered that the corrosion and oxygen embrittlement resistance of Ni_3Al (and other aluminides) could be significantly improved with small additions (~2%) of Cr, and that trace additions of B partitioned to grain boundaries, improving the ductility of slightly substoichiometric compositions. The alloys were solution-strengthened by additions of Mo, Zr, and Hf, with the latter two elements also improving weldability and castability. Oxide, carbide, and boride dispersions added additional strengthening to some alloys. Research eventually expanded beyond Ni_3Al to include NiAl, Fe_3Al, FeAl, TiAl, Ni_3Si, and Cr-Cr_2Nb [6], [7]. Numerous advances in scientific understanding resulted in design, demonstration, licensing, and deployment of intermetallic alloys, particularly centrifugally cast Ni_3Al for large furnace rolls and Fe_3Al for hot gas filters. The impacts of these research efforts were recognized with multiple R&D 100 awards (Table 2), the E. O. Lawrence Award, and the Humboldt Award. Today ORNL still receives wide recognition for our decades of intermetallic research, largely due to the substantial record of high-quality publications documenting our scientific leadership.

> *"The materials developed in the DOE program became the foundation for the material now going into aircraft engines."*
> —Krishan Luthra, who led GE Global Research's development of CMCs for 25 years [10]

Ceramic matrix composites. In the early 1980s, ORNL began investigating ceramic composites with a goal of enabling brittle ceramics to function as high-temperature, damage-tolerant structural materials systems. Chemical vapor infiltration (CVI) research for ceramic matrix composites (CMCs) began in 1982 under DOE FE, following years of chemical vapor deposition (CVD) research at ORNL for coating nuclear particle fuels. Invention of the forced-flow thermal gradient (FFTG) CVI process at ORNL [8] enabled SiC matrix infiltration of simple SiC-fiber pre-form geometries in days instead of the months typically required for thicker sections and allowed ORNL to establish significant leadership in CVI and CMC research [9]. In 1992 DOE launched the Continuous Fiber Ceramic Composite (CFCC) program under the DOE Office of Industrial Technologies. This >$100 million program, led by ORNL, supported a robust, decadelong series of research partnerships among national laboratories, industry, and academia, as well as strategic collaborations with the US Department of Defense. ORNL provided scientific leadership in developing the materials, processes, and SiC_{fiber}/SiC_{matrix} composite architectures, including the fiber interface coatings that enabled the key CMC pseudo-toughening mechanisms. Candidate applications included hot gas filters, radiant burners, carburized furnace fan blades, and turbine combustor shrouds. Gas turbine engines eventually emerged as the primary application target, and ORNL partnered closely with General Electric (GE) and other organizations to better understand the associated properties and high-temperature oxidation behavior for candidate SiC/SiC CMC systems and their protective coatings. After CFCC concluded, GE invested an additional 15 years to scale and qualify SiC/SiC CMCs commercially (using a melt infiltration process) for replacement of superalloys in static turbine engine components, particularly combustor shrouds. Modern CMCs offer one-third the density of superalloys and enable a 100–200°C increase in temperature. This new class of lightweight, higher-temperature structural materials entered commercial flight service in 2016 with the LEAP aero engine, which provided a 15% increase in efficiency. By 2017 GE reported over $150 billion in aero gas turbine engine preorders resulting from the efficiency advantages enabled by CMCs.

Additionally, the ORNL Fusion Energy Sciences program elucidated the degradation mechanisms of early SiC/SiC composites in nuclear environments and developed a new generation of composites capable of surviving extreme doses of high-energy neutrons [11]. This development led to nuclear applications of SiC technologies, including accident-tolerant nuclear fuels and the Transformational Challenge Reactor (TCR) core assembly research that integrated binder jet additive manufacturing (AM) and CVI to create near-net-shape SiC particle fuel containment systems with complex geometries. Current CMC research at ORNL is focused on nuclear, fusion, turbine, and aerospace applications, including cooperative experimental and computational CVI research with industry.

