AMERICAN CERAMIC SOCIETY
bulletin
emerging ceramics & glass technology
MARCH 2023

Sustainability in industry: Embracing new practices, materials, and systems

Managing mineral consumption | High-temperature ceramics | Thermal energy storage

contents

March 2023 • Vol. 102 No.2

feature articles

Cover image

Solar panels on the rehabilitated Par Moor Blackpool kaolin mining site in Cornwall, United Kingdom. Multinational group Imerys S.A. has numerous ongoing initiatives to sustainably manage the consumption of minerals. Credit: Philippe Zamora and Dominique Lecuivre

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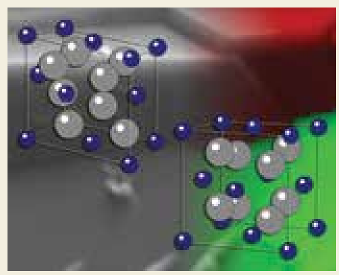
As seen on *Ceramic Tech Today*...


Credit: Edward Pang, Massachusetts Institute of Technology

Extensive modeling leads to new shape-memory zirconia with properties on par with shape-memory alloys

Even when a shape-memory ceramic's lattice compatibility is improved, it still often experiences cracking after just a few dozen transformation cycles. Researchers at the Massachusetts Institute of Technology improved the cyclability of shape-memory zirconia ceramics with the help of a multimode modeling approach.

Read more at www.ceramics.org/shape-memory-ceramics

Also see our ACerS journals...

Investigation of fracture behavior of typical refractory materials up to service temperatures
By E. Brochen, C. Dannert, J. Paul, and O. Krause
International Journal of Ceramic Engineering & Science

Influence of Ti_3AlC_2 addition on water vapor resistance of low-carbon Al_2O_3–C refractories
By G. Liu, N. Liao, Y. Li, et al.
International Journal of Applied Ceramic Technology

Determination of temperature dependent static Young's modulus of refractory ceramics using RUL tests
By M. Henze, W. Reichert, T. Tonnesen, et al.
International Journal of Ceramic Engineering & Science

A replacement of traditional insulation refractory brick by a waste-derived lightweight refractory castable
By Sk. S. Hossain, C. J. Bae, and P. K. Roy
International Journal of Applied Ceramic Technology

Journal of the American Ceramic Society | International Journal of Applied Ceramic Technology | International Journal of Applied Glass Science | International Journal of Ceramic Engineering & Science

Read more at www.ceramics.org/journals

American Ceramic Society Bulletin covers news and activities of the Society and its members, includes items of interest to the ceramics community, and provides the most current information concerning all aspects of ceramic technology, including R&D, manufacturing, engineering, and marketing. The American Ceramic Society is not responsible for the accuracy of information in the editorial, articles, and advertising sections of this publication. Readers should independently evaluate the accuracy of any statement in the editorial, articles, and advertising sections of this publication. *American Ceramic Society Bulletin* (ISSN No. 0002-7812). ©2022. Printed in the United States of America. *ACerS Bulletin* is published monthly, except for February, July, and November, as a "dual-media" magazine in print and electronic formats (www.ceramics.org). Editorial and Subscription Offices: 550 Polaris Parkway, Suite 510, Westerville, OH 43082-7045. Subscription included with The American Ceramic Society membership. Nonmember print subscription rates, including online access: United States and Canada, 1 year $135; international, 1 year $150.* Rates include shipping charges. International Remail Service is standard outside of the United States and Canada. *International nonmembers also may elect to receive an electronic-only, email delivery subscription for $100. Single issues, January–October/November: member $6 per issue; nonmember $15 per issue. December issue (*ceramicSOURCE*): member $20, nonmember $40. Postage/handling for single issues: United States and Canada, $3 per item; United States and Canada Expedited (UPS 2nd day air), $8 per item; International Standard, $6 per item.

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ACSBA7, Vol. 102, No. 2, pp. 1–48. All feature articles are covered in Current Contents.

letter from the editor

Eileen De Guire
Editor

The *ACerS Bulletin* prepares for a digital evolution

Dear readers

The *ACerS Bulletin* has undergone many transitions during its 102 years of existence. As the ceramic and glass industry has evolved and expanded, the *Bulletin* also has evolved and expanded its coverage in step with our industry.

Publishing, too, has evolved with time, and the digital version of the *Bulletin* is about to undergo its own transition.

Starting with the May issue, the digital *Bulletin* will transition from the cumbersome flipbook format to a more flexible, engaging interface. At the same time, the print version of the *Bulletin* will become an opt-in benefit for ACerS members that must be specifically requested (view sidebar: *How to opt in for print*).

Benefits to you

Already, less than half of the ACerS membership receive the *Bulletin* in print and instead read the *Bulletin* solely online in the PDF or flipbook formats. This transition to a new digital platform represents a significant improvement for the e-reading experience of our members.

The new platform will allow us to bring you dynamic content, such as video and audio content, alongside the traditional articles. Want to see what a glass pour looks like? We can show you. Want to hear a Ceramic Tech Chat podcast interview that relates to an article? We can link directly to it. Authors and advertisers can link to extra information, references can link directly to the resource, and more.

The platform is completely responsive, meaning the reading experience will be satisfying on desktops, tablets, and phones. Readers can still download a PDF to read offline at their convenience.

Articles will still be formatted as magazine articles, and we do not engage in "click bait," sensational headlines, or content rabbit holes. The professional quality you expect from the *Bulletin* will continue.

With more people these days working remotely or in hybrid onsite–remote environments, web-based publishing means the *Bulletin* comes to you where you are: at home, at the office, and on the road. While the current flipbook format offered this access in theory, the new platform will be much easier to navigate.

What to expect

Starting with the May issue, all members and subscribers will receive an emailed Table of Contents to the new digital platform. Reading the *Bulletin* will be as simple as perusing a website.

We recognize that some ACerS members will prefer reading the *Bulletin* in print. As content creators and consumers ourselves, we appreciate the value of paging through a favorite magazine or book.

If you wish to still receive the print version of the *Bulletin*, **you must let us know by opting in through the process described in the sidebar**.

The *Bulletin* editorial team is excited about this evolution for the *Bulletin* and the opportunities it opens for our contributors, advertisers, and especially you, our readers. There may be a few bumps along the way, but we will work through them together. We invite you to join us on this journey.

Sincerely,

Eileen

Eileen De Guire
Editor, *ACerS Bulletin*
edeguire@ceramics.org

How to opt in for print

ACerS members can use one of three convenient options to opt in to receive a print version of the *Bulletin*.

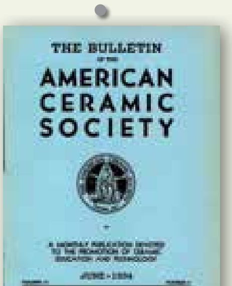
NOTE: This free print version is only available to members who already receive a complimentary print version with their current membership level.

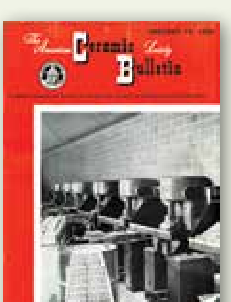
U.S. or Canada members

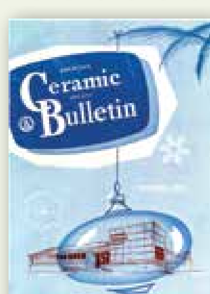
- Online: Login to your ceramics.org account using your membership credentials.
  - → "Purchase" a $0 subscription at https://myacers.ceramics.org/productdetails?id=a1B3u000006PMp8EAG.
- Phone: +1 866-721-3322
- Email: customerservice@ceramics.org

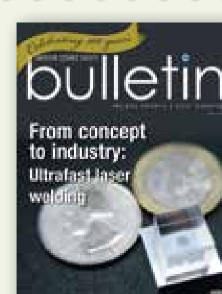
International members (except Canada)

- Online: Login to your ceramics.org account using your membership credentials.
  - → "Purchase" a $0 subscription at https://myacers.ceramics.org/productdetails?id=a1B3u000006PMp9EAG.
- Phone: +1 614-890-4700
- Email: customerservice@ceramics.org









news & trends

At home or on the go, EV charging innovations at CES 2023 have you covered

Infrastructure projects will be a main focus for many states in 2023 due to the historic investments provided by the Bipartisan Infrastructure Law. Among these projects, the National Electric Vehicle Infrastructure (NEVI) Formula Program is one sure to affect a large swath of the U.S. population.

The NEVI Formula Program will provide nearly $5 billion over five years to help states create a network of electric vehicle charging stations along designated Alternative Fuel Corridors, which are a national network for alternative fueling and electric vehicle charging infrastructure along national highway system corridors.

Last summer, states submitted plans for deploying the NEVI network within their respective jurisdictions. And already this year, some states started implementing their plan.

With rollout of the NEVI network, in addition to new tax credits for buyers of electric vehicles, the number of people buying electric vehicles is sure to increase. In turn, the pressure to innovate new charging systems will intensify as well. Luckily, there are plenty of charging solutions in the pipeline as showcased at CES 2023.

CES, or the Consumer Electronics Show, is said to be the world's largest annual consumer technology trade show. It takes place each January at the Las Vegas Convention Center in Winchester, Nevada.

This year, CES took place January 5–8 and welcomed more than 115,000 attendees and more than 3,200 exhibitors. During the four-day event, several key announcements were made regarding electric vehicle charging innovations (highlighted below).

Amazon partners with EVgo to streamline charging process

On the first day of CES 2023, e-commerce giant Amazon announced it will partner with EVgo, a maker of electric vehicle charging systems, to streamline the process of locating, paying, and initiating recharging sessions at an EVgo station. The new service, which will be powered by Amazon's Alexa voice assistant, will reportedly connect drivers to more than 150,000 U.S. public charging stations through EVgo's PlugShare map. It is scheduled for a late 2023 launch.

SparkCharge launches fleet services for mobile charging as a service

SparkCharge is a Massachusetts-based company that bills itself as the first company to create a mobile charging system. Their system, called Charging-as-a-Service (CaaS), allows users to request a portable battery charging unit be delivered to them wherever they are, be that at their home, work, or even a hotel while traveling.

On the first day of CES 2023, SparkCharge announced the launch of its new fleet services solution, which will allow fleet owners and operators to request charges for their vehicles through use of a centralized portal.

New charging products, systems, and components by Blink, EverCharge, and Skyworks

True to its December advanced promise, electric vehicle charging vendor Blink Charging Co. unveiled five new products at CES 2023 for a variety of automotive sectors, including retail, home, parking garage, and street charging.

- The Vision charging system is a two-in-one solution that comes with two 80-amp, 19.2 kW ports that can charge simultaneously. It also features a 55-inch LCD screen for media displays.
- The EQ 200 system, designed for European and South American markets, can fit into any location tailored for bidirectional, vehicle-to-grid systems.
- The PQ 150 smart charging cable, targeted for the European residential charging market, offers 22 kW of power with no need for installation due to its portable design. It also is Bluetooth, Wi-Fi, and SIM/GSM compatible.
- Series 3 is designed for the Asia-Pacific and Latin American markets for two- and three-wheeler electric vehicles. It provides 15 amps of output for installation at small shops, residential, and commercial parking.
- Series 9 is a 30 kW DC fast charger in a small footprint with an LCD touchscreen display for commercial charging sectors. It works with a Wi-Fi, Ethernet, or 4G connection with remote monitoring.

In contrast to Blink's range of products, EverCharge, a provider of electric vehicle charging devices and management systems, announced a single new charging system. Called COVE, this single-family home charging system is an addition to EverCharge's current multifamily systems. It is designed to be integrated into any electrical supply and is compatible with all electric vehicles on the market.

Also unveiled at CES 2023 was a range of new electronic components by semiconductor manufacturing company Skyworks Solutions Inc. that are meant to help shorten recharge time for electric vehicles. These components include next-generation Si89xx isolated analog amplifiers, voltage sensors, and delta-sigma modulator devices. ■

Cleaning up our waterways—addressing the abandonment of fiberglass boats in Virginia

After several years of record demand driven by the COVID-19 pandemic's outdoor-recreation boom, the boat market is expected to finally settle back to normalized levels sometime this year. The result of this buying bonanza is there are now many more fiberglass boats cruising the waterways than before.

The first fiberglass/polyester boat was built in 1942 by Ray Greene of Toledo, Ohio. Over the next few decades, innovations in resin and manufacturing techniques led to fiberglass becoming a dominant boat material.

The weight of fiberglass compared to aluminum is one reason fiberglass boats are so popular. Fiberglass boats are much heavier than aluminum boats, which means they can cut through waves more easily, thus making the ride more comfortable.

On the other hand, fiberglass boats are less durable than aluminum boats. As such, they require more maintenance than aluminum boats, and repairs are typically more expensive as it is more difficult to fix fiberglass than it is aluminum.

Once damage is extensive enough to no longer justify the cost of repairs, fiberglass boats are again at a disadvantage compared to aluminum boats. While the heavier weight of fiberglass is beneficial when boating, it means fiberglass boats are more expensive to dispose of than aluminum boats. Additionally, while aluminum can be sold or donated as a scrap material, methods for recycling fiberglass are still a work in progress, thus adding to the cost of disposal.

Because of the high disposal costs, some owners will choose to abandon their old fiberglass boats in public waters instead. Such dumping is an environmental hazard for numerous reasons. Not only does the fiberglass release microplastics into the water as it degrades, but a boat will often contain oil and other toxic chemicals that will leach into the surrounding environment.

To mitigate illegal dumping, some states, such as Florida, Oregon, and California, have state-run "turn-in" programs that offer owners a way to voluntarily surrender their unwanted vessels to the state free of charge. Establishing such programs offers both environmental and economic benefits, as disposing of a vessel while it still floats costs thousands of dollars less than removing an abandoned boat that has disintegrated.

Unfortunately for owners in the state of Virginia, such a program does not exist there, even though abandoned boats are a growing problem in Virginia waters. So, some Virginia residents, such as Mike Provost, are taking matters into their own hands.

Provost is a U.S. Navy veteran who enjoys cruising the Lynnhaven River near his home in Virginia Beach. During a cruise one day in 2021, he spotted an abandoned 36-foot cabin cruiser left tied to a tree in Long Bay Pointe. He called dozens of offices trying to find someone to remove the vessel, but he was explicitly told that if he personally did not take care of it, no one would.

In response, Provost started the Vessel Disposal & Reuse Foundation (VDRF). This nonprofit leverages charitable donations to hire expert marine salvage contractors to conduct the safe removal and disposal of derelict vessels.

The VDRF website states that, to date, the nonprofit has organized the disposal of 18 abandoned and derelict vessels, representing about 201,820 pounds of landfill debris and more than 14,620 pounds of scrap metal.


Credit: VDRF & VMS Videos, YouTube

The Vessel Disposal & Reuse Foundation coordinates removal of abandoned and derelict boats from Virginia waters.

Though a state-run turn-in program is not yet in the works, a June 2022 *Bay Journal* article reports that Virginia officials are discussing with a local cement plant the possibility of pursuing a fiberglass disposal method used in Rhode Island. The Rhode Island pilot program involves dismantling and reprocessing fiberglass into cement rather than dumping it in a landfill. Learn more about the project at https://rimta.org/index.php/environmental-programs. ■

Industrial sustainability: Environmental, social, and governance standards

By BCC Publishing Staff

The three pillars of environmental, social, and governance (ESG) define the standards and practices that, taken as a whole, reveal an organization's commitment to operating sustainably.

Thanks to ESG reporting, organizations can comprehend and communicate the risks and opportunities related to their business activities. Furthermore, with the help of ESG reporting, businesses can set goals and metrics, monitor performance, and manage change to make their operations more sustainable and more in line with the values of their shareholders.

With the world changing due to climate change, social awareness, and the COVID-19 pandemic, monitoring and progress in ESG at every stage of a company's supply and value chains are more crucial than ever. When designing new standardized value measures for ESG and core competencies, the following questions must be taken into consideration by manufacturers.

- Has the entire carbon footprint of your product been calculated, taking into account both your actions and those of third parties who provide you with goods and raw materials? Have you used this data to inform organizational innovation and portfolio management?
- Have you adapted your ESG goals to investors' and competitors' expectations by turning them into specific indicators and targets?
- Have you developed metrics that provide information about job-related competencies and skills across the organization, such as workforce planning?

The adoption of ESG principles is most common in Europe. Investors in Europe place greater importance on ESG (31%) compared to investors in North America (18%) and Asia-Pacific (22%). Europe also has the highest percentage of ESG users (93%) compared to North America (79%), Asia-Pacific (88%), and Latin America (89%). This adoption rate reflects the more established European ESG market and regulatory environment. In contrast, the lowest level of ESG conviction and the lowest proportion of ESG consumers are found in North America.

ESG principles are being adopted in numerous industries. BCC Research offers several reports covering these different industries, including

- ESG Trends in Chemical Industry (Report ENV056A, Dec 2022)
- ESG in the Automobile Industry (Report ENV057A, Jan 2023)
- ESG Trends in Pharmaceutical Industry (Report ENV061A, Feb 2023)
- ESG Trends in Agriculture Industry (Report ENV058A, Feb 2023)
- ESG Trends in Healthcare Industry (Report ENV064A, Feb 2023)
- ESG in Food & Beverages Industry (Report ENV063A, Feb 2023)
- ESG Trends in Mining Industry (Report ENV062A, Feb 2023)

Find all these reports at www.bccresearch.com.

