

Root cause analysis: Methods and procedures for unleashing ceramic potential



Zachariasen and the Manhattan Project | Entropy-inspired materials design



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feature articles



Analytical X-ray techniques for chemical and structural characterization of ceramics

X-ray techniques are key instrumental methods for chemical and structural analysis of ceramics. This article provides a high-level overview of several analytical X-ray technologies.

by Nathan Henderson, Tina Hill, David Sampson, and Julia Sedlmair



'There is always another way to destroy refractories!' Root cause analysis of a steel ladle argon system breakout

Determining the root cause of a refractory failure issue is essential for liability and safeguarding reasons. A proper root cause analysis must consider all potential sources of failure, from materials to installation to operational factors.

by Tom Vert



Discrete element modeling deepens understanding of microcracking phenomena in refractory materials

A new discrete element method provides a deeper understanding of the relationship between a refractory's microstructure and its macroscopic thermomechanical properties—paving the way to use microcrack engineering for commercial refractory production.

by Harikeshava Ranganathan, Damien André, Marc Huger, Ratana Soth, and Christoph Wöhrmeyer

Zachariasen and the Manhattan Project

Numerous ceramists played hidden but key roles in the Manhattan Project. This article remembers the work of one such scientist, William Houlder Zachariasen.

by Mario Affatigato

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As seen on Ceramic Tech Today...



Nature-inspired paint offers rapid and reversible color change

Many animals in nature have special pigment cells that allow them to change the color of their skin in response to various stimuli. Now, Northeastern University researchers combined one of those pigments, called xanthommatin, with titanium dioxide to create a paint that can rapidly and reversibly change color in response to light.

Credit: Alvssa Stone, Nort

Read more at www.ceramics.org/nature-inspired-paint

Also see our ACerS journals...

Failure criterion for brittle materials with U-notches: Unification of characteristic length-based and grain size-based criteria

By A. Wang, S. Wang, J. Liu, et al. Journal of the American Ceramic Society

Linking flexural strength and strength-limiting flaws in additively manufactured alumina with print parameter variations

By S. Boardman and C. E. Packard Journal of the American Ceramic Society

High temperature confocal scanning laser microscopy analysis of dead-burned magnesia aggregates

By T. Richards, V. Athavale, J. Smith, and R. O'Malley International Journal of Ceramic Engineering & Science

3D-printed alumina-based ceramics with spatially resolved porosity By S. Nohut, J. Schlacher, I. Kraleva, et al. International Journal of Applied Ceramic Technology

5 mm (B) 5 mm







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news & trends

Communicating the sustainability crisis: ACerS members help lead the charge for action with new paper, alliance

The transition to a more sustainable society faces challenges due in part to the definition that governments use for this concept.

The most used definition of sustainability comes from a 1987 report by the Brundtland Commission, which was established by the United Nations in 1983 and named after the first chairperson, Gro Harlem Brundtland. The report states that sustainable development "meets the needs of the present without compromising the

International Alliance of Societies for a Sustainable Future

INTERNATIONAL

The newly established International Alliance of Societies for a Sustainable Future aims to recognize, communicate, and actively work to counter the sustainability crisis.

ability of future generations to meet their own needs."

The report further states that sustainable development is not a fixed state of harmony, but rather "a process of change in which the exploitation of resources, the direction of investments, the orientation of technological development, and institutional change are made consistent with future as well as present needs."

This second part of the definition, however, is much less frequently quoted

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news & trends

because "it contains a holistic behavior change, which turned out to be less consensual in the political arena," three authors write in a recent open-access paper.

The authors are ACerS Fellows Jürgen Rödel and Dragan Damjanovic at the Technical University of Darmstadt, along with their colleague Alexander Frisch. In their paper, which published in October 2023, they expand on the initial entreaty that Rödel made in a September 2022 *Bulletin* "Letter to the editor" to urge scientists to help publicly communicate the sustainability crisis.

In addition to calling on individual scientists, the authors describe the important role of international scientific networks in communicating this crisis. As they explain, "the sustainability crisis consists of several parallel problems and is therefore systemic and integrative in nature," and so "changes in one aspect may affect another field."