Toughened ceramics. The Ceramic Technology Project (1983–1998), led by ORNL under the DOE Office of Transportation Technologies, sponsored a diverse portfolio of collaborative ceramic materials and processing research for development of an industrial technology base to provide reliable, cost-effective high-temperature ceramics for advanced heat engines. Industrial research collaborations included development, manufacture, and engine testing of Si_3N_4 valves for diesel engines used in the most severe environments, such as mining. In parallel, during the same era, DOE Basic Energy Sciences–sponsored fundamental research that resulted in development of new monolithic Si_3N_4 compositions. Reinforced microstructures were designed to effectively exploit the limited toughening mechanisms available in these high-strength but brittle materials, including promotion of elongated, reinforcing β-Si_3N_4 grain structures in a fine-grained matrix to bridge cracks and improve resistance to crack growth. Additionally, SiC whisker–reinforced alumina composites with excellent toughness were developed and patented [12] and adopted as an industrially significant material for cutting tools.

Alumina-forming austenitic alloys. A 2007 *Science* article introduced a new class of heat-resistant, higher-strength AFA stainless steels developed by ORNL [13]. The AFA family of alloys, primarily developed under DOE FE, the DOE Office of Energy Efficiency and Renewable Energy, and Advanced Research Projects Agency–Energy, offer significant opportunity to increase operating temperatures (500–1150°C) in aggressively oxidizing environments (e.g., steam) while also maintaining ability to use lower-cost ferrous alloys instead of Ni-base alloys. The key innovation was the design of chemistry and microstructure to enable a high-strength austenitic alloy that selectively oxidizes to form a protective external Al_2O_3-based scale instead of the typical Cr_2O_3-based scales that form on most stainless steels. Alumina scales are more stable and protective than Cr_2O_3-based scales, particularly at higher temperatures and in environments containing corrosive water vapor, carbon, and sulfur-based species. Additionally, significant improvements in creep strengths, as compared to other high-temperature stainless alloys, were achieved through nanodispersions of NbC and $M_{23}C_6$ and, more recently, by precipitation of γ'-Ni_3Al for AFA Fe-base superalloys. Cast variants capable of operation up to ~1,150°C have been developed more recently, with five distinct grades of AFA alloys developed thus far. The AFA alloys have received multiple awards (Table 2) and were licensed by Carpenter Technologies (2011) and Duraloy Technologies (2018). They have demonstrated success ranging from thin foils in turbine recuperators to cast components for industrial heat treating, chemical, and petrochemical processing, as well as potential for hydrogen energy environments. Their developmental story is highlighted in more detail in the second section of this article.

Cookstove alloys. Almost 3 billion people use open fire biomass cookstoves, which are typically highly inefficient and release large volumes of smoke and toxic emissions that can be extremely detrimental to user health and may contribute to climate change. Clean, low-cost cookstove technologies can help to address this complex issue. One of the most challenging components is the cookstove combustor, which needs to operate at high temperatures (often ≥600°C) in the presence of highly corrosive biomass fuels. Such conditions pose a significant challenge, as materials must be both durable and low-cost to permit widespread adoption. A 2007–2018 collaboration with Envirofit International (EI) and Colorado State University allowed ORNL to select, optimize and co-patent FeCrAl-based alloy compositions for clean biomass cookstove combustors [14]. This contributed to EI successfully producing new, globally affordable wood-fired cookstoves that improved fuel consumption by up to 60% and lowered smoke and toxic emissions by up to 80%, reducing the severe health effects related to cookstoves. EI reached its one-millionth clean cookstove customer by 2015, with many of these stoves using the FeCrAl alloy.