Table 1. Environmental, social, and governance standards

Environmental	Social	Governance
• Recyclability	• Customer satisfaction	• Board composition
• Pollution and emission	• Data protection and privacy	• Audit committee structure
• Hazardous waste	• Gender and diversity	• Bribery and corruption
• Raw materials consumption	• Employee engagement	• Executive compensation
• Climate change	• Community relations	• Lobbying
• Air and water pollution	• Human rights	• Political contributions
• Biodiversity	• Labor standards	• Whistleblower schemes
• Deforestation	• Product quality and safety	• Regulatory requirements
• Energy efficiency	• Health and safety of plant workers	• Compensation
• Water scarcity		

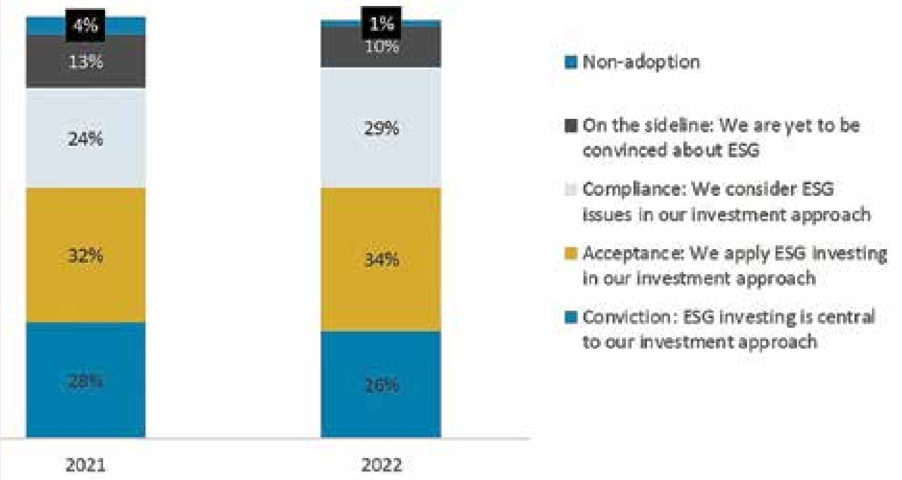


Figure 1. ESG adoption level globally across all industries. (Source: Harvard Law School Forum on Corporate Governance)

About the author

BCC Publishing Staff provides comprehensive analyses of global market sizing, forecasting, and industry intelligence, covering markets where advances in science and technology are improving the quality, standard, and sustainability of businesses, economies, and lives. Contact the staff at Helia.Jalili@bccresearch.com. ■

acers spotlight

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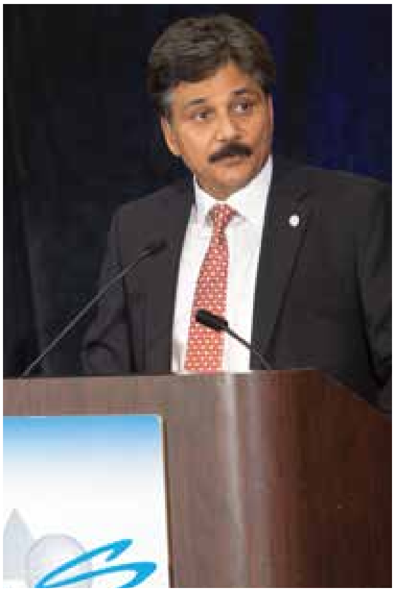

FOR MORE INFORMATION:

ceramics.org

ACerS Carolinas Section 2023 Annual Meeting

Sponsored by The American Ceramic Society's Carolinas Section and the Department of Materials Science and Engineering at Clemson

Title: Advances in Processing and Performance of Functional Ceramics

When: March 30, 2023, 1–7 p.m.

Where: Advanced Materials Research Lab, Clemson University, Clemson, S.C.

Agenda: Includes speakers, posters, Section business meeting, laboratory tours, and networking reception

For more information and to register, visit the Carolinas Section webpage at https://ceramics.org/members/member-communities/sections/carolinas-section. ■

New Jersey/New York Metro/Philadelphia Section plans inaugural event

Hosted by the Rutgers Department of Materials Science and Engineering, The Ceramics Association of New Jersey, and the ACerS New Jersey/New York Metro/Philadelphia Section

Title: 2023 Malcom G. McLaren Lecture Symposium featuring Benjamin V. Fasono

When: March 30, 2023

Where: Rutgers University, Busch Campus

For more information, visit the New Jersey/New York Metro/Philadelphia Section webpage at https://ceramics.org/members/member-communities/sections/new-jersey-metro-new-york-philadelphia-section. ■

58th Annual St. Louis Section / Refractory Ceramics Division Symposium on Refractories

Theme: Refractory sustainability

When: March 29–30, 2023, with a kickoff event to be held the evening of March 28

Where: St. Louis, Mo., at the Hilton St. Louis Airport Hotel

For more information and to register, visit the St. Louis Section webpage at https://ceramics.org/members/member-communities/sections/st-louis. ■

Pittsburgh Section members participate in Pittsburgh Region Future City competition

On Jan. 14, 2023, Pittsburgh Section members Glenn McIntyre (Harbison Walker International), Mark Morelock (Chiz Brother), Eric Young, and Bill Harasty participated as judges in the Pittsburgh Region Future City competition.

Future City is a hands-on, cross-curricular educational program that brings science, technology, engineering, and mathematics to life for students in grades 6–8. This year's focus was on climate change challenges.

Carson Carnahan (pictured), an eighth-grader from Marion Center Junior/Senior High School, earned the award for "Best Use of Ceramics." He proposed a futuristic city called Healtect, located on the coast of Texas, that addressed sea-level rise by building a rising sea wall made of permeable pavement, installing oyster reefs and marshes to absorb wave impact during storms, and employing a Wipe-A-Trap drainage system that kept storm drains clear while reusing organic matter and properly disposing of trash. He also proposed the use of a specialized calcium carbonate paint to lower the temperature by about 20 degrees, thus reducing the need for air conditioners in his city. ■

Ceramic Tech Chat: Jürgen Rödel

Hosted by ACerS Bulletin editors, Ceramic Tech Chat talks with ACerS members to learn about their unique and personal stories of how they found their way to careers in ceramics. New episodes publish the second Wednesday of each month.

In the January episode of Ceramic Tech Chat, Jürgen Rödel, professor and ceramics group leader at the Technical University of Darmstadt, discusses the most concerning effects of climate change, shares how he became active in advocating for sustainability, and describes what individual and organizational actions can be taken to preserve the Earth for future generations. Check out a preview from his episode, which features Rödel giving an example for why sustainability should be embraced now rather than later.

"Clearly if governments act now, it will cost more money. So therefore, not everyone will agree. In the long term, of course, the money we invest now will be much less than the money we will need later to mitigate the damage by storms and floods. [For example,] There was in 2021 a small river in Germany by the name of Ahr, in the Ahr valley. Most Germans have never heard of it. And it's usually one meter deep. It suddenly flooded. No one knows how high the river went, but there was a measurement device which broke off at six meters high. The damage supposedly is $30 billion. That was a small river, and it just destroyed everything in the whole valley. ... [So] I think everyone needs to try to do what they can do."

Listen to Rödel's whole interview—and all our other Ceramic Tech Chat episodes—at http://ceramictechchat.ceramics.org/974767. ■

Bioceramics Division YouTube contest winners announced

The Bioceramics Division is pleased to announce the winners of the recent YouTube video contest. The winning submissions showcase recent innovations and technological advancements in the bioceramics field.

Congratulations to the winners:

First place: *Advanced antimicrobial bioceramics*—**Sierra Kucko**, Alfred University

Second place: *Resorbable and deployable medical devices*—**Saswat Choudhury**, Indian Institute of Science

The winning videos can be viewed on the Bioceramics Division webpage at https://ceramics.org/members/member-communities/divisions/bioceramics. ■

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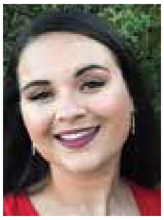
Volunteer spotlight

ACerS Volunteer Spotlight profiles a member who demonstrates outstanding service to the Society.



Rebecka Annunziata is currently a refractory engineer at AM/NS Calvert in Alabama. Before moving to southern Alabama, she received her B.S. in ceramic engineering from Missouri University of Science and Technology.

Annunziata joined ACerS in 2021 through the Young Professionals Network. She served ACerS as the YPN liaison to the Refractory Ceramics Division. She has led round table discussions with peers from academia, industry, and ACerS/CGIF leadership to recognize opportunities for growth and development of programs to encourage students to consider refractories.

Currently, Annunziata is developing a map of ACerS Sections and Material Advantage and Keramos Chapters to highlight opportunities to connect industry and academia.

Scott Thompson graduated from the Navy Nuclear Power School in 1991. Before exiting the Navy, Thompson was awarded with a Navy Achievement Medal. He then earned a double B.S. in chemical engineering and materials engineering at the University of Connecticut, followed by an M.S. in mate-

AWARDS
AND
DEADLINES

Electronics Division awards best student posters and oral presentations at EMA 2023

The Electronics Division presented awards for outstanding student presentations during their 2023 Conference on Electronic Materials and Applications held in Orlando, Fla., January 17–20. Congratulations to these students.

Poster presentation awardees

First place

Novel integration of graphene-based ceramics for enhanced supercapacitor energy storage
Jacob Strimaitis, Norfolk State University

Second place

Frequency dependence of domain switching in lead zirconate titanate
Rachel Beall, North Carolina State University

Third place

Processing optimization of novel high T_c piezoelectric ceramic
Brooke Nicole Richtik, University of Calgary

Oral presentation awardees

First place

Unravelling the domain formation during the growth of epitaxial ferroelectrics
Martin F. Sarott, ETH Zurich

Second place

Scanning nitrogen-vacancy microscopy for ferroelectrics and multiferroics
William Huxter, ETH Zurich

Third place

Impact of processing parameters on crystallization and ferroelectric behavior of hafnium oxide thin films
Samantha T. Jaszewski, University of Virginia

FOR MORE INFORMATION:

ceramics.org/members/awards

rials science. During this time, Thompson served as treasurer of the joint ACerS, TMS, and ASM chapter and represented the University of Connecticut in the 2001 ACerS Student Congress. Thompson also earned an MBA from Babson College and completed a post-graduate diploma in data science from Columbia University.

Thompson began his ceramics career as a ceramics engineer at Carpenter Technology Corporation, followed by a senior materials engineering role at Saint-Gobain. He joined CoorsTek in 2011 and was recognized at the 2015 CoorsTek Ignite Conference for Best Non-Technical White Paper on mentorship. As senior manager of computational materials engineering at CoorsTek, Thompson continues research in additive manufacturing of ceramics with a data science approach toward process improvements.

An ACerS member since 2012, Thompson petitioned to restart the ACerS Colorado Section in 2018. He served as secretary and chair of the Colorado Section and is currently advisor to the Section. The Colorado School of Mines Keramos Chapter inducted Thompson as an honorary member in 2018.

We extend our deep appreciation to Annunziata and Thompson for their service to our Society! ■

IN MEMORIAM

Harold Emrich

Charles R. Kurkjian

George Peterson

Norman Schoeppel

George Shillington

Some detailed obituaries can also be found on the ACerS website, www.ceramics.org/in-memoriam.

Nomination deadlines for Division awards: May 15 or May 30, 2023

Contact: Karen McCurdy | kmccurdy@ceramics.org

Division	Award	Nomination Deadline	Contacts	Description
GOMD	**Alfred R. Cooper Scholars**	May 15	Steve Martin swmartin@iastate.edu	Recognizes undergraduate students who demonstrated excellence in research, engineering, and/or study in glass science or technology.
EDiv	**Edward C. Henry**	May 30	Mina Yoon myoon@ornl.gov	Recognizes an outstanding paper reporting original work in the *Journal of the American Ceramic Society* or the *Bulletin* during the previous calendar year on a subject related to electronic ceramics.
EDiv	**Lewis C. Hoffman Scholarship**	May 30	Mina Yoon myoon@ornl.gov	Recognizes academic interest and excellence among undergraduate students in ceramics/materials science and engineering.

STUDENTS AND OUTREACH

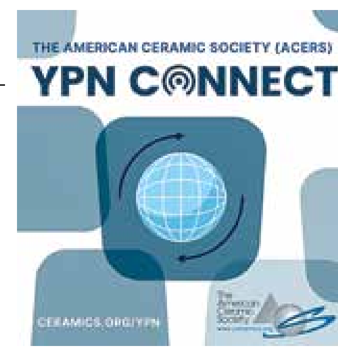
Basic Science GEMS Award: Eligibility deadline is April 3

Sponsored by ACerS Basic Science Division, the annual Graduate Excellence in Materials Science (GEMS) Awards recognize the outstanding achievements of graduate students in materials science and engineering. The award is open to graduate students making oral presentations in any symposium at MS&T23. To be eligible to apply for these awards, you must first submit your abstracts to MS&T2023 at www.matscitech.org/MST23 by **April 3, 2023**. ■

Apply today to be a part of the 2023–24 ACerS PCSA

The President's Council of Student Advisors (PCSA) is the student-led committee of ACerS composed of ceramic-and-glass-focused students. The PCSA is looking for dedicated and motivated undergraduate and graduate students to get involved and to help advance ACerS into the future. Interested students should visit www.ceramics.org/applypcsa to learn more and how to apply. Application deadline is **March 10, 2023**. ■

YPN Connect: Come network with other young professionals!



Join fellow young professionals at the monthly YPN Connect virtual networking event. YPN Connect is open to both ACerS YPN members and nonmembers, so be sure to invite your colleagues and friends!

Register by visiting www.ceramics.org/ypn so that we may send you the connection details. We look forward to seeing you there! ■

ACerS GGRN—the graduate student membership for ceramic and glass students

Build an international network of peers and contacts within the ceramics and glass community with ACerS Global Graduate Researcher Network membership.

GGRN is the ACerS membership that addresses the professional and career development needs of graduate-level research students who have a primary interest in ceramic and glass materials. GGRN members receive all ACerS individual member benefits plus special events at meeting, and free webinars on targeted topics relevant to the ceramics and glass graduate student community.

ACerS GGRN is only $30 per year. If you are a current graduate student focusing on ceramics or glass, visit www.ceramics.org/ggrn to learn what GGRN can do for you—and to join! ■

ACerS Associate Membership and Young Professionals Network

The American Ceramic Society offers one year of Associate membership at no charge for recent graduates who have completed their final degree. To receive the benefits of membership in the world's premier membership organization for ceramics and glass professionals, visit www.ceramics.org/associate.

Also, consider joining ACerS Young Professionals Network (YPN) once you have become an ACerS member. ACerS YPN is designed for members who have completed their degree and are 25 to 40 years of age. YPN gives young ceramic and glass scientists access to invaluable connections and opportunities. Visit www.ceramics.org/ypn for more information, or contact Yolanda Natividad at ynatividad@ceramics.org ■

FOR MORE INFORMATION:

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CERAMICANDGLASSINDUSTRY FOUNDATION

CGIF funds international outreach in Brazil


Credit: Isabella Costa

Isabella Costa (center, white shirt) with teacher Eduardo Siríaco Trezza (center, blue shirt) and students from Antônio Ferreira Martins Municipal School after a lesson demonstrating the Mini Materials Kit.

Tucked between sloping hills in a rural, southeast sector of Brazil, children in the municipal Maripá de Minas dream of becoming veterinarians and farmers. Many do not think of pursuing a higher education, likely because they do not know what opportunities await them in Brazil or beyond.

Isabella Loureiro Muller Costa, a Brazil native and third-year Ph.D. candidate in materials science and engineering at the University of California, Davis, plans to show these students what their future could entail with her outreach efforts.

"The students don't have the knowledge or don't open their eyes for what they can do. They feel that their life is this and nothing is going to change, they're going to still live on the farm," Costa says. "When I got into outreach, that was my first idea: 'Can I do something in Brazil?'"

Costa knew little about materials science until she learned about it during her time as an undergraduate student. She holds a master's in materials science and engineering from Pontifical University Catholic of Rio de Janeiro and a bachelor's in mechanical engineering from the University of Rio de Janeiro State, but her true passion lies in materials science.

Her goal is to expose students in Brazil to materials science at an earlier age. Costa hopes that this exposure will also encourage the students there to want to pursue a higher educational degree like she did.

"I know that it's difficult in Brazil to get a higher degree," Costa says. "But even though it's difficult to get, it's possible if they study and they work hard for it. So, I want to show them that they could do it, that they can reach that goal, and that there are a lot of opportunities out there."

After joining the President's Council of Student Advisors (PCSA) Outreach Committee last year, Costa began planning her first outreach project in Brazil.

With some help from the Outreach Committee chair and Nathan McIlwaine, a Ph.D. candidate at The Pennsylvania State University, Costa submitted a project grant application to the Ceramic and Glass Industry Foundation. Her project, titled "Materials' Magic," involved bringing CGIF Mini Materials Kits to a school in Brazil to expose students to materials science and spark their interest in the topic.

"She stood out so much because she had an idea, and it was a really good idea, and then she did it," McIlwaine says.


Credit: Isabella Costa

Students in Brazil explore one of the lessons from the CGIF Mini Materials Kit.

Costa first traveled to Escola Estadual Wallter Trezza in Maripá de Minas in February 2022 to introduce the students to one of the experiments from the mini kit. After her initial visit, she planned to return in May with more mini kits in her suitcase to carry out the full Materials' Magic project. However, due to the COVID-19 pandemic, Costa has been unable to return. Yet her goals remain the same.

"I want to make sure that they can change [their lives] if they want to," Costa says. "And I want to not only show that but also provide the resources they need to move forward if they want."

Last fall, the teachers continued the project themselves by experimenting with the mini kits each Friday. Although the project has not panned out exactly as planned, Costa remains optimistic that it will still leave a positive impact on the students.

"I feel that if I had this opportunity, the opportunity that I gave to them when I was in their position, my life would be a little bit different," Costa says. "So maybe this can change one person's life." ■

Three key allowances in ceramic refractory anchoring design to prevent failures

By Shawn Story, engineering manager for the Plibrico Company

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In extreme catastrophic ceramic anchor failure cases, refractory sections can fall out and leave major gaps or holes in the lining.

Credit: Plibrico Company, LLC

Research shows that more than 40% of monolithic refractory failures are the result of improper anchor design and installation. Failures commonly attributed to the refractory component are instead often caused by shortcomings in the actual anchoring system.