Encouragingly, the authors note a recent contribution by materials scientists to the arena of international networks. Specifically, the newly established International Alliance of Societies for a Sustainable Future (SFS Alliance).

The SFS Alliance, which was established in fall 2023, is a joint committee of the German Ceramic Society, The American Ceramic Society, the European Ceramic Society, and the German Materials Society. The alliance aims to

- Raise awareness of the global sustainability crisis,
- Promote understanding and application of sustainable practices, and
- Provide a platform to share knowledge and develop innovative ideas.

In addition to Rödel, who is chairperson of the SFS Alliance, ACerS past president Sanjay Mathur (2022-2023) helped initiate the formation of this alliance and serves on the founding Board.

People who are interested in getting involved with the SFS Alliance can email Rödel at roedel@ceramics.tu-darmstadt.de.

Green is not for granted: Commonly perceived sustainable practices do not always bring benefits

Just because certain manufacturing practices are generally considered beneficial, it is important to critically evaluate their potential effects before adoption to avoid unintended consequences, as demonstrated in a recent open-access paper.

The authors come from the Technical University of Darmstadt, and the study follows a "Letter to the editor" that the authors published in the September 2023 *Bulletin* on evidence-based sustainable development.

In the letter, the authors argued for conducting sustainability assessments during the early stages of product development to avoid difficult process modifications during later developmental stages when negative environmental impacts are identified.

Their new paper demonstrates the types of impacts that may be caught during early assessments. Specifically, they showed that microwave-sourced heating, which generally is believed to consume less energy than conventional heating sources, may actually consume more energy in certain cases.

This study's specific case was the synthesis of LCNC, or $(La_{0.9}Ca_{0.1})_2Ni_{0.75}Cu_{0.25}O_{4\pm x}$, a promising oxygen transport membrane material. The authors previously published an open-access paper that identified factors impacting sustainability when producing LCNC through a Pechini-based sol-gel process. The new study focused on the factor of electricity consumption.

Corporate Partners news Blasch Precision Ceramics announces leadership changes

Blasch Precision Ceramics announced the transition of Ted Collins to the role of executive vice president of global contract manufacturing and licensing. As part of this transition, Keith DeCarlo was promoted to executive vice president of operations and technology. https://www.blaschceramics.com/ company/news

Chiz Bros opens Detroit warehouse to provide ceramic fiber and refractory products

Chiz Bros, a provider of custom solutions for refractory and high-temperature applications in a wide range of industries, opened a warehouse in suburban Detroit, Mich. The facility carries the same inventory as the company's Pittsburgh-area location. https:// thermalprocessing.com/latest-news

Imerys commits to more sustainable abrasives by joining SEAM

Imerys joined the Sustainable European Abrasive Manufacturers (SEAM) program that helps improve the sustainability of the abrasive industry. SEAM was launched on Jan. 21, 2020, by the Federation of European Producers of Abrasives. https://www. imerys.com/media-room

Kyocera joins smart mobility infrastructure partnership

Kyocera Corp., Toyota Tsusho Corporation, Panasonic System Networks R&D Lab. Co., Ltd., and Nippon Signal Co., Ltd. announced the establishment of the "Smart Mobility Infrastructure Technology Research Partnership" to address challenges in transportation. https://global. kyocera.com/newsroom/index.html

Sierra Space advances commercial space station technology

Sierra Space successfully designed, manufactured, assembled, and tested its first full-scale, expandable space station structure, alongside exclusive softgoods technology partner ILC Dover. The full-scale unit reached 77 psi before it burst in a recent test, which well exceeds NASA's recommended level of 60.8 psi.

https://www.sierraspace.com/news

The authors compared the electricity consumption and environmental impacts from three production setups:

- Original Pechini-based sol-gel process.
- Reference process: same as original setup but with a reduction in calcination time (from 10 to 2 hours).
- Modified process: same as reference setup, but the heating sources were changed from a hot plate (for gelation) and electric resistance heating furnace (for pre-calcination and calcination) to a microwave-heating sourced furnace.