ATF FeCrAl alloys. Wrought, thin-wall fuel cladding made of ORNL's new C26M alloy (Fe-12Cr-6A-l2Mo-Si-Y) began commercial service exposure in 2018 in the Hatch-1 Nuclear Reactor in Baxley, GA. This new family of thin-wall FeCrAl alloy cladding for LWRs was rapidly developed (2012–2017) under the DOE NE ATF Campaign, partly in response to the Fukishima disaster, as a potential replacement for Zr-based cladding alloys. New FeCrAl compositions were designed to avoid the rapid (and exothermic) oxidation and hydrogen evolution that Zr-based alloys experience in a loss-of-coolant accident (LOCA) scenario. A balance of high-temperature oxidation resistance, manufacturability, mechanical properties, and radiation tolerance was achieved by optimization of Cr, Al, and solute additions [15]. These nuclear-grade cladding materials are designed to provide oxidation resistance in accident scenarios up to 1,400°C, compared to ~800°C for the current Zr-based alloys.

Cast AlCuMnZr alloys. A new family of higher-temperature, higher-strength cast AlCu-based alloys was developed (2013–2017) by ORNL in partnership with FCA US LLC and Nemak Corporation. The sponsor (DOE VTO Materials Program) funded three parallel, independent teams (one led by ORNL and two by industry) with identical materials development targets that strategically imposed a uniquely stringent combination of requirements, including (1) use of state-of-the-art ICME methods to develop a new cast lightweight alloy, (2) a 50°C increase in temperature capability over existing cast commercial aluminum alloys, (3) a 25% increase in strength at peak temperature, (4) excellent castability using existing commercial processes, (5) no more than a 10% cost increase, and (6) delivery of a full-scale reciprocating engine test of a cylinder head cast from the new material in only 4 years. The ORNL-led team met or exceeded all VTO requirements and delivered an alloy capable of a remarkable 100°C temperature increase (i.e, up to 350°C), in 4 years or less [16]. The team also solved a long-standing hot-tearing challenge for cast Al-Cu alloys. Further, only the ORNL-led team met all DOE requirements in 4 years. These alloys are presently being tested by General Motors as potential next-generation cylinder head and block alloys for higher-efficiency, lighter-weight engines for sport utility vehicles (SUVs) and light trucks [17]. In a parallel effort, an ORNL team supported by the Critical Materials Institute (DOE AMO), developed a new family of cast Al-Ce-based alloys that offer remarkable stability at higher temperatures [18].

High-temperature aluminum alloys designed for printing. There are presently very few commercial lightweight alloys available as printing feedstock. A multioffice collaboration between AMO and VTO (2018–2021) is currently investigating, designing, and demonstrating several families of new higher-temperature lightweight alloys tailored to specific AM processes. This research was motivated by the discovery that some alloy compositions exhibit remarkable changes in microstructure and properties when printed, as compared to their cast state. The extremely rapid cooling rates of some AM processes can result in nonequilibrium or far-from-equilibrium solidification paths that can deliver extreme microstructural refinement, as well as novel intermetallic phases with unique properties and stability [19]. New AM feedstock alloys developed at ORNL include multiple variants of Al-Cu and near-eutectic AlCeNi-based systems. One of the ORNL-designed printed alloys (AlCeNiMn) recently demonstrated the best creep resistance of any known bulk aluminum alloy at 300°C [20], as well as high-temperature fatigue behavior similar to or better than that of forged alloy 2618. One of the new alloys is presently being evaluated by General Motors for use as printed pistons for next-generation, higher-efficiency, lightweight engines for trucks and SUVs [17]. These new printable aluminum alloys were developed from concept to full-scale components in less than 3 years and offer very good printability and excellent mechanical properties up to 400°C.

EXAMPLE OF PRESENT MATERIALS DEVELOPMENT FOR EXTREME ENVIRONMENTS

This section introduces one example of a recent materials design philosophy and strategy by which ORNL has delivered multiple new advanced high-temperature steels precisely tailored for improved performance in extreme environments and cost. The example is also anticipated to be a precursor of future materials development at ORNL.