Like any material, refractories will expand and contract due to changes in temperatures. Expansion in refractories can be broken down into two different types: permanent linear change (PLC), and reversible expansion. PLC is a type of expansion stress that occurs during the initial heat-up when moisture is released from the refractory. Reversible expansion happens when the refractories go through thermal cycling, or in more detail, from an extremely high temperature to room temperature, and then back again to high temperatures.

Both types of expansion, PLC and reversable, are accounted for in mathematical terms as the rate of expansion, per inch, for every degree that the temperature increases. Engineers and refractory installers can find expansion rate numbers listed on technical data sheets.

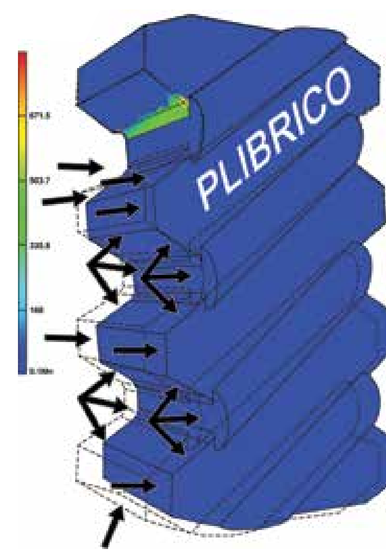
Ceramic anchors, as an integrated part of the overall refractory lining, will move with the monolithic refractories as it experiences these thermal cycling and initial heat-up PLC stresses.

So, a critical consideration when designing an anchoring layout for a suspended refractory application is factoring in movement of the anchor. If not accommodated, this movement can cause the ceramic anchor to fail, leading to a section of refractory dislodging. In the extreme, refractory sections could fall out and leave a major gap or hole in the lining.

We live in a three-dimensional world

Thermal expansion happens in all three dimensions: length, width, and height. For anchor designing purposes, the "height" aspect refers to the thickness of the installation material and is a minor consideration when designing for expansion allowance. Instead, the larger focus should be on the other two anchoring dimensions because the installation is far more likely to move in the length and width directions. Therefore, it is critical that allowances be made in the anchoring system to accommodate this movement.

Figure 1 illustrates the forces that act on a ceramic anchor in one of the directions of expansion. Arrows signify the pressure distributed across the various faces of a ceramic anchor, while the top of the anchor is constrained in place. Note that there is a concentration of stresses at approximately the point where an anchor clip would normally contact the anchor. If this clip or the beam that supports the clip does not allow the anchor to move to relieve this stress, the anchor will very likely fail.



Credit: Plibrico Company, LLC

Figure 1. Illustration of the forces that act on a ceramic anchor in one of the directions of expansion.

Preventing anchoring system failures

To create a strong anchoring system that accommodates movement, there are three simple steps that should be followed in the design and planning of a ceramic anchoring system.

1. Determine how much expansion the installation requires, including reversible expansion due to cycling, and the PLC that happens only during initial bake-out.
2. Choose an appropriate expansion scheme.
3. Select an anchoring system that will accommodate these expansion requirements, including number of anchors, anchor spacing, and anchor shape, size, and material. This point is commonly overlooked.

A strong anchoring system is key to maintaining monolithic refractory lining integrity and preventing cracking, dislodging, or a total structural collapse. And essential to a strong anchoring system is movement accommodation. By carefully determining expansion, and then designing the suspension system to accommodate for movement, you will greatly improve refractory life and prevent any possible catastrophic refractory lining failures due to a rigid and poorly designed anchoring system.

For more information on optimal ceramic refractory anchoring design, visit https://plibri.co/Plibrico_YouTube or contact Plibrico at contact@plibrico.com. ■

Crystallization of hybridized glasses provides a general and easy strategy for fabricating transparent ceramics

Researchers from South China University of Technology and Zhejiang University in China and a colleague from Nanyang Technological University in Singapore presented a general strategy for constructing dual-phase transparent ceramics from hybridized aluminosilicate glasses consisting of oxides and fluorides.

The current and primary sintering methods used to obtain transparent ceramics are restricted by extreme processing conditions such as high temperature and pressure or spark plasma, which is necessary to eliminate undesired micropores. Moreover, barring 3D printing techniques, these methods suffer from difficulties in material reshaping, and the available products are usually in bulk form. Thus, downsizing transparent ceramics to the microscale level remains challenging.

In contrast to these conventional processing routes, the crystallization of glass is a newer approach for creating transparent ceramics that holds several advantages. For example,

- **Accessible processing conditions**. Producing transparent ceramics through glass crystallization only requires heat treatment at atmospheric pressure, and the heat-treatment temperature is commonly below 1,000°C.
- **Easily downsized**. Without the restriction of pressurization conditions, downsizing the transparent ceramics becomes easier and more convenient.
- **Easily shaped**. Glass has the advantage of being easily shaped through mature molding technologies. By using these technologies to shape the precursor glass, transparent ceramics of different shapes can be readily achieved.

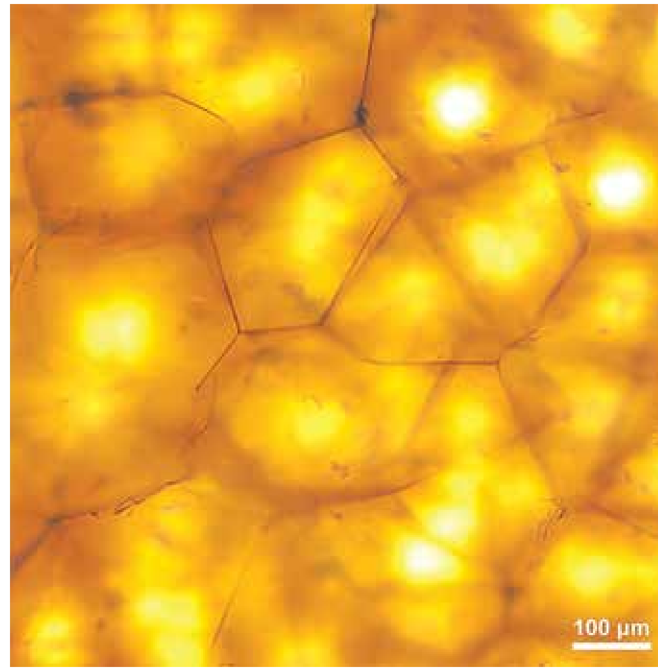
However, there are challenges to satisfying the harsh and conflicting requirements of excellent glass-forming ability and inherent dense crystallization habits while fulfilling the requirements for high transparency. So, researchers have produced only a limited number of glass-derived transparent ceramics to date.

In the new paper, the researchers explain that compared to other glass systems, hybridized glasses containing oxides and fluoride exhibit strong flexibility in the crystallization process.

"The introduction of fluoride in the hybridized glass breaks the network of glass, which causes a lower viscosity of the glass matrix, making diffusion and migration easier. Thus, the hybridized glass has lower energy barrier to crystallize," they write.

Additionally, "the notable contrast in the crystallization tendency of oxides and fluoride from the oxide matrix allows modification of the crystallization coordinate curve into various discrete stages, enabling dense crystallization under mild conditions," they add.

For their study, the researchers synthesized hybridized $BaAl_2Si_2O_8$–LaF_3 (BASL) glasses using the melt-quenching



Credit: Shifeng Zhou

Microscopy image of a $BaAl_2Si_2O_8$–LaF_3 transparent ceramic derived from a hybridized glass.

method. They then heat treated the glass at various temperatures between 780°C and 860°C for 2.5 hours in air to induce crystallization.

The sample heat treated at 860°C achieved the highest crystallinity (~92%). Microscopy analyses revealed it featured a multiscale and interconnected microstructure consisting of nanoscale LaF_3 crystalline domains homogeneously embedded in the microscale $BaAl_2Si_2O_8$ crystalline phase.

Interestingly, the refractive indexes of the $BaAl_2Si_2O_8$ and LaF_3 crystals were 1.61 and 1.60, respectively, so scattering was avoided between them. Additionally, the refractive indexes of the glass and transparent ceramic were measured to be 1.603 and 1.598 at a wavelength of 633 nm, respectively, and this similarity contributed to the good transparency of the sample.

Once analysis of the bulk samples was completed, the researchers used the same process to crystallize glasses with a fiber geometry. The resulting transparent ceramic fiber consisted of $BaAl_2Si_2O_8$ and LaF_3 in multiple crystalline phases but with an overall highly homogeneous crystalline structure. Like the bulk sample, the transparent ceramic fiber also demonstrated excellent optical transparency.

Based on these encouraging results, the researchers tried fabricating other hybridized glass compositions. The new compositions—$BaAl_2Si_2O_8$ replaced with $SrAl_2Si_2O_8$ (SASL) and LaF_3 replaced with GdF_3 (BASG)—also demonstrated high crystallinity (89% and 93%, respectively) and optical transparency. Achieving these results required only a small modification to the ideal heat treatment temperature (lowered from 860°C to 830°C and 850°C, respectively). Transparent ceramics based on the hybridized systems of $Ba_3Si_5O_{13}$–BaF_2 and $NaAlSiO_4$–LiF were also successfully fabricated.

The researchers also demonstrated the possibility of functionalizing the transparent dual-phase ceramics through doping with various luminescent rare earth activators. BASL transparent ceramics doped with cerium, europium, terbium, dysprosium, and samarium under excitation with ultraviolet light (365 nm) exhibited bright blue, azure, aquamarine, yellow, and orange luminescence, respectively.

Additionally, the researchers used the transparent ceramic to construct a radiographic imaging device and successfully demonstrated its application for X-ray imaging.

Ultimately, the researchers concluded that this strategy demonstrates a wide variety of useful features, including

1. **Generality**, where the strategy is suitable for transparent ceramics and fibers with various chemical compositions, phases, microstructures, and morphologies;
2. **Easy processing**, where the strict external conditions of conventional ceramic technology, such as high temperature and pressure, can be avoided; and
3. **Potential for further functionalization**, where the ceramic can be activated with luminescent centers for different photonics applications.

The paper, published in *Advanced Materials*, is "Hybridization engineering of oxyfluoride aluminosilicate glass for construction of dual-phase optical ceramics" (DOI: 10.1002/adma.202205578). ■

Accidental discovery leads to microprinting method for highly curved, complex surfaces

Through an accidental discovery, National Institute of Standards and Technology researcher Gary Zabow discovered a new microprinting method based on sugar and corn syrup that allows microscale arrays to be deposited with precision on highly curved, complex surfaces.

Zabow is group leader of the Magnetic Imaging Group in the Applied Physics Division of NIST. He needed to send some micromagnetic dots to colleagues in a biomedical lab, and he found that burying the dots in hardened chucks of sugar served as excellent packaging material. Unlike more conventional water-soluble materials, sugar left no harmful plastics or chemicals behind when dissolved in water to free the dots upon arrival.

One day, Zabow found a forgotten beaker in his lab containing a leftover sugar chuck embedded with arrays of micromagnetic dots. When he dissolved the sugar and rinsed out the beaker, he found that instead of releasing into the water, the dots had transferred to the beaker's bottom, where they cast a rainbow reflection. The colorful reflection indicated to Zabow that the arrays of microdots had retained their unique pattern.

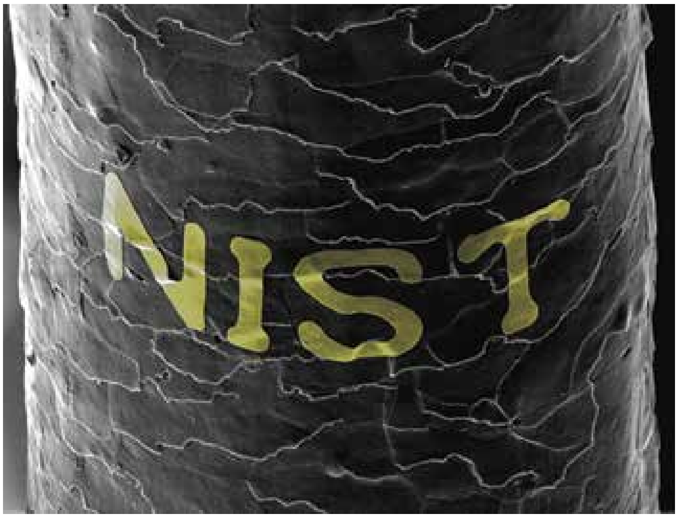
This discovery inspired Zabow to explore if regular table sugar could be used to transfer microchips onto new and unconventional surfaces. A new microprinting process was thus born that overcomes some challenges experienced with conventional transfer microprinting processes.

Conventional transfer processes use a solid carrier, such as flexible tapes or elastomers, or a liquid medium. Solid methods cannot conform to sharp curves nor transfer fragile structures without damage; liquid methods have limited placement accuracy.

In contrast, Zabow's new process, called REFLEX (REflow-driven FLExible Xfer), enables "accurately positioned, ultraconformal printing over a wide array of surfaces, including those too topographically challenging to be patterned by existing methods," he writes in a paper on the process.

The REFLEX process uses a simple combination of caramelized table sugar (sucrose) and corn syrup, which is obtained after heating with water. The corn syrup prevents crystallization, which can produce inhomogeneous surfaces.

Once the mixture is cooled, the resulting solid can be melted or redissolved in water for pouring over micropatterns



Credit: Gary Zabow, NIST

Using sugar and corn syrup, NIST researcher Gary Zabow transferred the acronym "NIST" onto a human hair in gold letters, shown in false color in this grayscale microscope image.

or structures that are to be transferred. Any remaining water is then removed via evaporative heating.

After all water is removed, the sugar mixture hardens and can be released with the pattern embedded, sometimes by dissolving an underlying sacrificial layer. The pattern can then be redeposited on another surface by reflowing the sugar mixture, with the high reflow viscosity of the resulting fluid helping maintain the relative positions of structures during transfer.

Advantages of the REFLEX process include

- Maintaining long-range order while deforming locally;
- Near room-temperature and tailorable glass transition temperatures;
- Full dissolution in water, eliminating the need for harsh solvents;
- Accurate positioning, with micrometer-level precision;
- Eliminating resistance to both bending and stretching;
- Selective release with widely available photoresists or other acetone soluble materials;
- Printing over potentially unlimited surface curvatures or features with extreme sharpness; and
- Applicability to a wide range of materials, including metal, plastic, paper, glass, polystyrene, semiconductor, elastomer, hydrogel, and multiple biological surfaces.

In his paper, Zabow used the REFLEX process to make a variety of structures, including an array of microfabricated disks, which double as reference markers, that were transferred onto a surface with recessed holes. The entire surface was patterned, including down vertical sidewalls and over edges with nanoscale radii of curvature, for both rigid and flexible microstructures.

He also printed onto the sharp point of a pin and wrote the acronym "NIST" in microscale gold lettering onto a single strand of human hair. Plus, he successfully transferred magnetic disks, 1 micrometer in diameter, onto a floss fiber of a milkweed seed. The fiber reacted in the presence of a magnet, proving successful transfer.

As a new process, REFLEX may require some adjustments to achieve peak efficiency. For example, to ensure optimum spreading over a surface and to avoid dewetting of the heated mixture, it may be necessary to pretreat the surface, apply gentle pressure, or use transfer layers a few millimeters thick. Additionally, directional heating can help avoid trapping air pockets, which prevent complete pattern transfer. To accommodate locally varying surface chemistries, targeted surface pretreatments or heating profiles may offer further control.

Zabow has filed a patent application for the new process. Future research will look at testing different sugars as well as other possible materials for encasing/transferring the micromagnetic dots and other structures. A better understanding of the process, its opportunities, and limitations is needed to fully take advantage of REFLEX and scale it up for manufacturing.

The paper, published in *Science*, is "Reflow transfer for conformal three-dimensional microprinting" (DOI: 10.1126/science.add7023) ■.

Keeping water metal free: One-step method produces functionalized MXenes for fast mercury removal

Researchers from Drexel University and Temple University developed a simple one-step method to fabricate functionalized $Ti_3C_2T_x$ MXenes for mercury removal from water.

Heavy metals such as mercury and cadmium cause negative effects on human health by binding to cells and preventing them from performing their functions. Heavy metals show up regularly in mining and industrial operations. The common practice of establishing such operations near water sources can lead to these metals entering the aquatic ecosystem, contaminating the fish we eat and water we drink.

Most heavy metals do not undergo microbial or chemical degradation. Thus, they must be removed from the water through various developed remediation technologies.

Adsorption is a widely used process for removing heavy metals from water because of its low cost, availability, and eco-friendly nature. It involves placing a solid adsorbent into contaminated water to attract and bind the heavy metal particles to its surface.

Traditional sorbents such as activated carbons, clays, and zeolites are not efficient for heavy metal removal due to their weak affinity with most metal ions, low surface area, and pH instability. In contrast, 2D materials with special structural features and abundant functional groups can be ideal candidates for this purpose.

MXenes are one 2D material family with great potential as adsorbents for heavy metals. These 2D transition metal carbides, nitrides, and carbonitrides feature high specific surface area and functional groups on the MXene surface, which not only provide sites for direct ion exchange but also reduce some organic molecules and cations. Additionally, compared to other 2D materials such as graphene oxide and molybdenum disulfide, MXenes feature a larger d-spacing (distance between planes of atoms), which aids in ion diffusion into the pores and interlayer.

Titanium-based MXenes, particularly titanium carbide ($Ti_3C_2T_x$), are the most widely studied MXenes for environmental applications due to element abundance and nontoxic decomposition products. However, $Ti_3C_2T_x$ decomposes to TiO_2 crystals in aqueous media due to surface oxidation, hindering its use in water remediation.

Researchers have investigated functionalization of the $Ti_3C_2T_x$ surface to delay degradation and improve the rate of adsorption. For this study, functionalization meant introducing carboxyl functional groups on the surface of the $Ti_3C_2T_x$ MXene. This choice stems from the belief that "carboxyl groups stabilize MXene layers, owing to higher energy formation compared to the OH–terminated $Ti_3C_2T_x$," the researchers write.