While each setup resulted in the production of LCNC membranes with comparable functionalities, the reference process consumed 6 kWh less electricity than the original production setup. However, the modified process consumed more electricity than the reference process, by more than 65% for primary LCNC and more than 90% for secondary LCNC.

In an email, first author and TU Darmstadt graduate student Rishabh Kundu explains that the increased consumption in the microwave-sourced heating process appears to be due to energy losses in the furnace.

"The energy consumption of the furnace used for the study can be measured in two ways: through an energy meter plugged into the socket powering the furnace, or by mathematically integrating the power against time graph obtained through the software used to control the furnace," he says.

He explains that the latter method does not account for any energy losses and simply states the magnetron power with respect to time. It also does not account for energy consumed by other nondetachable components, such as the ventilation system software controller. As such, if energy consumption is reported using this method, microwave-sourced heating appears more sustainable than the reference process.

However, the first method accounts for all kinds of energy losses, including from the magnetron, and energy consumed by all components because it records the actual energy consumption. Using this method resulted in the conclusion that the microwave-sourced heating process was less energy efficient for this specific case study.

So, "while methods for pursuing sustainable materials development are generally broadly applicable, this study reemphasizes the need for manufacturers to evaluate the impact that comes from using each method within their specific context," Kundu says.

The open-access paper, published in *Open Ceramics*, is "All that seems green might be a smokescreen—a case study on microwave-integrated process development of oxygen transport membrane material" (DOI: 10.1016/j. oceram.2023.100534).



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William H. "Bill" Payne, ACerS past president and DLM, 1941-2023

William H. "Bill" Payne, the so-called Grandfather of Angel Investing, died on Dec. 19, 2023. His wife, Ann Colvin Payne, and family members were with him at the end.

Payne was an international expert in the angel investing asset class, after a successful career as an engineer, CEO, and entrepreneur. He served as president of The American Ceramic Society in 1989–1990, and he was named an ACerS Distinguished Life Member in 2000. He was a member of the Electronics Division. Born and raised in Peoria, Ill., Payne earned a B.S. and M.S.



in ceramic engineering from the University of Illinois Urbana-Champaign (UIUC). After graduation, he was employed as a research engineer at Interpace Corp. (Glendale, Calif.). During the 1960s, he worked for Hughes Aircraft developing thermal control coatings for the Surveyor unmanned lunar missions.

In 1971, Payne founded an electronics materials startup, Solid State Dielectrics (Burbank, Calif.), which he sold to DuPont Corp. in 1982. Making one of his first angel investments, he encouraged his friend and colleague Andre Galliath to start Novacap, an electronic component manufacturer, in 1979. Payne was the first investor and served as director until the company was sold to Dover in 1987.

Payne served as an entrepreneur-in-residence for the Ewing Marion Kauffman Foundation in Kansas City, Mo., from 1995 to 2007. During that time, he helped found the Angel Capital Association and initiated the angel education development program. He continued to share his knowledge in angel investing by developing and delivering workshops for accredited investors and entrepreneurs for more than two decades. In 2009, he received the prestigious Hans Severins Award, presented annually to the most influential U.S. angel investor.

During his lifetime, Payne invested in more than 60 companies, and his speaking engagements and educational workshops took him to eight countries. In 2010, Payne received the New Zealand ArchAngel Award for his impact on angel investing in the country, which he considered "the most beautiful in the world."

In 2016, Payne received the Alumni Award for Distinguished Service from the College of Engineering at UIUC. He was also recognized for his outstanding service by the New York State Center for Advanced Ceramic Technology at Alfred University in 1994.

In 2004, Payne mentored student entrepreneurs by serving as the Anheuser Busch Entrepreneur-in-Residence at the McGuire Center for Entrepreneurship at the University of Arizona. Additionally, after moving from San Diego to the Las Vegas area in 2003, he served in an advisory role to the Rebel Venture Fund, a student-led venture capital group at the University of Nevada, Las Vegas.