Alloy design. Alloy design strategies for high-temperature structural environments strongly depend on the combined requirements of target applications and components (e.g., combustion chambers, heat exchangers, steam generators, tubes/pipes, gas turbines, pressure reactor vessels, production furnaces, chemical/petrochemical plant components, internal combustion vehicle engines and its components), in which the materials are to be exposed at various temperatures in either static or dynamic stress conditions, within different levels of oxidizing/corrosive environments [21], [22]. The balance of mechanical performance, surface protection, manufacturability, and affordability are key for material selection, and these features must always be considered and satisfied in any new alloy designs. For example, improvement of steam power energy conversion system efficiency has been vigorously promoted in past decades to reduce greenhouse gas emissions, which creates an intensified demand for structural materials capable of improved high-temperature mechanical performance, environmental compatibility (fire-side and steam-side), and cost-effectiveness. Higher-temperature operation requires not only improved mechanical properties at elevated temperature but also advanced surface stability because the various detrimental corrosive/oxidizing environments become exponentially more aggressive as temperatures increase. Further, although some existing Ni- and/or Co-base alloys could meet or exceed the performance requirements of many of these applications, the materials systems are cost-prohibitive for most large-volume industrial applications.

Thus, for high-volume, extreme energy environment applications, new Fe-base alloy development has been important, typically with an overarching target of extending material life through a combination of creep–deformation resistance, oxidation resistance, and affordability of materials and manufacturing. Hereafter, an example of successful development of a new class of heat-resistant Fe-base alloys at ORNL is introduced as one of the examples meeting multiple key property and manufacturing requirements for current and potential future structural applications with extreme operating environments.

Alumina-forming austenitic alloys: A new class of heat-resistant alloys. The new AFA alloys, based on Fe-Cr-Al-Ni-Nb-C as major constituents with additional minor elements and developed at ORNL for structural use in aggressive oxidizing environments in the temperature range of 500°C–1,150°C, exhibit a unique combination of oxidation resistance through protective alumina-scale formation—instead of the chromia scales formed on most austenitic stainless steels—and improved creep–rupture performance via precipitation strengthening at elevated temperatures, together with inexpensive raw material cost as Fe-base alloys. The development concept was to pursue, not a single alloy composition, but instead a new alloy design strategy that balanced both oxidation and creep resistance, to offer a wider composition range that could tailor performance (and cost) characteristics and also offer the option of either wrought or cast forms. The result was five major grades of ORNL-developed AFA alloy series, which are summarized in Table 3 [23]. The first three are wrought grades—standard AFA, AFA^{LN}, and AFA^{HP}—which cover a wide temperature range (650°C–950°C). The cast grade of AFA offers higher-temperature capability

Table 3. Major grades of wrought AFA alloys [23]

Designation	Composition, wt.%	Target/remarks
AFA	Fe-(14-15)Cr-(2.5-3.5)Al-(20-25)Ni-(1-3)Nb with Mn, Si, Mo, W, Cu, B, C, P	Up to ~700-850°C, wrought, baseline AFA
AFA^{LN} (low Nickel)	Fe-14Cr-2.5Al-(12-15)Ni-(0.6-1)Nb-(5-10)Mn-3Cu with Si, C, B, etc.	Up to ~650°C, wrought, lower-cost, low Ni AFA
AFA^{HP} (high performance)	Fe-(12-15)Cr-(3.5-4.5)Al-(25-30)Ni-(1-3)Nb-0.1Hf or Zr-0.02Y-2Mn-(0-4) Mo+W-0.5Cu +B, C, P	Up to ~800-950°C, wrought, highly alloyed AFA for higher temperatures
Cast AFA	Fe-(20-35)Ni-(14-25)Cr-(3.5-4.5)Al-1Nb-2Mn-(0-4)Mo/ W-0.5-1Si-0.5Cu-(0.2-0.5)C + B ± Hf, Zr, Y	up to ~750-950°C (for 25Ni grade), or >1100°C (for 35Ni grade)
High Nickel AFA with $L1_2$ strengthening	Fe-(14-19)Cr-(2.5-3.5)Al-(30-35)Ni-3Nb with Ti, Si, C, B, etc.	Up to ~750-850°C, (up to 900°C for 45Ni grade)