They created the carboxylated $Ti_3C_2T_x$ MXenes by adding 1.7 grams of chloroacetic acid to a 1 mg/mL delaminated $Ti_3C_2T_x$ colloidal solution at 0°C. They stirred the solution for two hours to convert –OH groups on the MXene surface into carboxyl groups. The mixture was then neutralized with distilled water.

Credit: Tom Friedel, Wikimedia (CC BY 3.0)

Sign warning visitors of mercury contamination in the Florida Everglades.

Analysis of the carboxylated $Ti_3C_2T_x$ MXene revealed its surface exhibited a more negative charge than pristine $Ti_3C_2T_x$ MXene, over a pH range of 2.0–8.5. Such negativity increased the electrostatic interactions between mercury ions and the carboxylated $Ti_3C_2T_x$ MXene. Plus, addition of the carboxyl groups increased interlayer spacing of the $Ti_3C_2T_x$ nanosheets and their oxidation stability.

Compared to pristine $Ti_3C_2T_x$ MXenes, which have pH range values of 2–6, the carboxylated sample demonstrated increased stability and an improved rate of mercury ion adsorption. For example, at an initial concentration of 200 ppm, pristine $Ti_3C_2T_x$ removed about 70% of mercury ions after 20 minutes; the carboxylated version removed the same amount in just 1 min.

Additionally, leaching of adsorbed mercury ions from the carboxylated $Ti_3C_2T_x$ MXene was much lower than that from the pristine $Ti_3C_2T_x$ MXene. However, the leached mercury for both samples remained much lower than the safe limit defined by the U.S. Environmental Protection Agency.

Based on these results, the carboxylated $Ti_3C_2T_x$ MXene "has industrial potential for efficient removal of heavy metal ions, as it has a higher mercury-ion uptake capacity than commercially available adsorbents reported in the literature," the researchers conclude.

The paper, published in *Journal of Hazardous Materials*, is "Efficient mercury removal from aqueous solutions using carboxylated $Ti_3C_2T_x$ MXene" (DOI: 10.1016/j.jhazmat.2022.128780).

Nanoparticle spray reduces sunburn damage in pineapples

Researchers from São Paulo State University and Santa Clara Agrociência Industrial Ltd. in Brazil tested the potential of spray-on calcium carbonate nanoparticles to protect pineapples from sunburn.

Sunburn in fruits and fruiting vegetables is a big concern for farmers because it affects the food's marketability. Shade is the main defense farmers have to protect fruit from sunburn. However, when events such as storms or immoderate pruning cause damage to the good leaf cover in canopies, it puts the fruit at risk of excessive sun exposure. While artificial shading is an option, it is not practical for large acreages.

For sunburn protection at a field scale, use of spray-on films can reduce or eliminate sunburn. These spray-on films, which typically are based on kaolin clay, calcium carbonate, or talc, leave a white particle film on the fruit that must be washed or brushed off at harvest.

The budding field of nanotechnology has allowed for the production of calcium carbonate nanoparticles that, when used as a spray-on film, do not cause residual stains on the fruit surface. Thus, "fruit quality may benefit from nanotechnology development," the researchers write in their paper.

The experiment took place in the municipality of Severínia, Brazil, with pineapple seedlings of the cultivar "Pérola" (the most consumed pineapple variety in Brazil). Two sprayings were made with the calcium carbonate nanoparticles during the vegetative growth phase. Pineapples were harvested in the final stage of ripening for evaluation.

The researchers found that, compared to untreated fruit, pineapples treated with the nanoparticles had a darker peel color and a lower level of yellowing on the peel and the pulp, indicating decreased solar radiation damage.

The treated pineapples were also firmer than the untreated ones, which the researchers attribute to the calcium reacting with pectic acid to form pectates that preserve the cell membrane permeability characteristics. Additionally, the application of calcium carbonate nanoparticles led to an increase in sugar content and decrease in organic acids, providing desirable fruit flavor characteristics.

Based on these results, "The spraying of calcium carbonate nanoparticles on pineapple fruit was effective to control fruit sunburn … [and] may be a new strategy to improve fruit quality with sustainability as it does not harm the environment and can also reduce losses during commercialization," the researchers conclude.

The paper, published in *South African Journal of Botany*, is "Spraying of calcium carbonate nanoparticles on pineapple fruit reduces sunburn damage" (DOI: 10.1016/j.sajb.2022.04.004). ■

Pineapples are mainly grown in tropical regions and so are at high risk of excessive sun exposure.

Insights into the internal oxidation processes of ceramic matrix composites

Though ceramic matrix composites (CMCs) for aircraft have entered commercial operation, there still are some knowledge gaps regarding the oxidation of these materials. Two researchers from the University of California, Santa Barbara, conducted an experiment on internal CMC oxidation that provided new insights into the oxidation processes and highlighted deficiencies in the current standard oxidation model.

The researchers are graduate student researcher Victoria Christensen and Frank Zok, ACerS Fellow and Distinguished Professor of Materials. They explain that the oxidation process of silicon carbide composites with boron nitride fiber coatings occurs through multiple coupled steps involving mass transport, reaction, and volatilization.

However, critically assessing the event sequence and mechanistic elements of these steps by direct observation is challenging because, after oxidation, open gaps will appear between the composite constituents. These gaps make the material highly friable and difficult to prepare for analysis with transmission electron microscopy or scanning electron microscopy, both common analysis tools used by ceramic scientists.

In their study, Christensen and Zok prepared samples for scanning electron microscopy analysis using a method based on ion-mill sectioning/polishing. They used unidirectional minicomposites consisting of 800 Tyranno ZMI silicon carbide fibers coated with boron nitride and silicon carbide via chemical vapor deposition.

They oxidized the minicomposites by placing 1-centimeter-long specimens in a quartz tube furnace at 1,000°C for 12 hours in flowing, dry air (water content ≈ 10 ppm). Scanning electron microscopy analysis was performed on the samples both before and after oxidation. Additionally, phase distributions were obtained from secondary electron imaging and backscatter electron imaging modes, as well as energy-dispersive spectroscopy maps.

Notably, the oxidized test specimens consisted of both broken and unbroken samples so as to provide a clearer picture of the internal oxidation mechanisms. The unbroken sample featured a polished transverse cross section and was sectioned longitudinally for examination. The other sample was broken in a tensile test and was sectioned longitudinally for examination as well.

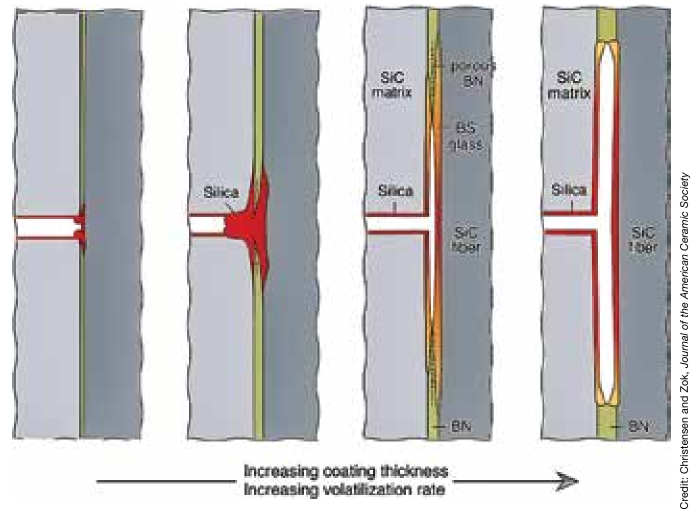
According to Christensen and Zok, this experimental design yielded "observations of the oxidation processes with arguably unprecedented fidelity." Specifically, they gained new insights into the event sequence leading to both coating recession and gap closure.

In general, they determined that when the coatings are thin and volatilization is slow, only a small amount of boron nitride needs to be consumed before the gaps for gas transport are sealed and the process effectively ceases. For somewhat thicker coatings, the amounts of boron nitride removed and oxide produced are greater, and the time required to seal the recession gap is longer.

On a more detailed level, their observations revealed the closure process involved the transport of oxidants along the coating/fiber and coating/matrix interfaces ahead of the recession front. "Gap closure therefore occurs in subsurface regions near the recession front rather than at the matrix surface," they write.

Additionally, even though the water content in the dry air was at mere ppm levels, volatilization by reaction of boria with water to form HBO_2 gas was sufficient to cause measurable amounts of recession even following relatively short exposures at 1,000°C. If water was present in even larger concentrations, it would also accelerate silica formation "as water is a more potent oxidant of SiC than oxygen," Christensen and Zok write.

Based on these observations, they determined that the current standard model for internal CMC oxidation processes



Schematics illustrating transitions in recession and closure behavior as the coating thickness and volatilization rate increase (from left to right) in SiC–BN–SiC ceramic matrix composites.

Research News

Novel electrode material boosts supercapacitor performance for electric vehicles

Researchers at Dongguk University in South Korea designed and synthesized a novel hybrid composite electrode material that significantly enhances the performance of supercapacitors for use in hybrid electric vehicles. This composite electrode, which was created using a wet-chemical strategy, is composed of cobalt selenide nanorod-copper selenide polyhedron-decorated over graphene oxide. The resulting asymmetric supercapacitor device demonstrated a capacitance of 192.8 F/g at 1 A/g; energy density of 54.6 Wh/kg; power density of 700 W/kg, and capacitance retention of about 82.5% over 10,000 cycles. For more information, visit https://www.dongguk.edu/eng/article/63820/list.

is only applicable to the extreme case where coatings are very thick and volatilization is rapid. In every other case, the standard model overpredicts recession lengths by a significant margin due to three underlying assumptions.

1. Gap closure occurs at the top of the recession channel, not at its base.
2. The SiC oxidation rate is unaffected by the presence of boria.
3. The oxidation-induced volume expansion is accommodated purely by displacement normal to the oxidizing surfaces, without physical constraint and without flow parallel to the surfaces.

"The current experimental observations call into question these assumptions and point to the need for more refined models to capture the observed behavior," they conclude.

The paper, published in *Journal of the American Ceramic Society*, is "Insights into internal oxidation of SiC/BN/SiC composites" (DOI: 10.1111/jace.18834). ■

Preserving photographic plates—the potential role of glass alteration in gelatin delamination

Researchers from the Smithsonian Museum Conservation Institute investigated how formation of an amorphous surface layer on historic glass photographic plates due to water exposure can impact delamination of the image-containing gelatin layer.

When the daguerreotype, the first photographic process, debuted in the 1830s, the material used to capture the images was a highly polished, silver-plated copper sheet. This material served as the basis of photography for the next 20 years, until the invention of a collodion wet plate process in the 1850s.

The collodion wet plate process involved pouring a 2% solution of collodion over a glass plate and then placing the plate in a solution of silver nitrate. When removed from the silver, the collodion film contained a translucent yellow compound of light-sensitive silver iodide. The plate was exposed while still wet and then developed by inspection under red light.

Unlike the daguerreotype process, which only produced a single image at a time, the collodion wet plate process created a negative image that could be copied numerous times onto paper for wide distribution. However, disadvantages of this technique include the need for a darkroom and a time limit on developing the plate before the collodion emulsion dried.

In the 1870s, a dry plate process was developed. Unlike the collodion wet plate process, which required the plate to be prepared just before exposure and developed immediately after, the dry plate process involved coating a glass plate with a gelatin emulsion of silver bromide. The prepared plate could then be stored until exposure, and after exposure, it could be brought back to a darkroom for development at leisure.

The dry plate process allowed for the mass production of both negatives and positive transparencies, popularly known as lantern slides. Some of the most well-known positive trans-

Credit: National Museum of American History

An example of the composite positive transparencies from the *Animal Locomotion* series (Series 1478, Plate 598). This series of glass photographic plates are widely regarded as the immediate predecessor to the development of motion pictures.

parencies produced using this technique are from the 1887 *Animal Locomotion* series by Eadweard Muybridge, which depict humans and various animals performing simple motions and are widely regarded as the immediate predecessor to the development of motion pictures.

The Smithsonian Institution's National Museum of American History houses 528 composite positive transparencies from the *Animal Locomotion* series. (The composites consist of individual transparencies arranged in sequence on a larger glass support panel.) As these photographs are now approximately 150 years old, they are beginning to exhibit a range of degradation phenomena and products, including alteration of the glass plates.

"Alteration" refers to the formation of surface (alteration) layers when the silicate glass is exposed to water and begins to dissolve. This silica, along with other glass components or exogenous elements supplied by the solution, form an amorphous, porous, and hydrated interfacial surface layer by two processes.

1. Reorganization via hydrolysis/condensation reactions, in which SiO_2 tetrahedra are not completely detached from the glassy network.
2. Dissolution and reprecipitation of species in the aqueous solution.

Even without alteration, glass photographic plates commonly experience delamination of the image-containing gelatin layer from the glass support. This delamination occurs because gelatin coatings, when subjected to significant changes in relative humidity, tend to curl, creating tensile stress at the interface with the photographic support. Understanding the role an alteration layer may play in this existing delamination process can aid conservators in improving preservation protocols.

For their study, the Smithsonian researchers worked with a collections specialist in the Photographic History Collection at the National Museum of American History to examine previously broken fragments of both the image-bearing glass plates and larger support glass panels from the *Animal Locomotion* series. Compositions of the glasses were obtained through quantitative scanning electron microscope–energy-dispersive spectrometry, while electron imaging was used to perform cross-sectional analysis.

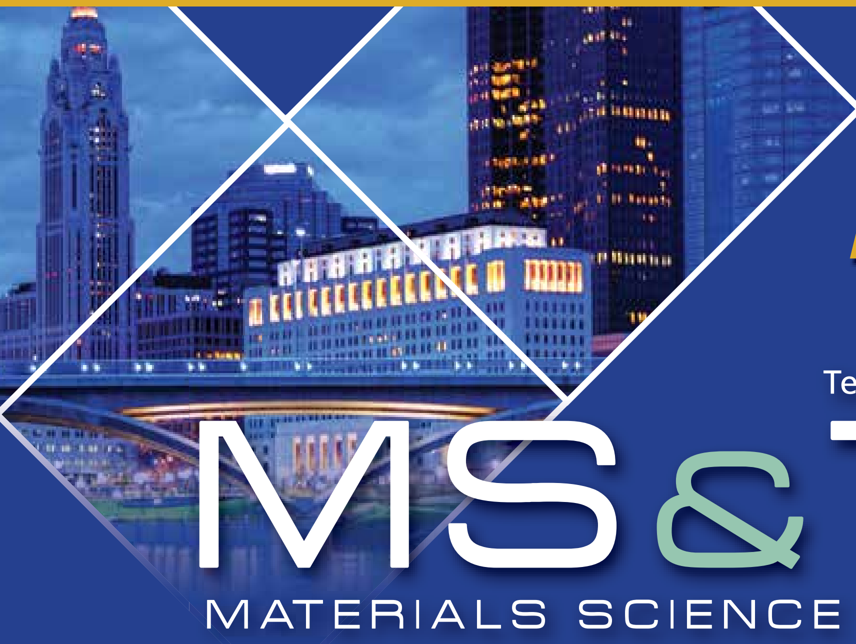
Imaging identified a visible sodium-depleted alteration layer (~5 μm thick) on the image-bearing glass plates. The layer was apparent on both the gelatin-coated and uncoated faces of the glass. In scanning electron microscope images of the glass, the researchers clearly saw that as the gelatin lifted off the glass, it carried with it the alteration layer.

This observation "suggests that while the delamination of the image layer observed in these objects is driven by the tensile stress caused by the curling of the polymeric gelatin, the interfacial point of failure is not between the gelatin and the glass, but between the glass alteration layer and the underlying unaltered glass," the researchers write.

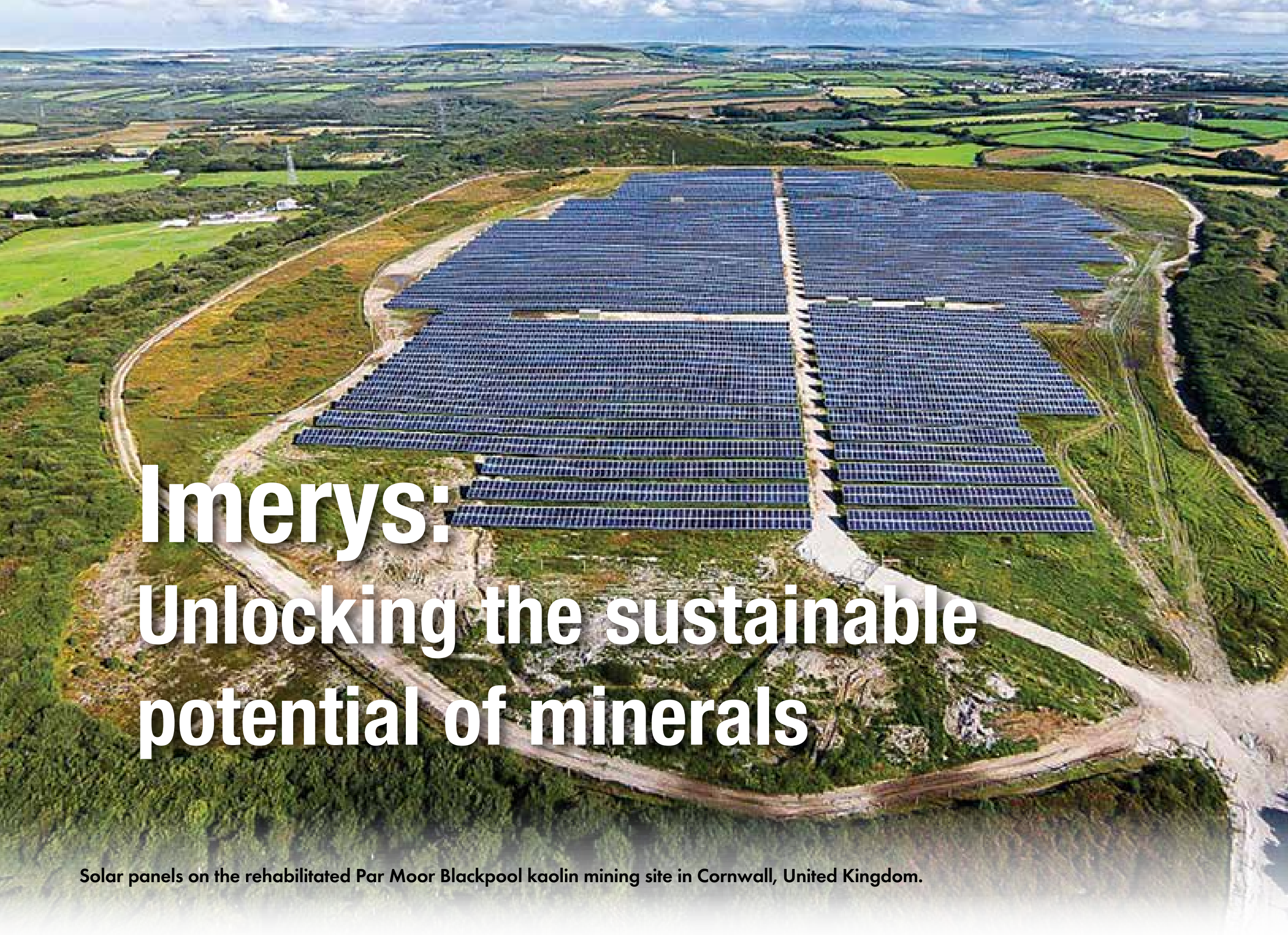
As such, "It is plausible that had the glass not been altered, the curling of the gelatin would not have been sufficient to cause delamination from an unaltered glass surface," they add.