Although Payne was a victim of early onset osteoarthritis, enduring 18 joint surgeries beginning at the age of 50, it did not slow him down much. He remained an avid hiker and bicyclist and enjoyed time with family.

ACerS International Northeast India Chapter announces winners of essay competition

The ACerS International Northeast India Chapter's highly anticipated essay competition, which drew more than 100 submissions from across the region, showcased a diversity of perspectives and insights. Following meticulous evaluation, the judges selected winners in two categories, Senior and Junior.

Senior category

First place: **A. Peer Mohamed** Second place: **Nitiksha Sharma** Third place: **Rajkrishna Hota**

Junior category First place: Paulette William Xavier Second place: Sayan Maity Third place: Ahaana Paikray

ACerS Carolinas Section 2024 Annual Meeting

Sponsored by ACerS Carolinas Section and the University of South Carolina.

Theme: Additive manufacturing of advanced ceramics

When: April 16, 2024

- Where: University of South Carolina, Columbia, S.C.
- Agenda: Includes invited talks, student poster competition, and tour of the McNair Aerospace Center and the Solid Oxide Fuel Cell Center at the University of South Carolina

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

59th Annual Greater Missouri (St. Louis) Section / Refractory Ceramics Division Symposium on Refractories

Theme: Unleashing refractory potential: Root cause analysis

- When: March 27–28, 2024 (kickoff event the evening of March 26)
- Where: St. Louis, Mo., at the Hilton St. Louis Airport Hotel

For more information and to register, visit the Greater Missouri Section webpage at https://ceramics.org/members/member-communities/sections/greater-missouri.



Top row (Senior category): A. Peer Mohammad (first place), Nitiksha Sharma (second place), and Rajkrishna Hota (third place). Bottom row (Junior category): Paulette William Xavier (first place), Sayan Maitiy (second place), and Ahaaha Paikray (third place).

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Volunteer spotlight: Scott J. McCormack and Kiyoshi Shimamura

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



Scott J. McCormack is assistant professor of materials science and engineering at the University of California, Davis. He received a B.E. in materials engineering at the University of Wollongong, Australia, and a Ph.D. in materials science and engineering from the University of Illinois at Urbana-Champaign.

McCormack's research focuses on thermochemical and thermophysical properties of materials in extreme environments for applications in hyper-

sonic platforms, nuclear fission/fusion, and space exploration. He is a recipient of the Nuclear Regulatory Commission Faculty development award (2020), National Science Foundation Early Career Award (2021), and Excellence in Teaching Award from UC Davis College of Engineering (2023).

Outside the lab, McCormack is passionate about STEM outreach. He has served as chair of the ACerS Northern California Section since 2020.



Kiyoshi Shimamura is deputy director of the Research Center for Electronic and Optical Materials at the National Institute for Materials Science (NIMS) and CEO of E-Crystal, Inc., which was founded in 2015 as a spinoff from NIMS. He is also a visiting professor in the Graduate School of Advanced Science and Engineering at Waseda University, Japan.

Shimamura received a B.E. in chemical engineering from Waseda

University, Japan, and an M.S. and Ph.D. in chemistry from Tohoku University, Japan. His research focuses on the design, growth, and characterization of novel single crystal materials, mainly for optical, piezoelectric, and semiconductor applications.

Shimamura is an ACerS Fellow and member of the Engineering Ceramics Division. As of January 2024, he is now chair of the ACerS International Japan Chapter.

We extend our deep appreciation to McCormack and Shimamura for their service to our Society! \blacksquare

IN MEMORIAM

Daniel Button William Campbell Zaharia Cohn Thomas Eddy Samuel Etris Ronald Kilgore Murli Manghani William H. "Bill" Payne Arthur Petty

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

Names in the news

Members—Would you like to be included in the Bulletin's Names in the News? Please send a current head shot along with the link to the article to mmartin@ceramics.org. The deadline is the 30th of each month.