than the wrought alloy series. Finally, the $L1_2$ strengthened AFA "superalloys," with higher Ni contents, are suitable for applications requiring a higher allowable stress. To date, one of the cast versions of AFA (Fe-25Cr-4Al-35Ni wt.% base), has demonstrated excellent oxidation resistance at 1,100°C in a water vapor–containing environment, as shown in Figure 1 [24], [25]. By comparing commercially available, chromia-forming cast austenitic stainless steel HP, the AFA alloy coupon specimen maintained its morphology and the continuous alumina layer on the surface in the cross-sectional view, suggesting significantly superior protective characteristics even in such an aggressively oxidizing environment. It should be emphasized that both alloys exhibit comparable creep–rupture performance at 1,100°C. The cast AFA alloys were licensed by Duraloy Technologies in 2018 and have demonstrated successful commercial use as furnace rollers by an industrial steel fabricator [24].

The present AFA alloys offer the potential for use in atmospheres containing steam, exhaust gas, coking, syngas, sulfurizing, carburizing, hydrogen fuels, as well as a solid-oxide fuel cell balance of plant, with promising surface protection. Some advantages are also recognized in supercritical CO_2, molten salt, and metal dusting environments, under certain conditions [26].

Why alumina? Oxidation resistance is one of the essential performance characteristics that preserves the durability of heat-resistant alloys, particularly in systems where protective coatings are not feasible or affordable. Surface protection through formation of an external, thermally grown continuous layer of a slow-growing, thermodynamically stable oxide phase is the key to peak oxidation resistance because subsequent oxidation is limited by diffusion of metal or oxygen species across this oxide layer [27]. For high-temperature applications above ~600°C, Cr_2O_3 (chromia) and Al_2O_3 (alumina) are the principal oxides that form as external scales and are most widely used for the protection of metallic alloys. However, chromia-forming alloys can become less oxidation-resistant as temperatures increase, especially when the environment contains moisture [28]. Formation and volatilization of chromium oxyhydroxide deteriorates the surface protectiveness of many alloys designed to be chromia formers. In contrast, alumina scales are thermodynamically stable to much higher temperatures, even in a moisture-containing environment, and the oxide growth kinetics are nearly two orders of magnitude slower than chromia scales at a given condition.

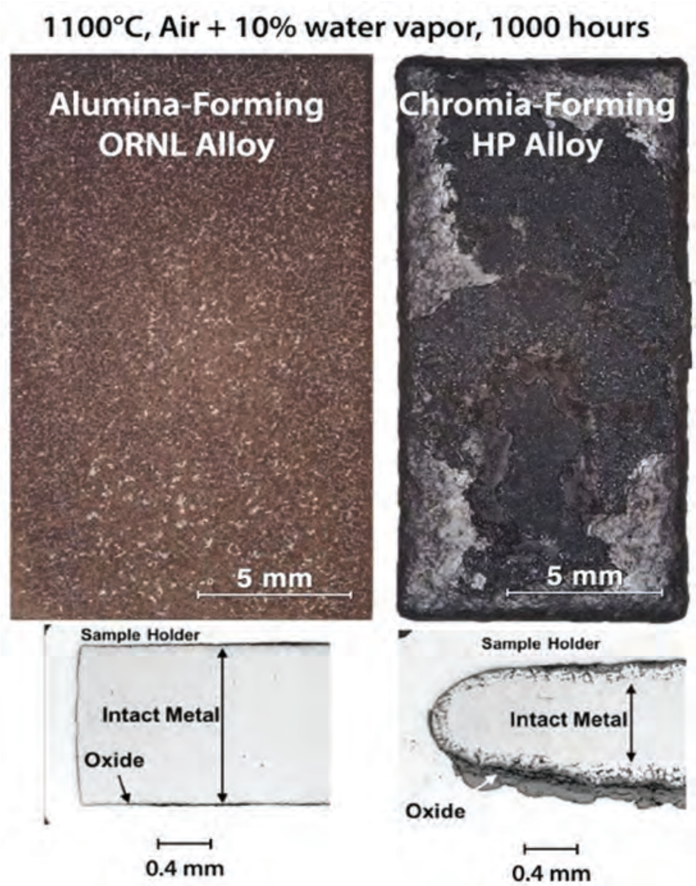

Figure 1. Oxidation-tested coupon specimens and cross-sectional images of an AFA alloy (Fe-25Cr-4Al-35Ni wt.% base) and commercial Cr2O3-forming cast austenitic stainless steel HP (Fe-25Cr-35Ni wt.% base), after cyclic exposure at 1,100°C in air + 10% water vapor for total 1,000 h [24], [25].