The researchers conclude that further modeling is needed to fully explain the relationship between the alteration layer and delamination of the gelatin. Additionally, further modeling is needed on the mechanical properties and dissolution mechanisms of glasses with more complex chemistries, such as these photographic plates.

The paper, published in *Journal of the American Ceramic Society*, is "Glass alteration in 19th century glass photographic plates: Potential role in gelatin delamination" (DOI: 10.1111/jace.18880). ■



Imerys: Unlocking the sustainable potential of minerals



Solar panels on the rehabilitated Par Moor Blackpool kaolin mining site in Cornwall, United Kingdom.

Credit: Philippe Zamora and Dominique Lecuivre

By Eileen De Guire

In an interview, Imerys global sustainability director Nancy Bunt discusses the work Imerys is doing to sustainably manage the consumption of minerals and how this work applies to the refractories industry.

Bunt

Refractories are essential to the industries that we as a society rely on. From steel, aluminum, and glass manufacturing to the cement industry, from hydrocarbon processing industries to paper and even food processing, refractories work behind the scenes in a crucial capacity anywhere that involves thermal processing.

As these industries commit themselves to reducing their carbon footprints, for example, by adopting alternative energy sources such as hydrogen, refractory manufacturers will need to develop new products that can support customers in reaching their goals. In turn, the raw materials suppliers that work with the refractories industry have a role to play in supporting these sustainability initiatives.

Imerys S.A. (Paris, France) is a multinational group that specializes in the production and processing of industrial minerals, including for the refractories industry. In an email exchange, *Bulletin* editor Eileen De Guire talked with ACerS Fellow Nancy Bunt, global sustainability director of Imerys' Refractory, Abrasives, and Construction Business Area, about the need to sustainably manage the consumption of minerals and how Imerys is working toward that goal.

Sustainability at Imerys

Q. *What is Imerys' approach to sustainability?*

A. In the last two years, we have seen a dramatic acceleration of the importance of sustainability and corporate social responsibility in the eyes of the public. Our stakeholders' expectations are rapidly changing.

As consumption levels around the world increase, the growing demand for natural resources places pressure on our natural systems. Our expertise and innovative mindset as the world's leading supplier of minerals-based specialty solutions enable us to extract and transform minerals responsibly.

Q. *What is the Imerys SustainAgility Framework, and how did it come about?*

A. Launched in 2018, our SustainAgility program focuses on continuous improvement to empower our people, care for our planet, and build for the future by fostering positive change and creating value for our shareholders.

SustainAgility is structured around six pillars and 16 interconnected themes, allowing us to unlock better futures for our people, our customers, and our planet. Through SustainAgility, we create value for our stakeholders, and we are aligned with the operations of the United Nations Global Compact Ten Principles, which we became a signatory of in 2016. We strategically act to advance nine of the United Nations Sustainable Development Goals, with more than 365 community initiatives since 2012 and 55 initiatives launched in 23 countries in 2021.

Q. *What are some of the sustainability initiatives taking place within the SustainAgility Framework?*

A. Decarbonizing our operations is a massive challenge for us, and we now have made the future commitment to our planet to accelerate toward the 1.5°C trajectory, using science-based targets to reduce emissions by 42% in absolute terms by 2030. We are working on increasing our energy efficiency, increasing our use of renewable electricity, changing our energy mix to further integrate biomass waste, investing in innovative technologies, and accelerating our partnerships with value chain partners.

Imerys' own native plant nursery in Milos, Greece, for land rehabilitation and restoration.

Credit: Jean Philippe Siblet

Environmental management is based on eight environmental protocols. All our sites have been audited for environmental management using a maturity matrix for self-assessment, which is then audited against by auditing teams. Of course, as a mining company, land rehabilitation and biodiversity have been on our radar for years. The proper management of biodiversity is key to the social acceptance of our mining activities, mineral extraction, and to our reputation; as regulations increase, our ability to access resources and sustain our operations for the long term is key.

We have made the commitment to operate with no net loss of biodiversity as a signatory of Act4nature, which requires us to comply with 10 public commitments on biodiversity. By 2024, we will have achieved the ambitious targets set forth by Act4nature. We will have biodiversity action plans at 100% of our quarries and mines.

But we go further by acknowledging that optimizing use of natural resources and water at our sites—plus recycling—is key. In particular, we focus on water management requirements for our sites in areas where water scarcity is an issue.

Q. *What is your role within the SustainAgility Framework?*

A. Within this framework, my role is to lead Imerys' Refractory, Abrasives, and Construction (RAC) Business Area to drive sustainable performance. We cascade Business Area ambitions to our teams to engage them at all levels within our organization. Practically, this approach involves training, communications, and partnering with our refractory and other customers to help deliver sustainable solutions that create value for both them and us.

Additionally, as a diversity and inclusion ambassador, I facilitate a team of 29 D&I ambassadors within our Business Area to foster a diverse, equitable, and inclusive workplace. Imerys is committed to promoting a culture based on mutual respect and appreciation, where the value and contribution of each individual is welcomed and recognized. Our diversity and inclusion program has focused on gender equality as well as awareness campaigns on mental health, the LGBTQ+ community, multiculturalism, and disabilities.

In 2023, we will launch a new diversity and inclusion index to measure our progress on female participation in senior, managerial, expert, and professional roles; reducing the pay gap; increasing the percentage of underrepresented nationalities in senior managerial roles; increasing the percentage of employees with disabilities; and increasing our diversity and fairness treatment as measured through an employee engagement survey.

Diversity and inclusion are strong drivers of innovation, contribute to recruitment and retention of employees, and ultimately support improved financial performance. The Imerys Board of Directors has specific responsibility to oversee our

Imerys: Unlocking the sustainable potential of minerals

Imerys' andalusite mine in Glomel, Brittany, France. It is one of the many mines where monitoring for no net loss of biodiversity is continuously performed.

diversity performance (gender in particular), and customers and investors are increasingly demanding on this topic.

Sustainability in the refractories industry

Q. *What are the key sustainability challenges for refractory manufacturers?*

A. The key sustainability challenges are the same for refractory manufacturers as they are for us. First is our impact on the **environment**, whether it be climate change and decarbonization; energy efficiency; biodiversity; natural resource efficiency, especially water usage and conservation; and the secondary use of raw materials and recycling.

Second is the **social aspects of business**, whether it be occupational health and safety of employees, labor rights, human rights, diversity and inclusion, community engagement/involvement, and the social impact of supply chains. The questions refractory manufacturers should be asking include: Do their suppliers of raw materials and goods comply with human rights and practice a duty of care?

Lastly, like all businesses, the **governance** side of their business is essential. Governance encompasses everything from risk management, business model resiliency, business code of conduct and ethics, information security, legal compliance, and data protection, just to name a few.

The refractory industry must adapt to the changing conditions and requirements of the thermal processing industries they serve as customers. As these industries decarbonize and change technologies, the refractory industry will adapt to these changing environmental conditions, enabling their customers to change process environments and reduce their environmental footprint.

Q. *How can a raw materials supplier help the refractories industry meet its sustainability goals?*

A. As a raw materials supplier, enabling refractory producers to meet their sustainability challenges by adapting raw materials will be key to addressing their customers' needs.

As a leader in both specialty minerals and as a raw material supplier to the refractories industry, Imerys can help navigate the dimensions of sustainability and offer guidance and solutions that many other suppliers will not be able to do. We partner with our customers to provide sustainable solutions with products that have been verified for life cycle analysis through third party independent verification using ISO methodology.

We assess our products using the SustainAgility Solutions Assessment, a methodology adapted and aligned to the Portfolio Sustainability Assessment framework that was developed by the World Business Council for Sustainable Development. It is a scientific, fact-based tool to measure social and environmental impacts from cradle to grave to identify and steer the portfolio toward "sustainable solutions."

Q. *A recent corporate presentation states Imerys is committed to recovering and dealing with wastes and recycling. In practical terms, what do these commitments look like for a materials supplier to the refractories industry?*

A. Optimizing the use of our natural resources and contributing to resource recovery by finding destinations for all our wastes will be key going forward. In our manufacturing processes, we will continue to introduce non-virgin materials for virgin materials, all the while developing products that enable circular economy downstream. We know we must reduce our environmental footprint by increasing circularity.

Q. *What can a minerals company do to support downstream circular economies?*

A. By reassessing where waste is most prevalent in their value chains, companies can learn to close those loops to get more from the resources and minerals they use. The refractories industry has been part of the circular economy for years mainly for economic reasons, and many refractories and raw materials are used and designed with circularity in mind. We must continue to support this circularity and find homes for all the waste stream minerals and resources we produce.

Q. *Any final thoughts?*

A. After spending 37 years in the sales and technical support of minerals to primarily the refractory and traditional ceramics industries, the opportunity to change focus late in my career has been a rewarding, challenging, and eye-opening experience. I learn something new every day, and, more importantly, I feel like I am doing my small part to leave the world a better place, using our resources wisely and channeling my inner Girl Scout.

Sustainability is at the core of our strategy, operations, and innovation. By reducing the environmental footprint of our operations, we are leading the industrial minerals industry to solve global challenges. This result will in turn help our customers to achieve their sustainability targets and to develop sustainable solutions that meet societal needs. We must drive this sustainable performance at all levels of our organization, and I am proud to contribute to this mission.

For information, contact Bunt at nancy.bunt@imerys.com. ■

Structure and thermodynamics of oxides/carbides/nitrides/borides at high temperatures

By Qi-Jun Hong, Sergey V. Ushakov, Kristina Lilova, Alexandra Navrotsky, and Scott J. McCormack

The 2nd Structure and Thermodynamics of Oxides/carbides/nitrides/borides at High Temperature (STOHT2) conference took place at Arizona State University from Oct. 4–7, 2022. This article provides a snapshot of the meeting, including a look at currently used experimental and computational techniques, their key limitations, and possible future directions for research.

Humankind has an innate appetite for exploration, energy, and speed. These areas all require materials that operate in extreme environments, for example, temperatures above 1,500°C.

While exploring the universe can be cold (about –270°C in deep space), reentry into a planet's atmosphere can be hot (about 1,500°C on Earth). Energy production through nuclear fission can reach temperatures of up to about 1,700°C and even higher for nuclear fusion, while nuclear thermal propulsion systems require temperatures up to about 2,800°C to provide thrust to propel next-generation spacecrafts to Mars and beyond. When traveling at hypersonic speeds on Earth, leading edges can reach temperatures of about 2,700°C at Mach 8.

High-temperature thermal barrier systems as well as high-temperature environmental barrier coatings are required to protect both people and equipment on board from these high temperatures. To effectively design high-temperature material systems, one must have a clear understanding of both their thermodynamic properties and atomic structure. Understanding thermodynamics is essential to determining the longevity (stability) of a system in its operating environment, while atomic structure influences the desired material properties (e.g., mechanical, thermal, electrical, optical). There is a direct interplay between thermodynamics and atomic structure, and thus both need to be understood in the design of next-generation high-temperature materials.

This need for high-temperature material systems led researchers to organize the 1st Structure and Thermodynamics of Oxides at High Temperature (STOHT1) conference, which was held at the University of California, Davis, in 2016. After several delays due to the COVID-19 pandemic, the 2nd Structure and Thermodynamics of Oxides/carbides/nitrides/borides at High Temperature (STOHT2) conference at Arizona State University took place from Oct. 4–7, 2022 (Figure 1).

The core goal of the STOHT2 meeting was to bring together both high-temperature experimental and computational experts to discuss (i) current state-of-the-art high-temperature techniques and methodologies, (ii) key experimental and computational high-temperature limitations, and (iii) directions to overcome these limitations.

The meeting began with a CALculation of PHAse Diagram (CALPHAD) workshop that focused on FactSage, PyCalphad, and Extensible Self-optimizing Phase Equilibria Infrastructure (ESPEI). The remaining three days focused on a series of invited 40-minute presentations, with 10 minutes of questions and answers from experts in experimental and computational thermodynamics and material structures.

This article provides a snapshot of the meeting and our take on the currently used experimental and computational techniques, their key limitations, and possible future directions for the study of the structure and thermodynamics of oxides/carbides/nitrides/borides at high temperatures. In line with the spirit of the *ACerS Bulletin,* citations throughout are not exhaustive and are used to highlight key bodies of work from authors at the STOHT2 meeting.

Current state-of-the-art high-temperature techniques and methodologies

There is a broad range of techniques available that enable the collection and processing of all-important high-temperature thermochemical and thermophysical data. These techniques can be separated into (i) commercial high-temperature characterization systems, (ii) high-temperature levitation, (iii) combined extreme environment testing, and (iv) computational techniques.

Commercial high-temperature characterization systems

Commercially, there is a wide variety of high-temperature techniques to probe thermochemical and thermophysical properties up to about 2,800°C. For example, Netzsch designed a laser flash apparatus (LFA 427) that can measure thermal diffusivity up to 2,800°C. This instrument, combined with the Netzsch dilatometer (DIL 402) and differential scanning calorimeter, enables thermal conductivity measurements as a function of temperature. These thermophysical properties are of great importance for the development of next-generation hypersonic platforms.

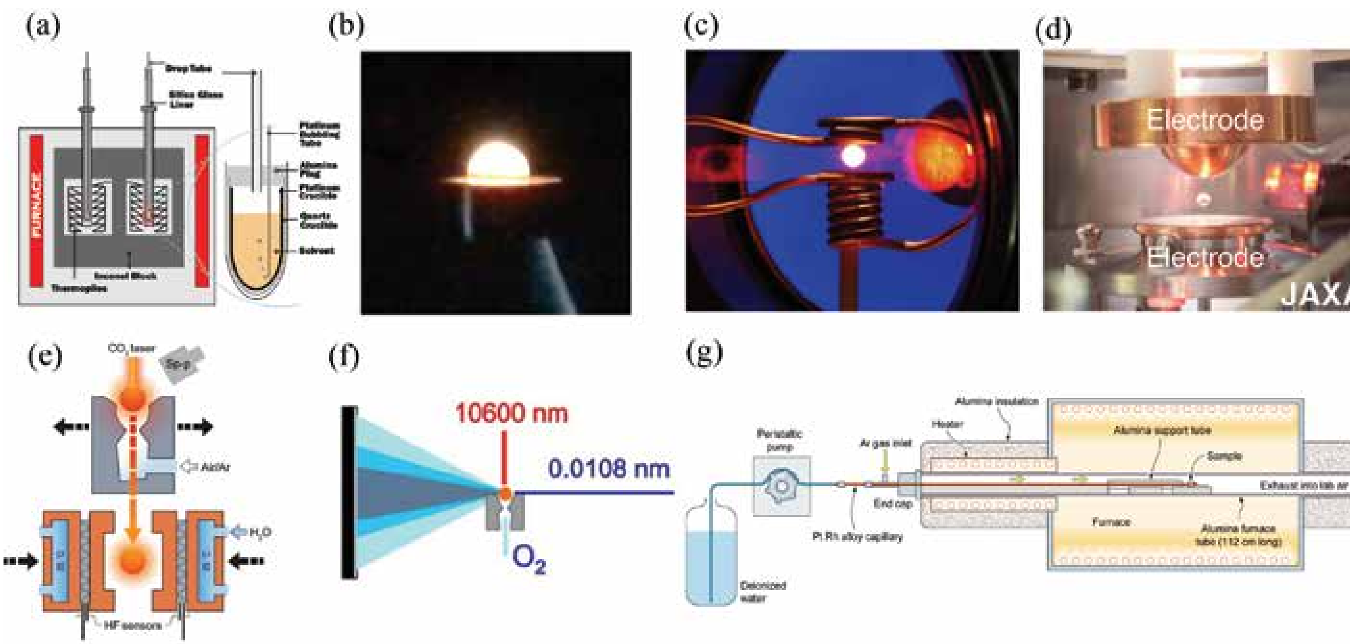
Setaram has a high-temperature differential thermal analyzer (Setsys) that can operate at temperatures up to 2,500°C and a differential scanning calorimeter (Labsys) that operates to 1,600°C and uses highly sensitive 3D sensors for reliable heat capacity measurements. Setaram also offers a high-temperature Calvet calorimeter (Alexsys, Fig. 2a) that can be used to measure enthalpy of formation and enthalpy of mixing of refractory materials.

Costa et al. used the Setaram MHTC 96 calorimeter to determine rare earth silicate and zirconate stabilities with respect to $CaO–MgO–Al_2O_3–SiO_2$ melts,[1] which is of great importance for next-generation barrier coatings that protect jet engines against volcanic ash, sand, and similar threats. Using the Setaram Alexsys systems, Hayun et al. measured formation enthalpies of multicomponent ($n > 5$) metallic alloys,[2] and Goncharvo et al. measured formation energies of uranium mononitride compositions for thermal nuclear propulsion fuel applications.[3] These properties are all essential for the CALPHAD method and are thus required to push our understanding of phase equilibria to high temperatures.