Aldo R. Boccaccini, FACerS, head of the Institute of Biomaterials at the University of Erlangen-Nuremberg, was elected Fellow of Biomaterials Science and Engineering by the International Union of Societies for Biomaterials Science and Engineering. The induction ceremony will take place at the 12th World Biomaterials Congress in Daegu, Republic of Korea, May 26–31, 2024.



Manoj Choudhary, FACerS, adjunct professor of materials science and engineering at The Ohio State University, was invited to give the AGC/Professor Michael Cable Memorial Distinguished Speaker Award Lecturer at the ESG15/NCM15/SGT combined conference organized by the Society of Glass Technology. The conference will be held July 15–19, 2024, in Cambridge, U.K. ■

Ceramic Tech Chat: Geoff Brennecka and Rajendra Bordia

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 third Wednesday of each month.



In the December 2023 episode of Ceramic Tech Chat, Geoff Brennecka, Herman F. Coors Distinguished Professor of Ceramic Engineering at Colorado School of Mines, discusses the importance of having degree programs that focus specifically on ceramics, recalls the history and evolution of ACerS

President's Council of Student Advisors, and describes how the Ceramic and Glass Industry Foundation's new Teacher Training Workshops provide K–12 teachers guidance on effective ways to teach materials science.

Check out a preview from his episode.

"Forty years ago, there were a lot of metallurgy and ceramics programs across the country and across the world. And as the broader materials science education grew out around this, it's understandable that people would want to merge because there are a lot of overlaps between the fundamental understanding and the fundamental behavior of metals and ceramics and polymers and semiconductors ... But in that process, we lost a little bit of depth. And so I think there's value in having a population of people that know the breadth and a population of people that know the depth. When you go into an engineering team at a company somewhere, it's going to be valuable to have a diverse set of backgrounds, a diverse set of perspectives."



In the January 2024 episode of Ceramic Tech Chat, Rajendra Bordia, the George J. Bishop, III Chair Professor of Ceramics and Materials Engineering at Clemson University, shares his somewhat unplanned pathway from mechanical into ceramic engineering, describes his approach to mentoring students, and

discusses his goals as this year's president of The American Ceramic Society.

Check out a preview from his episode.

"Almost always when I have a new student join my group, within the first six months, they will come and ask me, 'How long will it take for me to get my Ph.D.?' I tell



them that as a Ph.D. student, I am training you to be my colleague. So, in your journey, I need to see two transitions, two milestones. The first one is that right now, I have given you a problem to work on. I want to see you take ownership of this problem. When it becomes your problem, that's the first transition. ... And the second milestone is when you teach me something that I don't know. At that point, you have become my colleague."

Listen to Brennecka and Bordia's whole interviews—and all our other Ceramic Tech Chat episodes—at https://ceramictechchat.ceramics.org/974767.



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Oacers spotlight -

AWARDS AND DEADLINES



STUDENTS	
AND	
OUTREACH	



FOR MORE **INFORMATION:** www.ceramics.org/students

Nomination deadlines for Division awards: May 15 or May 30, 2024

Contact: Vicki Evans | vevans@ceramics.org

Division	AwardNominationContactsDeadline		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. May 30 Henry		Aiping Chen apchen@lanl.gov	Recognizes an outstanding paper reporting original work in the <i>Journal of the American</i> <i>Ceramic Society</i> or the <i>Bulletin</i> during the previous calendar year on a subject related to electronic ceramics.		
EDiv	Lewis C. Hoffman Scholarship	May 30	Aiping Chen apchen@lanl.gov	Recognizes academic interest and excellence among undergraduate students in ceramics/materials science and engineering		

Grad students: Choose GGRN to advance your career

Build an international network of peers within the ceramic and glass community by joining the Global Graduate Researcher Network (GGRN). GGRN is ACerS membership option that addresses the professional and career development needs of graduate-level research students who have a primary interest in ceramics and glass.

Membership in GGRN is only US\$30 per year. Visit www.ceramics.org/ggrn to learn how GGRN membership can help you in your future career. Contact Yolanda Natividad, ACerS senior mem-



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bership manager, at ynatividad@ceramics.org with any questions.

ACerS Associate membership and Young Professionals Network (YPN)

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 are 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 vnatividad@ceramics.org.