Protective alumina scale formation has already been used in Ni-base and FeCrAl ferritic alloys to achieve high-temperature surface protection. However, the former requires a trade-off of expensive material costs, and the latter does not offer adequate high-temperature strength for many structural applications because of the weak body-centered cubic-Fe (BCC-Fe) structure [13]. Austenitic Fe-base alloys can provide the balanced performance of both high-temperature strength from the close-packed face-centered cubic (FCC-Fe) structure matrix and cost-effectiveness due to lower Ni content. However, the Al addition strongly stabilizes BCC-Fe (ferrite) relative to FCC-Fe (austenite), which made the development of materials with both "alumina-forming" and "austenite matrix" more challenging. In fact, various historical attempts [29], [30] failed to find a single alloy composition demonstrating both protective alumina-scale formation and sufficiently high mechanical properties at elevated temperatures. Success of ORNL's AFA alloy development relied on computational thermodynamics to significantly reduce the experimental iteration required to find the compositional range of austenite single-phase matrix with adequate Al addition, combined with a maximized supersaturation of the strengthening second-phase precipitates [31]. By combining with an experimental approach to characterize the microstructure, oxidation resistance, and creep–rupture property, relatively straightforward compositional criteria were developed to achieve the targeted AFA performance characteristic, as listed below.

1. Identify the allowable Ni content range based on the targeted material cost, service temperature, strengthening mechanism to be applied, and comparison with competitive materials.
2. Maintain an austenite single-phase matrix (minimize/eliminate ferrite phase) at the target temperature, by balancing major and minor alloying elements such as Cr, Al, Nb, C, Mn, and Si.
3. Allow a relatively high Cr content, which reduces the required Al content to form a protective alumina scale (excess Al content not only destabilizes austenite but can also negatively impact high-temperature strength).
4. Avoid or minimize the use of Ti and V, and add Nb (or Ta), to control the strengthening second-phase precipitation without interfering with the formation of the external alumina scale.
5. Maximize the supersaturation of second-phase precipitation in the austenite matrix for precipitation strengthening at elevated temperatures.

Minimum required amounts of major elements (Cr, Al, Ni, and Nb) vary depending on the target temperatures, but in general, the AFA alloys require more than 12Cr, 2.5Al, 20Ni (or 12Ni when combined with a Mn addition), and 0.6Nb, wt.% for external alumina-scale formation at or above ~600°C. It is also necessary to maintain less than 0.3 wt.% of Ti+V and 0.02 wt.% of N to preserve the alumina-scale formability and stability [27]. Within the compositional guidelines, minor element additions must be controlled to optimize the precipitation of strengthening second phases.

Precipitation-strengthening. Because of the requirement of major elements (Cr, Al, Ni, Nb, and C) in the AFA alloy design, formation of multiple second-phase precipitates is expected in the alloys at the target service temperatures. Among various second phases, B2-NiAl, Laves (C14)-Fe_2Nb, $L1_2$-Ni_3Al, $M_{23}C_6$, and MC can contribute to high-temperature strengthening.