Other companies offer even higher temperature commercial systems. For example, the conical nozzle levitator system (CNL, Fig. 2b) by Materials Development Inc. (Evanston, Ill.) levitates samples in a gas stream, enabling containerless measurements. The CNL can be coupled with a carbon dioxide laser (400 W, 10.6 µm) to heat levitated samples to about 3,400°C, with a dual

Credit: Sergey Ushakov

Figure 1. (Top) Attendees and presenters from the STOHT2 conference. Left to right: Brandon Buckland, Heng Wang, Joerg Neuefeind, Zi-Kui Liu, Wenhao Sun, Philip Spencer, Richard Otis, and Scott McCormack. (Bottom) Students and presenters from the STOHT2 conference. Clockwise starting at top (royal blue shirt): Fox Thorpe, William Rosenberg, Stuart Ness, Nakeshma Cassel, Shivani Srivastava, Randi Swanson, Manuel Loffler, Wenhao Sun, and Mark Asta.



Credits: (a) Ushakov and Navrotsky, *Journal of the American Ceramic Society*, (b) Scott J. McCormack, (c) Seidel et al., *J Phys Conf Ser*, (d) Paradis et al., *Materials Science and Engineering: R: Reports*, (e) Ushakov et al., *Journal of the American Ceramic Society*, (f) Ushakov and Navrotsky, *Journal of the American Ceramic Society*, and (g) Golden and Opila, *J Eur Ceram Soc*

Figure 2. (a) High-temperature oxide drop solution calorimeter,[29] (b) conical nozzle levitator equipped with 400 W carbon dioxide laser, (c) electromagnetic levitator,[4] (d) electrostatic levitator,[6] (e) drop-and-catch calorimeter,[12] (f) high-temperature levitator coupled with X-ray diffraction,[29] and (g) steam-jet furnace.[24] Each figure reproduced with permission from respective journals and/or authors.

carbon dioxide and ytterbium fiber laser (500 W, 1.06 μm) to about 3,700°C (unpublished communication, achieved on a molten HfO_2 with diameter 2.5 mm), and with a calorimeter.

High-temperature levitation

The levitation techniques coupled with laser heating include electromagnetic levitation (EML, Fig. 2c);[4] electrostatic levitation (ESL, Fig. 2d);[5,6] aerodynamic levitation,[7] which includes the previously mentioned CNL; and acoustic levitation.[8] For most levitation techniques, the typical samples are about 2–5 mm diameter spheroids.

These techniques can achieve the highest temperatures while maintaining sample purity, which is essential for accurate thermochemical and thermophysical measurements. Using a CNL with uniaxial laser heating, ceramic spheroids at about 3,000°C can have temperature gradients up to about 500°C/mm (depending on processing), which can be reduced to about 15°C/mm if the sample is a perfect sphere that spins on all axes. When molten, temperature gradients are reduced to about 5°C/mm through convection.[9] Temperature gradients can also be reduced by using multiple lasers to heat from the sample top and bottom simultaneously.

Electromagnetic levitation, which can be used for electrically conductive carbides, nitrides, and borides, provides bulk heating by induction, which reduces the thermal gradient, allows the levitation of larger samples, and is not limited to spheroids. Levitation melting of an 8 mm sample of uranium carbide in EML was demonstrated by Knights et al. in 1971 using induction heating only.[10] However, so far, EML is applied mostly to metal alloys. EML has been combined with laser heating, and this approach was used to preheat semiconductors for levitation or for pulsed laser calorimetry.[11]

High-temperature levitation experiments can be coupled with noncontact diagnostics that enable property measurements at temperatures limited only by sample evaporation. Examples include thermal expansion, heat capacity, thermal diffusivity, and thermal conductivity measurements.

Thermal expansion or density variation as a function of temperature can be measured using high-speed cameras that take advantage of edge detection to determine volume. Through incorporation of a pulsing laser, the heat capacity, thermal diffusivity, and thermal conductivity can also be extracted. Fukuyama et al. performed such measurements on several materials at high temperatures.[11] Additionally, levitating molten samples can be pulsed mechanically, causing them to oscillate. By observing this oscillation using high-speed cameras, high-temperature surface tensions and viscosity can be extracted.[5]

An ESL system was incorporated into the International Space Station because near zero gravity measurements can lead to enhanced accuracy in viscosity and surface tension measurements. This project is being led by the Japan Aerospace Exploration Agency.

A drop-n-catch calorimeter (DnC) was developed in Navrotsky's group at Arizona State University in collaboration with Materials Development Inc. (Fig. 2e).[12] DnC combines a splitable nozzle aerodynamic levitator with laser heating and a calorimeter operating at room temperature. Fusion enthalpies are obtained from measurements on the samples heated to above and below their melting points before the drop. The DnC uses samples several orders of magnitude smaller in size than those used for conventional drop calorimetry up to the 1970s.[12] The calorimeter design and software were further improved by Materials Development Inc. and are now commercially available.

Levitation-based high-temperature environments are now available in the user programs at several national synchrotron and neutron facilities. In the United States, CNL is in operation at beamline 6-ID-D at Argonne National Laboratory's Advanced Photon Source (Fig. 2f). ESL and CNL systems are available at beamline 1B (NOMAD) at Oak Ridge National Laboratory's Spallation Neutron Source. A hyperbaric EML system is also proposed as one of the environments for neutron diffraction.[13] In Japan, CNL is available at beamline BL04B2 at Super Photon ring-8 GeV (SPring8). These in-situ high-temperature X-ray and neutron diffraction experiments have been used to observe phase transformations,[14] phase diagram construction,[15,16] thermal expansion measurements,[17,18] and liquid local structure measurements,[19–21] to name a few.

Gallington et al. demonstrated that molecular dynamics techniques based on machine learning and density functional theory can be coupled with in-situ scattering local structure data to build interatomic potentials.[22] This approach was applied to amorphous and molten HfO_2.

Yashima et al. implemented the maximum entropy method, which allows researchers to obtain more detailed electron densities from diffraction data, to map atom transport pathways in oxides.[23] To date, this technique has not been applied to in-situ high-temperature diffraction data collected via levitation techniques. The maximum entropy method will be useful in studying lambda transitions in refractory oxides and carbides to better understand sublattice melting phenomena at the highest of temperatures.

Combined extreme environment testing

Coupling other extreme environments with high-temperature testing is required to best study materials under their operating conditions.

For example, environmental barrier coatings are required for next-generation aircraft engines to ensure stability in chemically corrosive environments. The Opila group designed a high-temperature furnace that injects high-velocity hot water (Fig. 2g) to simulate the effects of steams on degradation of the ceramics.[24] Oxyacetylene torch testing as well as arc jet testing are used to simulate atmospheric reentry conditions.[25]

High-temperature mechanical testing setups that use four-point bend tests exist within the Fahrenholtz and Hilmas lab at Missouri University of Science and Technology. The temperature limits of these mechanical systems are limited by the eutectics of the graphite grips with the material being tested. Because of this limitation, diborides can only be tested up to about 2,300°C. New sintering techniques take advantage of electric fields to enhance densification.[26] Close examination of these systems led to the observation of interesting grain boundary phase transitions.[27] Now there is a push to incorporate surface effects into phase equilibria and the construction of grain boundary and nanophase phase diagrams.[28]

Computational techniques

Recent progress in developing first-principles methods has led to successful high-temperature discoveries.

To compute high-temperature materials properties, density functional theory (DFT) can be used on two levels: with lattice dynamics quasiharmonic approximation to calculate free energies of reactions at relatively low temperatures; and in conjunction with molecular dynamics (MD) techniques to obtain data at high temperatures, e.g., in the study of molten salts (Fig. 3e).[30] In addition, DFT and MD simulations generate a large amount of data, which are crucial to CALPHAD modeling and machine learning.

The CALPHAD method employs computational thermodynamics to predict materials properties of multicomponent systems. CALPHAD allows one to combine thermodynamic data from experiment or computation with data on phase equilibria in multicomponent systems to develop predictions for complex systems or locate the range of possible compositions for desired crystal structures. The reliability of these predictions depends on the thermodynamic description of all phases (stable, metastable, and unstable), across the entire compositional range, not only in the range of their stability or of technological interest.

Machine learning approaches can expedite the searches and prediction of properties. The Materials Genome Initiative resulted in the development of several materials databases, including the Materials Project, led by the Ceder and Persson group at UC Berkeley; Automatic Flow (AFLOW), led by the Curtarolo group at Duke University; and Open Quantum Materials Database (OQMD), led by Chris Wolverton at Northwestern University. Machine learning models were built from such databases to predict materials characteristics, especially refractory-materials-related high-temperature properties.

Experimental and computational high-temperature limitations

To date, the key limitations of high-temperature experimental and computational tests are (i) environment control in high-temperature experiments to prevent unwanted reactions, (ii) controlling and measuring temperature with high accuracy, (iii) database limitations, (iv) high-temperature computation, and (v) integrating physics with machine learning.

Environment control

When at high temperatures, everything reacts with everything. Material systems that may remain in the metastable states indefinitely at room temperature have sufficient energy at higher temperature to achieve their equilibrium states, overcoming kinetics barriers.

In general, furnaces that operate above 1,800°C are graphite furnaces. Samples can become contaminated with carbon in these furnaces. There are ways to reduce contamination, such as sample encapsulation using other materials like tungsten, but even those can react. Here high-temperature levitation really shines, as it is containerless and the sample is shielded by its surrounding levitation gas.

Material systems with components that have high vapor pressure can sublimate, making them very difficult to study at high temperatures even when using levitation techniques. To date, most levitation systems are designed for studying metals and oxides and are not designed to study the more refractory and high-temperature carbides, nitrides, and diborides. There is a direct need to further develop high-temperature levitation to extract property data from these more challenging high-temperature materials.

Controlling and measuring temperature

Temperature control and measurement is challenging at extreme temperatures. High-temperature thermocouples can degrade when operating above 2,400°C due to diffusion across their junction. This degradation can be somewhat overcome by consistent calibration, but this method is not ideal. Pyrometers are the next best tool for measuring temperature, but they come with even higher temperature errors than thermocouples. These errors are predominantly due to thermal gradients and uncertainty in emissivity. As mentioned previously, there are multiple ways to reduce thermal gradients, but it is difficult to eliminate them.

Database limitations (for both CALPHAD and machine learning)

Despite recent rapid developments, databases are still limited in quantity and variety. It requires extensive efforts to build databases, e.g., the SpMCBN database for refractory carbide, nitride, boride, and silicide systems and the newly assessed Zr–B–C–O system.[31,32] In addition, CALPHAD and machine learning models are only as good as the quality of the data they are trained on. Including new data can be time-consuming for CALPHAD and ML as databases grow and evolve.[33] Additionally, integrating data from different sources and approaches is challenging, as they are often subject to different and poorly known systematic errors.

High-temperature computation

High-temperature material properties are often significantly more expensive to compute than properties at 0 K. They require molecular dynamics or other approaches to include entropy effects. The high temperature leads to disordering and defects, which require, in principle, an extensive sampling of the configurational space (Fig. 3b).[34,35] Lattice dynamics quasi-harmonic approximation starts to fail at high temperatures as anharmonic effects grow. Liquid phases are considerably more challenging to model compared to solids.

Integrating physics with machine learning

Machine learning models are only as good as the underlying physical principles on which they are built. Machine learning typically does not come with a straightforward analytical expression, which is both a strength and a weakness. While it greatly increases its applicability, it becomes challenging to integrate physics into the machine learning algorithms. Without the guidance of physics, machine learning models inevitably break physical laws, resulting in unreasonable "predictions."

Directions to overcome these limitations

The innovations required to overcome the limitations discussed above include (i) further development of novel high-temperature systems that push the limitations of composition control, (ii) improved temperature measurements at the highest of temperatures through improved pyrometry, and (iii) new computational methods to simulate high-temperature properties via DFT, ML, and CALPHAD.

Levitation at high pressure has been attempted since the 1990s to improve processing and environmental control. However, existing levitators at synchrotron and neutron facilities still operate only at ambient pressure.

A hyperbaric aerodynamic levitator was constructed by David Lipke (Missouri Science and Technology), and the results of these experiments were presented at the STOHT2 conference. These levitation systems provide novel environmental control that will be essential for characterizing materials in combined extreme environments. The ability to control levitation gas composition in hyperbaric conditions opens an entire new field of high-temperature thermochemistry, where solid–gas reactions can be studied in situ as functions of temperature and pressure.

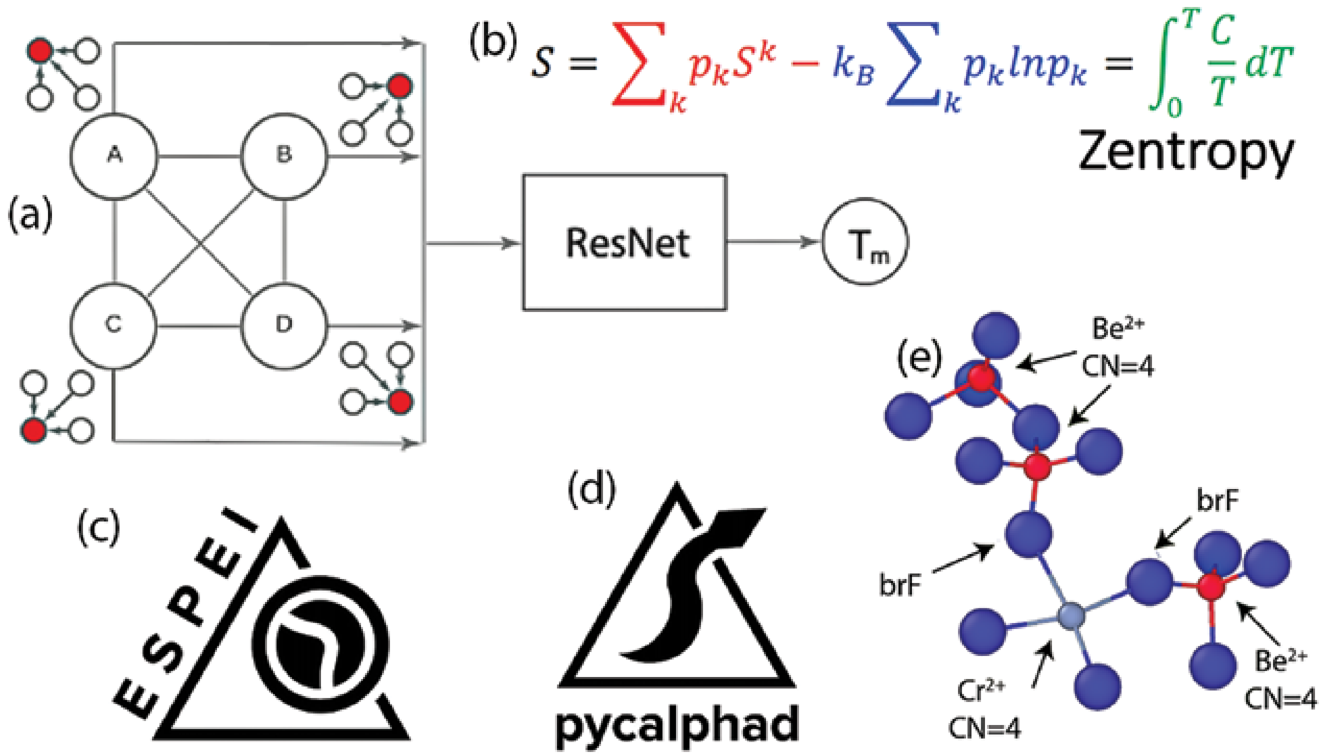
Of particular interest is reducing sublimation of high-vapor-pressure components, further expanding the composition space that can be studied at the highest of temperatures. Nitrides are a specific material example that will benefit from these types of systems. They sublimate before melting, which makes them extremely difficult to study at high temperatures while accurately controlling their composition. An ESL system with controlled atmosphere was recently able to observe AlN formation in Ni–Al in situ at high temperatures.[39] These sorts of experiments have the potential to provide great insight into in-situ oxidation of high-temperature refractory materials at temperatures, e.g., carbides, nitrides, and diborides.

These comments highlight the need for more levitation systems that can take advantage of atmospheric controls at high temperatures to study reactions in extreme environments. This system can then be coupled with synchrotron and neutron sources to obtain structural information in situ at high temperatures.

Noncontact temperature measurements have always been difficult because the sample surface serves as the sensor. Spectral band or "single-color" pyrometers are currently used on levitators at the beamlines for measurement of the sample temperature. They provide the fastest acquisition time, but they require knowledge of emissivity, which, for a levitating spheroid, will depend on temperature, wavelength, surface curvature, and angle of observation. Surface reduction or oxidation is also often accompanied by drastic changes in emissivity.

During diffraction measurements on levitated samples, the practical way to overcome uncertainty in surface emissivity and in thermal gradient is by calibration with known or independently measured temperatures of phase transition and melting, which can be observed directly from diffraction patterns.[14] Spectropyrometers, in which ratio of intensities on multiple spectral bands are evaluated, provide emissivity-free temperature measurements and have been commercially available from a small U.S. company called FAR Associates. They are successfully used in lab-based levitators in Navrotsky's group at Arizona State University and in Lipke's group at Missouri University of Science and Technology. Lu et al. in 2009 demonstrated the application of CMOS sensors as three-color 2D pyrometers,[40] but this application is not yet commercialized.