CERAMICANDGLASSINDUSTRY FOUNDATION

The Ceramic and Glass Industry Foundation welcomes new program manager

The Ceramic and Glass Industry Foundation (CGIF) is pleased to announce Lori Houghton as CGIF's new program manager. Houghton brings a background in education, business, organizational management, and program management to the team.



"It is a true privilege to be chosen to be the next program manager of CGIF," Houghton says. "It is my passion to help others develop and grow, and this opportunity will help me positively impact others in the growing field of materials science."

Amanda Engen, former CGIF program manager,

Houghton

is now the director of communications and workforce development at ACerS as of

Jan. 1, 2024. Throughout her time with CGIF, Engen helped develop numerous student and educator outreach programs,

such as the Teacher Training Workshops, Outreach in a Box, and the IGNITE MSE Professional Development Symposium.



"My time at CGIF was incredibly rewarding. I enjoyed working closely with educators and students alike to introduce them to the hands-on world of materials science," Engen says. "I look forward to seeing how Houghton will grow the programs to reach even more audiences and support the brilliant minds shaping the future of ceramic and glass materials science."

Engen

Support the CGIF and help inspire the next generation of ceramic and glass professionals through innovative programs by visiting ceramics.org/donate. Interested in volunteering with the CGIF? Contact Houghton at Ihoughton@ceramics.org.

ACerS' diverse networks benefit all members



Members at the 2023 Glass & Optical Materials Division annual meeting in New Orleans, La.

Be a part of ACerS' growth! Invite your friends and colleagues to join you as a member of ACerS and help connect old and new friends together. ACerS is the gateway through which diverse groups of professionals and students interact, exchange information, and develop tomorrow's technologies.

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business and market view

A regular column featuring excerpts from BCC Research reports on industry sectors involving the ceramic and glass industry.



Nondestructive testing equipment and services

By BCC Publishing Staff

The global market for nondestructive testing equipment and services was valued at \$28.6 billion in 2022 and is expected to grow at a compound annual growth rate (CAGR) of 10.1% to reach \$50.7 billion by 2028.

Nondestructive testing involves analyzing materials, components, or assemblies for differences in characteristics or discontinuities without destroying the part or system. Because it allows for inspection without interfering with a product's final use, nondestructive testing provides an excellent balance between quality control and cost-effectiveness.

Visual inspection of materials and surfaces with the human eye is the most basic nondestructive testing method. However, computerization and automation advancements in the past 20 years have led to the development of new techniques and increased usefulness of existing methods.

Established nondestructive testing methods, as recognized by the American Society of Nondestructive Testing, include

- Ultrasonic testing: High-frequency sound waves travel through the test object and are reflected when they encounter defects in testing.
- Radiography testing: X-rays or gamma-rays are used to produce an image of the test object on film.
- Visual inspection: A person with special training, such as knowledge of the product and process, inspects the test object using their eyesight.
- Eddy current testing: A localized electric current is induced within the test object. Discontinuities in the object, such as a void or deep crack

in the surface, will interrupt or reduce the current's flow.

- Magnetic particle inspection: Finely divided magnetic particles, either in powder form or in a liquid suspension, are applied to the surface of a magnetized test object, and the particles accumulate at the site of any flaws.
- Acoustic emission testing: Detects elastic waves generated within a test object by such mechanisms as plastic deformation, fatigue, and fracture.
- Liquid penetrant inspection: Reveals surface-breaking flaws by bleed out of a colored or fluorescent dye from the flaw.
- Infrared thermography testing: Converts radiated or reflected heat into real-time pictures or images.

The oil and gas sector drives demand in the nondestructive testing market as crucial infrastructure ages and operations become more complicated. Also, demand for equipment and services is rising in the aerospace industry, which requires novel techniques for inspecting new composite materials.