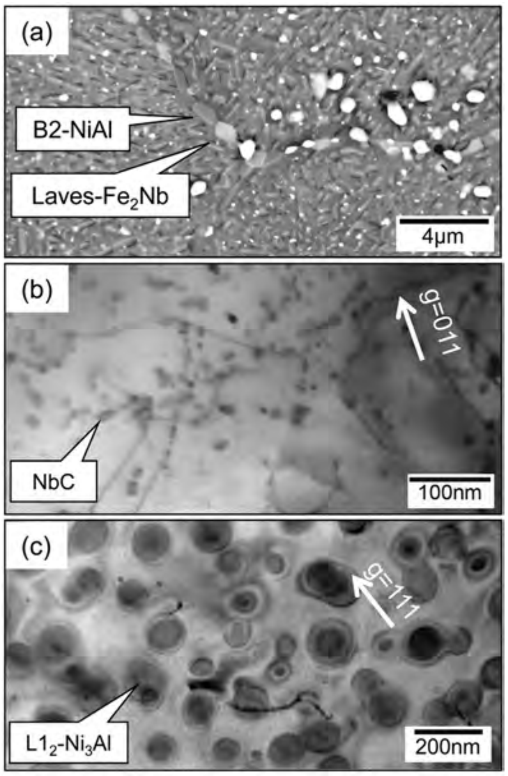

Figure 2. Scanning electron microscopy–backscattered electron image (a) and transmission electron microscopy bright field images (b and c) showing the second-phase precipitation formed in wrought AFA alloys after creep–rupture testing at 750°C: (a) dispersion of B2-NiAl and Laves-Fe2Nb [31], (b) nanoscale NbC [31], and (b) coherent L12-Ni3Al [32].

Thus, alloy design focuses on identifying the composition ranges that can dissolve some or all of these second phases during the solution heat treatment (e.g., 1,100°C–1,200°C), and then precipitates at the service conditions (e.g., 600°C–900°C), for precipitation strengthening. Submicron-size precipitates of B2-NiAl and Laves-Fe_2Nb form at both grain boundary and grain interior, as shown in Figure 2a, and this grain boundary precipitation effectively prevents grain boundary sliding during creep–deformation [31]. The AFA alloys are designed to form either nanoscale NbC (or $M_{23}C_6$ where M = mainly Cr) or coherent $L1_2$-Ni_3Al precipitates inside the austenite matrix (Figures 2b and 2c, respectively), depending on the target alloy design [31], [32]. These significantly increase the creep–deformation resistance by pinning dislocations. The best AFA creep–rupture performance to date has been achieved by a $L1_2$-Ni_3Al strengthened alloy based on Fe-15Cr-3Al-35Ni-Nb-Ti-C wt.%, which demonstrated creep strength comparable to the state-of-the-art chromia-forming austenitic stainless steel Sanicro25 (Sandvik, Fe-23Cr-25Ni-3W-3Cu-1.5Co wt.% base) at 750°C [33].

Production. To date, ORNL-developed AFA alloys have attracted interest from multiple industries seeking cost-effective, heat-resistant steels with improved oxidation/corrosion resistance. Sheet production through commercially available manufacturing facilities has been conducted to evaluate material durability in various industrial environments. A recuperator for a combined heat and power system, made of an AFA alloy, was produced and evaluated for up to 5,000 h service inside an operating microturbine with the inlet gas temperature of ~720°C [34]. A feasibility evaluation of sheet materials for a solid-oxide fuel cell balance of plant is in progress [35]. Centrifugal cast AFA tubes are also being evaluated for the use of furnace roller components [24]. In addition, AFA alloy tubes would be a strong candidate for reformer/cracking tube applications because of an advantage of AFA alloy characteristics for hydrogen production processes that heavily involve high-temperature steam environments. It should be emphasized that the production of AFA alloys does not require any specific modification of existing manufacturing facilities, so that many types of alloys are considered to be ready for industrial production.

FUTURE MATERIALS

The latest modern computational approaches, such as data-driven material optimization through machine learning, artificial intelligence, and advanced physics-based computational life prediction models with support from computational thermodynamics, are strong tools to guide or identify new alloy composition ranges with optimized performance without sole reliance on time-consuming experimental iteration. In addition, advanced manufacturing processes, such as AM and digital metallurgy, offer remarkable opportunities to expand the possibilities of future heterogeneous materials development with localized control of structure and properties. Hybridization of both materials and processes also offers a host of opportunities for designing new heterogeneous materials systems with uniquely valuable property sets, particularly for extreme environments.

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