Computational tools and packages were built to automate the processes for CALPHAD and DFT methods, providing



Credits: (a) Hong et al., *Proceedings of the National Academy of Sciences*, (b) Liu et al., *J Phase Equilibria Diffus* and Liu, *Mater Res Lett*, (c) Bocklund et al., *MRS Commun*, (d) Otis and Liu, *J Open Res Softw*, and (e) Winner et al., *J Mol Liq*

Figure 3. (a) a graph neural network model for melting temperature prediction,[36] (b) the Zentropy method,[34,35] (c) ESPEI (which uses PyCalphad to develop CALPHAD databases),[37] (d) PyCalphad (which uses the databases for calculations),[38] and (e) molecular dynamics to study chromium in 2LiF-BeF_2.[30] Each figure reproduced with permission from respective journals and/or authors.

frameworks for material property calculations. PyCalphad is a Python library for computational thermodynamics (Fig. 3d),[37] based within the CALPHAD method.[38] ESPEI (Fig. 3c) is a tool for creating and integrating CALPHAD databases,[36] as well as evaluating the uncertainty of CALPHAD models.[37] The Solid and Liquid in Ultra Small Coexistence with Hovering Interfaces (SLUSCHI) package implements the small-cell coexistence method for direct DFT melting temperature calculations.[39,41] All tools and packages are free and open source.

Ensemble models were built to calculate the uncertainty of ML prediction (Fig. 3a) and detect outliers.[42] A manual review helps resolve the two possible causes for each outlier. Either (i) the data point is wrong due to data issues (so we should correct or remove the data point), or (ii) the data point is correct and thus essential to the mapping (so more sampling is needed to anchor the ML model in the vicinity accurately).

In the synthesis of inorganic materials, reactions often lead to unexpected nonequilibrium kinetic products instead of thermodynamic equilibrium phases. Understanding the competition between thermodynamics and kinetics is a fundamental step toward the rational synthesis of target materials. Building a machine learning model for materials synthesizability requires considering all possible reaction pathways[43]; merely the reactant and product are insufficient.

New computational approaches, such as the small-size coexistence method for melting temperature calculations, were built to compute high-temperature materials properties directly from DFT. For example, the Hf–C–N system was computationally predicted to be the material with the world's highest melting temperature based on DFT MD calculations using the SLUSCHI package.[42,44] This discovery was also later confirmed independently from experiments.

Conclusions

The STOHT2 meeting highlighted how current state-of-the-art experimental and computational methods can be incorporated in tandem to study materials at the highest of temperatures.

High-temperature levitation techniques have shown to be indispensable to the study of structural, thermodynamic, and thermophysical properties at high temperatures. DFT combined with MD offers essential data to guide experiments, and after experimental validation, it can provide experimentally inaccessible data to build CALPHAD-type databases.

Although there are many successes, work remains to be done. At high temperatures (>2,500°C), it can be difficult to control the chemical environment and measure the temperature with high accuracy using thermocouples and pyrometers. Ab initio molecular dynamic computations at high temperatures when quasiharmonic approximations in MD start to fail are time and resource demanding. However, the developed packages, such as SLUSCHI, allow automation of DFT melting temperature calculations.

Thermodynamic analysis is especially relevant for high-temperature materials and processes. However, CALPHAD databases for ceramic materials above 2,000°C are very limited and mostly based on experimental data obtained decades ago.

These challenges have led to opportunities. Coupling levitation with lasers and induction heating with high-pressure chambers offers the possibility to explore high-temperature environments not previously achievable in controlled experiments. The development of hyperbaric aerodynamic and electromagnetic levitation as sample environments on synchrotron and neutron sources can open new vistas for structural characterization of high-temperature materials and provide experimental data for benchmarking computations and building CALPHAD databases.

In addition to commercially available CALPHAD software and databases, the new generation of free open-source software is becoming available, such as ESPEI. This software allows for uncertainty analysis of phase diagrams to be generated using all available experimental and computational data; the building and optimization of CALPHAD-type databases in a top-down manner in addition to the traditional bottom-up approach; and integration with PyCalphad, which allows for the implementation of new models by the users. Such software advances will undoubtedly democratize CALPHAD and will provide faster integration of new experimental and computational data into the models.

Considering both successes and challenges, the high-temperature materials field has a bright future.

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Regarding workshops, Jean-Philippe Harvey (Ecole Polytechnique de Montreal, Canada) presented at the FactSage workshop. Richard Otis (NASA Jet Propulsion Laboratory, Calif.) and Brandon Boucklund (Lawrence Livermore National Laboratory, Calif.) presented at the PyCalphad & ESPEI workshop.

The invited speakers include (in order of presentation) Alexandra Navrotsky (Arizona State University), Richard Weber (Materials Development Inc., Ill.), Chris Benmore (Argonne National Laboratory, Ill.), Shinji Kohara (Tokyo University of Science, Japan), Joerg Neuefeind (Oak Ridge National Laboratory, Tenn.), Maxime Bourdon (Setaram, France), David Lipke (Missouri Science and Technology), Elizabeth Sobalvarro Converse (Lawrence Livermore National Laboratory, Calif.), Gustavo Costa (NASA Glenn, Ohio), Sergey Ushakov (Arizona State University), Shmulik Hayun (Ben-Gurion University of the Negev, Israel), Zi-Kui Liu (The Pennsylvania State University), Philip Spencer (Spencer Group Inc., N.Y.), Jean-Philippe Harvey (Ecole Polytechnique de Montreal, Canada), Heng Wang (Netzsch, Mass.), Qi-Jun Hong (Arizona State University), Wenhao Sun (University of Michigan), Mark Asta (University of California, Berkeley), Elizabeth Opila (University of Virginia), Erica Corral (University of Arizona), Randall Hay (Air Force Research Laboratory, Ohio), Jian Luo (University of California, San Diego), Xiaofeng Guo (Washington State University), Masatomo Yashima (Tokyo Insitute of Technology, Japan), and Hiroyuki Fukuyama (Tohoku University, Japan).

The poster presenters include Stephen Wilke (Materials Development Inc., Ill.), Jakob Trammel (University of Arizona), Dwight Myers (East Central University, Okla.), Manuel Loffler (Institut fur Werkstoffwissenschaft, Germany), Benjamin Brugman (Arizona State University), Manuel Scharrer (Arizona State University), Miguel Bustamante (Arizona State University), Megan Householder (Arizona State University), Shivani Srivastava (University of California, Berkeley), Stuart Ness (University of California, Davis), William Rosenberg (University of California, Davis), Randi Swanson (University of California, Davis), Fox Thorpe (University of California, Davis), Kyle Kondrat (University of California, Davis).

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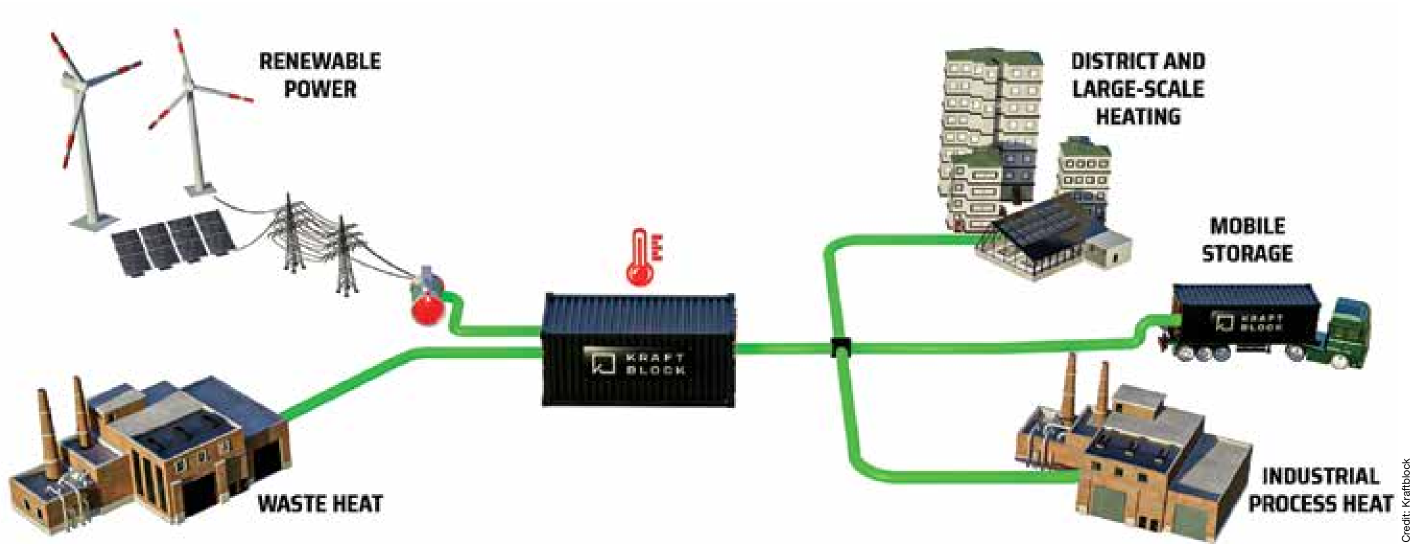


Figure 1. Kraftblock's high-temperature heat storage system is widely applicable to numerous thermal processing industries.

Value-add of thermal energy storage systems in the ceramics industry

By Martin Schichtel

Kraftblock (Sulzbach, Germany) has developed a widely applicable high-temperature thermal energy storage system that could help reduce emissions in the ceramics industry.

Thermal energy accounts for approximately 45% of global-energy-related CO_2 emissions worldwide. Specifically, 20% of these emissions comes from industrial heat.[1]

The ceramics industry significantly contributes to these emissions. Each year, the energy consumption for firing ceramics using natural gas is approximately 182 TWh.[2] At an average CO_2 release rate of 0.22t/MWh, this firing results in roughly 40 million tons of carbon dioxide emission every year. As wealth increases and more countries industrialize, a study by the Long Duration Energy Storage Council estimates industrial heat generation will increase by up to 60% by 2050, resulting in even higher levels of emissions.[1]

Since the 1980s, ceramic and glass manufacturers have dedicated themselves to reducing energy consumption.[3] While alternative fuels and heat generation sources are being explored, at present, harnessing waste heat is the most immediately accessible approach to improving efficiency and reducing emissions.

Technologies to improve energy efficiency

Currently, there are two main approaches to achieving a highly efficient combustion process. The first approach uses high-pulse (or high-speed) burners. These burners greatly increase the turbulence inside a furnace by directly returning hot gases back into the combustion chamber via high outflow speeds. The second approach simply uses pure oxygen instead of ambient air for the combustion process, which results in a reduced volume flow and thereby reduced exhaust gas losses. But the energy used for the combustion is still a fossil fuel, resulting in undesirable emissions.

In the last few decades, several components and processes were developed to further improve the efficiency of thermal systems by utilizing waste heat to provide power, refrigeration, and process heat.[4]

Regarding power usages, thermal energy from flue gases can be converted into electricity using thermoelectric, piezoelectric, or thermal photovoltaic technology. Most existing heat-to-electricity conversion systems are used to power sensors or smaller control units. Depending on the quantity and quality of heat, external systems such as Stirling engines, Kalina systems, and organic Rankine cycle engines can convert 5–15% of the heat into electricity. Such systems work well for up to 2 MW of waste heat power. If more waste heat is available, especially at higher temperatures, electrical power is generated by steam turbines with efficiencies between 20% and 45%.

Absorption or adsorption chillers are used to feed a refrigerating or cooling system. Such chillers are comparable to vapor compression cycles. Typically, the electric motor and compressors are replaced by a thermal compressor system, so that thermal energy is used instead of mechanical energy. These types of chillers use lithium bromide for space conditioning, or a mixture of water and ammonia for other applications, such as warehouses, cooling chambers, and so on.[5]

To use thermal energy as heat, heat exchangers, heat pumps, and thermal storage systems are the technologies of choice. The well-known recuperative and regenerative burners, which directly reuse heat from flue gases to preheat the combustion air, are currently the best use of waste heat because they offer the highest efficiencies. These latter systems comprise a type of intermediate thermal energy storage system.

For other processes, heat exchangers transfer thermal energy from the flue gas to pure air, thermal oil, steam, or simply hot water. The efficiency is determined by the surface area, the transfer coefficient, and the temperature of the receiving media. Typical structures for heat exchangers are pipe bundle, plate, double pipe, lamella, spiral, fin-tube, or even rotational heat exchangers.

Heat exchangers face several drawbacks that hinder their usage in the ceramics industry. For one, all types of heat exchangers are generally limited to an upper operation temperature of 700–800°C. Systems that can withstand even higher temperature are costly and rarely found in application.

Besides a limited temperature range, heat exchanger performance is frequently affected by contamination in the combustion air. Burning fossil fuels in ambient air results in various contaminations, such as carbon monoxide, nitrogen oxides, and carbon black, as well as several ashes. These "solid-state" contaminants might stick to the surface of the heat exchanger or even block the interconnection. Additionally, flue gases in the ceramic and glass industry can be contaminated by fluorine, sulphur, boron, lead, and other substances. In combination with often present humidity, these contaminates frequently cause corrosion problems.

According to a study by the French-German Institute for Environmental Research,[6] contamination from flue gases depends strongly on the type of ceramic being produced. Sintering of roofing tiles released the highest quantity of fluorine (up to 120 mg/m^3), followed by refractories, floor tiles, sanitaryware, and porcelain. Similar results were found for ammonia (refractories was highest, up to 2,500 mg/m^3) or organic contamination (up to 250 mg/m^3 for floor tiles or grinding materials). All these measurements are related to heat production and utilization.

Instead of heat exchangers, a thermal energy storage system developed by Kraftblock (Sulzbach, Germany) offers a more effective way of using waste heat in the ceramics industry (Figure 1).

Kraftblock's thermal energy storage system

Kraftblock has developed a widely applicable high-temperature thermal energy storage system that can store thermal energy up to 1,300°C. It includes all necessary components needed to operate a storage unit, such as state-of-the-art charging and discharging units that are designed on a project-by-project basis. This customized design approach makes it possible to serve a wide range of thermal processing industries with the same basic storage unit, from batch processes to continuously running systems.

The thermal energy stored in Kraftblock's system is stored between 350°C and 1,300°C. Up to 1.2 MWh of thermal energy can be stored per cubic meter of filling. This energy can be used for different applications, including

- Process heat (also with other heat transfer media),
- Refrigeration (adsorption or absorption chillers),
- Compressed air generation,
- Electricity generation (or as support for existing organic ranking cycle engines), and
- Feeding into heat networks.

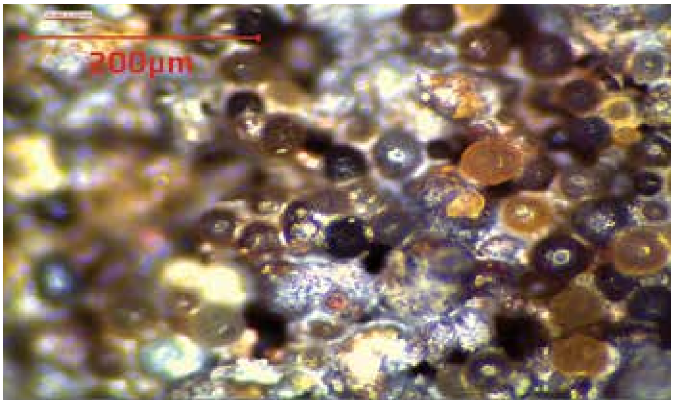
This wide range of applications is made possible by, among other things, the specially developed storage material (Figure 2). The storage material was developed according to many sustainability criteria and contains up to 85% recycled materials.

Steel slag is a main component of Kraftblock's storage material. The usage of steel slag to store thermal energy is not a new idea. The European Union Slagstock project already showed that steel slags can be used to store thermal energy.[7]

In the Slagstock project, pure slag (1–3 cm diameter) was charged by molten salt (T_{max} = 560°C) and exhibited a not-well-

Credit: Kraftblock

Figure 2. Kraftblock heat storage granules.



Credit: Kraftblock

Figure 3. Microscopic view into the storage material.

defined charging and discharging behavior. Due to a low heat conductivity (less than 0.8 W/mK), a lagging effect was observed. In other words, when a higher temperature from the core of the particles in the first slag layer was discharged, it caused particles in the second slag layer to partially charge again. This process resulted in a very inefficient cycle behavior. The lagging effect was even worse when air was used as the heat transfer media due to the different fluid dynamics of gases and liquids.

In the Kraftblock system, the steel slag acts as a capacity filler. It gets milled down to less than 200 µm to reduce the latency in the heat transfer. At this point, the conductivity still is rather low (less than 0.8 W/mK), and so the Kraftblock team combined the slag powder with an inorganic phosphate binder.

Phosphate binders, specifically monoaluminium phosphate, are well known in the refractory industry. This material also is used as a highly conductive protective coating for graphite electrodes in aluminum melts. In all cases, the "binder" must be sintered above the expected application temperature. The phosphate binder undergoes a chemical reaction that causes it to harden during the materials production process; so, all thermal granule production takes place at room temperature.

The round-shaped grains in Figure 3 are the milled slag particles, while the intergranular white layers are the hardened phosphatic binder, which transports the heat into the core of the storage pellets. There is even a protective layer of phosphate on the outer shell of the pellets, which provides high stability against chemical corrosion, especially during the condensation phase of the process. Overall, this composition makes the Kraftblock storage material completely stable, both thermally and chemically.

The storage material is placed into modular storage containers, generally 10 or 20 feet wide. Individual storage modules can be delivered as "turn-key" systems and can also be used as mobile heat storage units. This approach proves useful in two cases:

1. There is so much waste heat that the potential cannot be used internally in the plant. In this case, the "recycled" waste heat can be sold to external third parties.

2. Heat source and sink are located so far apart in the plant that laying pipe systems is too complex, expensive, and/or comes with big losses. In this case, mobile storage units can move the heat within the plant.

Credit: Kraftblock

Figure 4. Example of a 10-foot Kraftblock storage that can store 4.2 MWh of waste heat at a max 600°C.

A third argument for a modular high-temperature storage system is scalability. Modules can be interconnected to build stationary "large-scale" storage systems—which can even be expanded with additional modules in a second stage.

Ideally, heat is taken directly from the flue gas and transferred to the material. In this case, the storage unit is integrated into the waste heat system as a "bypass"—if possible, without a heat exchanger. The cooled flue gas is fed back into the actual process at a suitable point, which is why the system can usually comply with all environmental regulations. The same applies to decoupling of the heat into the useful process, as this step is done by connecting a suitable heat exchanger. Variants are possible here. Of course, exhaust gas values—particularly dust load, sulphur, nitrogen oxides, and fluorine content—are accounted for during concept development.

Application examples

A simple example of an application for the Kraftblock system is its use as an external recuperator or regenerator with better storage properties. In this case, a waste heat output of approximately 500 kW at a usable temperature level of about 600°C is available from a gas-fired batch furnace, according to combustion calculations. Thus, during the heating and soak phases, about 4 MWh of waste heat can be stored.

Based on these parameters, a small 10-foot system (Figure 4) can be charged and discharged at a rate of 1 MW per hour (i.e., it will take 4 hours to reach maximum storage capacity). An additional suction-pull blower, coupled to the furnace control system, adjusts the delivery pressure accordingly. After loading of the storage tank is completed (during the soak phase or beginning of the cooling phase of the furnace), the heat is retained until the next furnace run.

During discharging, the furnace chamber is preheated to 300°C. The remaining storage energy is used to generate heat and process water, which corresponds to cascading heat utilization. Thus, the primary energy demand for the kiln plus heating water can be reduced by about 20%, and up to 30% of CO_2 generation can be avoided.

Depending on local conditions, the stored energy could first be used to support or completely replace the heating system for the drying process. This three-way cascade makes efficiency considerations and potential savings even more interesting. Plus, this type of storage can be used to transport heat to a remote location as well. "Waste heat" gains commercial value by selling to third parties.

A good alternative to decarbonizing a process is the complete electrification of heat. In this case, the fossil-fired system is replaced with a combined power-to-heat and thermal storage system. The power-to-heat system converts electricity—preferably generated from renewable sources—to heat. Ideally, this conversion only takes place for three to four hours every day when prices are low. From this point on, the stored heat could discharge up to 24/7.

For low-temperature applications, PepsiCo is building such a system in the Netherlands with Kraftblock and Dutch energy supplier Eneco.[8] This system, which should be operational by the end of 2023, will replace a fossil-fired boiler used to make deep fried snacks.

These applications and the possible combination of multiple technologies show the potential of high-temperature thermal energy storage systems to help the ceramics industry become more sustainable and efficient in the future.

About the author

Martin Schichtel is cofounder and CEO of Kraftblock GmbH in Sulzbach, Germany. Contact Schichtel at welcome@kraftblock.com.

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Together again for Electronic Materials and Applications 2023 in Orlando

Credit: ACerS (all photos)

Attendees met for the first time in person since 2020 for the Electronic Materials and Applications Conference in Orlando, Fla., Jan. 17–20, 2023.

Students and young professionals gather for an outdoor reception at EMA 2023. This year is the first time attendees were able to meet in person since 2020 due to the COVID-19 pandemic.

The COVID-19 pandemic forced organizers to present EMA in virtual format in 2021 and 2022. While organizers and speakers did a great job creating an EMA virtual experience, all agreed that attending in person provided far better opportunities for discussion and interaction.

For EMA 2023, Electronics Division organizers were Edward Gorzkowski (Naval Research Laboratory) and Matjaz Spreitzer (Josef Stefan Institute, Slovenia). Basic Science Division organizers were Amanda Krause (Carnegie Mellon University) and Ricardo Castro (University of California, Davis).

Close to 270 attendees from 20 countries attended the three-day conference. Of the 40 students at EMA 2023, for many of them, this meeting was their first time attending a professional conference due to travel restrictions during the pandemic. So, conference organizers included a student and young professional reception, poster session, student poster and presentation awards, and a lunch-and-learn career panel discussion that were all designed to accelerate student engagement and access to everything the conference had to offer.

Plenary lecturer Jeffrey Rickman, left, receives a plenary recognition certification from Amanda Krause, secretary of the Basic Science Division and coorganizer of EMA.

The conference opened both of its full-day sessions with a plenary lecture. The first plenary lecture was presented by Andriy Zakutayev from the National Renewable Energy Laboratory in Golden, Colo. He talked about the discovery and design of electronic materials using high-throughput experimental methods, focusing specifically on ferroelectric materials for energy technologies and computing (transistors and capacitors).

"Energy-efficient computing is an important and ripe problem for materials design and discovery," he says.

Lehigh University professor and ACerS Fellow Jeffrey Rickman delivered the Day 2 plenary lecture on interfacial phase transitions at grain boundaries and their impact on thermal and mechanical properties.

As delightful as Florida was this year, it also marked the end of an era. Electronics Division and Basic Science Division leaders announced at the conference's reception that the meeting will move next year to Denver, Colo., and will be held Feb. 13–16, 2024. Without question, the Rocky Mountains will provide a spectacular backdrop for EMA 2024!

Check out all the images from EMA 2023 on ACerS Flickr page at bit.ly/EMA_2023. ■

Andriy Zakutayev, left, responds to questions after his plenary lecture while Edward Gorzkowski, vice chair of the Electronics Division and coorganizer of EMA, looks on.

Students and young professionals took advantage of the career lunch-and-learn on Wednesday, Jan. 18 to ask questions about career paths in industry, government, and academia. Here, Charlie Hill from 3M (second from left) shares his experiences as an astrophysicist working in industry as a materials scientist.

A big 'Hello, again!' at ICACC in Daytona Beach

Credit: ACerS (all photos)

The 47th International Conference on Applied Ceramics and Composites, organized by ACerS Engineering Ceramics Division, took place in person in Daytona Beach, Fla., Jan. 22–27, 2023.

ECD chair Balaya Palani welcomed everyone to the conference during Monday's plenary session and presented the ECD's Jubilee Global Diversity award and Global Young Investigator award. Student poster awards from 2022 were announced and presented, along with ECD's Global Star awards.

Palani then introduced conference chair Young-Wook Kim, who shared the good news that more than 874 abstracts from 47 countries were accepted, which is close to pre-pandemic levels. With formalities concluded, four excellent lectures followed.

- Mueller Award lecture: Jonathan Salem (NASA Glenn), "Testing and design of ceramic structural materials and components at NASA"
- Bridge Building Award lecture: Paolo Colombo (University of Padua), "Additive manufacturing of ceramics from liquid feedstocks"
- Plenary lecture: Rita Baranwal (Westinghouse Electric), "Westinghouse fuel innovation leveraging advanced ceramics"
- Plenary lecture: Huisuk Yun (Korea Institute of Materials Science and University of Science & Technology), "New challenges for ceramic additive manufacturing"

ICACC attendees chatted with vendors at the expo.

The conference included 19 symposia; four focused sessions; and a special symposium in honor of Tatsuki Ohji, ACerS Distinguished Life Member, Fellow, and past president. The symposium, "Emergent materials and sustainable manufacturing technologies in a global landscape: International symposium in honor of Dr. Tatsuki Ohji," was a fitting testimony to the impact and reach of Ohji's research.

The expo and poster session on Tuesday and Wednesday provided an opportunity for attendees to talk with vendors about the latest products and services. The concurrent student poster session extended stimulating scientific discussions well into the evening.

ACerS President's Council of Student Advisors held its annual shot glass drop competition on Tuesday evening. Student groups used pipe cleaners to construct protective cages for shot glasses provided by SCHOTT. The University of North Dakota "Fighting Sioux" team prevailed in a field of 11 teams with a winning drop from a height of 145 inches (about 12 feet).

President Sanjay Mathur (left) and ECD chair Balaya Palani (right) recognized conference chair Young-Wook Kim (middle) during the plenary session.

Students and young professionals availed themselves of other valuable opportunities, including a journal publishing workshop focused on effective abstract writing and a lunch-and-learn career panel with (slightly) older colleagues who already navigated the student-to-professional transition.

The strongly international character of the conference carried over to the Student and Young Professional Networking Mixer cosponsored by the ACerS Young Professionals Network and the ECerS Young Ceramists Network, which attracted a record attendance of about 150 people.

The ACerS Diversity, Equity, and Inclusion Subcommittee, chaired by Theresa Davey of Tohoku University, Japan, held a Diversity in Ceramics lunch. Davey created a set of eight realistic scenarios that could arise in the workplace, from gender, racial, and cultural situations to more subtle challenges such as language, religious practices, health issues, and family care situations.

The 48th ICACC will be Jan. 28–Feb. 2, 2024, in Daytona Beach, Fla. View images from the conference at https://bit.ly/ICACC-2023. ■

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UPCOMING DATES

2023 GLASS & OPTICAL MATERIALS DIVISION ANNUAL MEETING (GOMD 2023)

HOTEL MONTELEONE, NEW ORLEANS, LA.

ACerS Glass & Optical Materials Division will hold its annual meeting and conference in New Orleans, La., from June 4–8, 2023.

ACERS 2023 STRUCTURAL CLAY PRODUCTS DIVISION & SOUTHWEST SECTION MEETING IN CONJUNCTION WITH THE NATIONAL BRICK RESEARCH CENTER MEETING

OMNI AUSTIN HOTEL DOWNTOWN,
AUSTIN, TEXAS

If you are involved in the structural clay industry—and that includes manufacturing, sales and marketing, consultants, and material or equipment suppliers—then join us June 5–8, 2023, in Austin, Texas.

MATERIAL CHALLENGES IN ALTERNATIVE AND RENEWABLE ENERGY 2023 (MCARE 2023) COMBINED WITH Energy Harvesting Society meeting (EHS 2023)

A joint meeting effort organized by ACerS Energy Materials and Systems Division and the Korean Institute of Chemical Engineers (KIChE)

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BELLEVUE, WASH.

If your research seeks sustainable energy solutions on a global scale, you should attend this conference.

Calendar of events

March 2023

19–24 ➨ ECI – Electric Field Enhanced Processing of Advanced Materials III: Complexities and Opportunities – Hotel dos Templários, Tomar, Portugal; http://engconf.us/conferences/materials-science-including-nanotechnology/electric-field-enhanced-processing-of-advanced-materials-iii-complexities-and-opportunities

28–30 58th Annual St. Louis Section/Refractory Ceramics Division Symposium on Refractories – Hilton St. Louis Airport Hotel, St. Louis, Mo.; https://ceramics.org/event/58th-annual-st-louis-section-refractory-ceramics-division-symposium-on-refractories

28–30 IMFORMED Mineral Recycling Forum 2023 – Dubrovnik, Croatia; http://imformed.com/get-imformed/forums/mineral-recycling-forum-2023

May 2023

1–3 8th Ceramics Expo co-located with Thermal Technologies Expo – Suburban Collection Showplace, Novi, Mich.; https://www.ceramicsexpousa.com

17–19 ➨ 8th Highly-functional Ceramic Expo Osaka – INTEX Osaka, Osaka, Japan; https://www.ceramics-japan.jp/en-gb.html

30–June 1 MagForum 2023 – Grand Hotel Dino, Baveno, Lake Maggiore, Italy; http://imformed.com/get-imformed/forums/magforum-2023

June 2023

4–8 ACerS Glass & Optical Materials Division Annual Meeting (GOMD 2023) – Hotel Monteleone, New Orleans, La.; https://ceramics.org/gomd2023

5–8 ACerS 2023 Structural Clay Products Division & Southwest Section Meeting in conjunction with the National Brick Research Center Meeting – Omni Austin Hotel Downtown, Austin, Texas; https://ceramics.org/SCPD2023

14–16 13th Advances in Cement-Based Materials – Columbia University, New York, N.Y.; https://ceramics.org/event/13th-advances-in-cement-based-materials

July 2023

2–6 XVIIIth Conference of the European Ceramic Society (ECerS) – Lyon, France; https://www.ecers2023.org

August 2023

21–24 Materials Challenges in Alternative & Renewable Energy 2023 (MCARE 2023) combined with the 6th Annual Energy Harvesting Society Meeting (EHS 2023) – Hyatt Regency Bellevue, Bellevue, Wash.; https://ceramics.org/mcare-ehs-2023

27–31 ➨ The International Conference on Sintering 2023 (Sintering 2023) – Nagaragawa Convention Center, Gifu, Japan; https://www.sintering2021.org

30–31 EMC Ceramists Additive Manufacturing Forum (yCAM) 2023 – Leoben, Austria; https://euroceram.org/2023-ycam-forum-in-leoben

September 2023

12–15 China Refractory Minerals Forum 2023 – InterContinental, Dalian, China; http://imformed.com/get-imformed/forums/china-refractory-minerals-forum-2023

26–29 ➨ Unified International Technical Conference on Refractories (UNITECR) with 18th Biennial World-wide Congress on Refractories – Kap Europa, Frankfurt am Main, Germany; https://unitecr2023.org

October 2023

1–5 ACerS 125th Annual Meeting with Materials Science & Technology 2023 – Columbus Convention Center, Columbus, Ohio; https://matscitech.org/MST23

November 2023

5–10 ➨ 15th Pacific Rim Conference on Ceramic and Glass Technology – Shenzhen World Exhibition & Convention Center, Shenzhen, China; https://ceramics.org/event/15th-pacific-rim-conference-on-ceramic-and-glass-technology

July 2024

14–19 International Congress on Ceramics – Hotel Bonaventure, Montreal, Canada; www.ceramics.org

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Entries in **BLUE** denote ACerS events.

➨ denotes meetings that ACerS cosponsors, endorses, or otherwise cooperates in organizing.

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Olivia Brandt
Guest columnist

Improving thermal management: Using ceramic coextrusion to fabricate high-temperature heat exchangers

With 80% of industrial heat emissions coming from the burning of fossil fuels, it is no wonder that process heat accounts for approximately 21% of global CO_2 emissions.[1] A long-term solution to mitigating CO_2 emissions from this sector is to find alternative fuels and heat generation sources. However, in the short term, we can mitigate emissions by increasing heat management through improved heat exchanger efficiency.

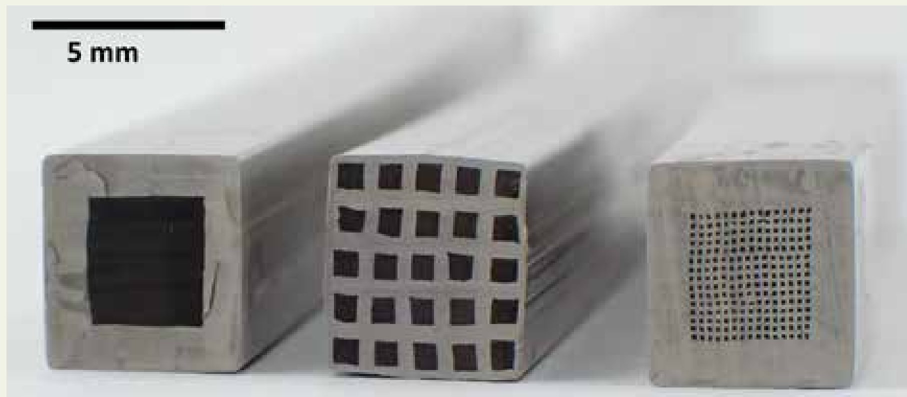
Heat exchangers transfer thermal energy from one medium to another. By increasing the amount of thermal energy that a heat exchanger can transfer, the overall efficiency increases.

Heat exchanger efficiency can be improved by operating the device at high temperatures (above 1,000°C). Additionally, the design of a heat exchanger impacts its efficiency, with a larger surface area-to-volume ratio typically corresponding to better performance.

Traditional metal heat exchangers face several drawbacks, such as their tendency to deform when subjected to high temperatures. On the other hand, nonoxide ceramics such as silicon carbide or silicon nitride are oxidation resistant and can maintain their strength at elevated temperatures.

To form ceramics into complex shapes, techniques such as injection molding and direct ink writing are often used. These techniques, which add polymeric binders to ceramic powders to improve formability, are still limited in terms of minimum feature size.

My research focuses on using a coextrusion process to improve the design and thereby thermal efficiency of high-temperature ceramic heat exchangers.* Coextrusion is a processing technique wherein two or more thermoplastic blends are extruded simultaneously through a reduction die. The blends usually consist of a ceramic powder mixed with thermoplastic polymers as well as a fugitive (sacrificial) material mixed with thermoplastic polymers. The blends are then compression molded above the glass transition temperature of the polymer system to create a feedrod, which can be extruded multiple times to reduce feature size without distortion. Once the desired feature size is reached, the extruded feedrods undergo a pyrolysis step to remove the fugitive material and polymer binders before sintering.



Credit: Olivia Brandt

Figure 1. Example of feedrods that have been extruded one, two, and three times (left to right). Each successive extrusion step reduces the square feature size by a factor of 5. The feedrods that have been extruded three times have 225 channels, each with a square opening of 120 mm x 120 mm.

Previous studies have used coextrusion to create fibrous monoliths[2] and solid oxide fuel cells.[3] My current study aims to use coextrusion to create high-temperature silicon carbide heat exchangers that consist of a series of alternating hot and cold unit cells, with each containing hundreds of microchannels. These microchannels increase surface area-to-volume ratio and thus, theoretically, will improve efficiency.

Though my research is in its early stages, my colleagues and I already showed the feasibility of creating unit cells from blends of silicon carbide, polymers, and carbon black (fugitive material). These blends are molded into feedrods with carbon black cores and silicon carbide walls. The feedrods are then coextruded three times to create hundreds of micron-size channels (Figure 1).

Future work in this study will include how to assemble the unit cells into a 6-by-6 array that will become the heat exchanger body.

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Olivia Brandt is a fourth-year Ph.D. candidate at Purdue University. Her research focuses on forming techniques for silicon carbide and is supported by an ARPE-E grant through the HITEMMP program in collaboration with the Massachusetts Institute of Technology. She was the 2021–2022 chair of the PCSA and enjoys mountain biking.

*Catalytic converters are another honeycomb-structured extruded ceramic device with plasticizers that burn out. However, catalytic converters are usually extruded in one step, whereas we can extrude multiple times due to using several different ceramic and polymer systems at once, allowing us to obtain a finer resolution.


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