Nondestructive testing equipment and services are governed by various rules and regulations adopted by different governments and authorities. For example, in the U.S., several federal and state agencies regulate these products, including

- The American Society for Nondestructive Testing (ASNT): The ASNT develops and publishes standards for nondestructive testing practices and procedures. These standards are used by nondestructive testing professionals and organizations worldwide.
- The American Society of Mechanical Engineers (ASME): The ASME publishes standards for the design, construction, and testing of pressure vessels and other equipment. These standards often include requirements for nondestructive testing.

Table 1. Global market for nondestructive testing equipment and services, by type, through 2028 (\$ millions)									
Туре	2022	2023	2028	CAGR % (2023-2028)					
Equipment	19,336.2	20,813.4	31,796.0	10.3					
Services	9,250.2	10,534.2	18,875.2	12.4					
Total	28,586.4	31,347.6	50,671.2	10.1					

- The Federal Aviation Administration (FAA): The FAA requires nondestructive testing for various aircraft components, including fuselages, wings, and engines.
- The Department of Defense (DoD): The DoD has a set of nondestructive testing requirements for military equipment.
- State and local regulations: Besides federal laws, some states and local jurisdictions have their own non-destructive testing requirements.

The Asia-Pacific region is expected to be the fastest-growing market for nondestructive testing equipment and services, followed by North America and Europe. This growth is driven by the increasing demand for nondestructive testing in emerging economies, such as China and India, as well as the growing focus on safety and quality assurance in these countries.

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.

Resource

BCC Publishing Staff, "Nondestructive testing equipment and services: Ultrasonic, radiographic, eddy current and others" BCC Research Report MFG016J, December 2023. https://bit.ly/BCC-December-2023nondestructive-testing

oceramics in biomedicine

Strategies for improving adhesion strength of plasma sprayed bioactive glass coatings

Researchers from the University of Barcelona in Spain improved the adhesion strength of bioactive glass coatings deposited on orthopedic implants via atmospheric plasma spraying (APS).

Ceramic coatings, specifically hydroxyapatite, deposited by APS are widely used in the medical field. But bioactive glass coatings deposited by APS, though they have a higher bioactive capacity, have to date demonstrated low adhesion strength.

The researchers evaluated several strategies to enhance the adhesion strength of bioactive glass coatings on a titanium substrate, including

- Changing the morphology of the feedstock powders through agglomeration;
- Incorporating hydroxyapatite as a support material, either as an anchor layer or blended with the glass powder; and
- Applying heat before or after the spraying process to reduce internal stresses in the coating.

After testing each coating, the researchers drew several conclusions about the different strategies.

- Morphology. A notable increase in bond strength was observed with the agglomerated glass powder, which had lower density, higher porosity, and higher specific surfaces than the commercial glass powder. The researchers hypothesize that this improved strength is due to the agglomerated powders melting more quickly.
- Hydroxyapatite addition. A significant improvement in the bond strength was achieved with both the bilayer and blended hydroxyapatite coatings. The researchers attribute this improvement to the lower mismatch in the coefficient of thermal expansion between hydroxyapatite and the titanium alloy in contrast to the bioactive glass.
- Heat treatments. The researchers previously showed the benefits of heat treatments on adhesion strength in a 2021 paper. This study confirmed those earlier results, which they attribute to the formation of some crystalline phases within the coating.

In line with the ASTM regulations for calcium phosphate and metallic coatings, coatings adhered to dense metal substrates require a minimum adhesion strength of 22 MPa to be suitable for orthopedic applications. The bioactive glass coatings that met this requirement were mainly heat-treated samples, with the blended coating being the only exception.

The researchers conducted additional tests to determine the coatings' ability to stimulate bone regeneration and degradation behavior. Based on this information, they determined that the blended coating—the only coating to achieve the required adhesion strength without heat treatment—is the most promising candidate to improve the osseointegration process.

The open-access paper, published in *Surface and Coatings Technology*, is "Improving the bond strength of bioactive glass coatings obtained by atmospheric plasma spraying" (DOI: 10.1016/j.surfcoat.2023.129837).



The various coatings types investigated in this study: a) reference, b) agglomerates, c) bilayer, and d) blended. 45S5 = bioactive glass; HA = hydroxyapatite.

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•research briefs

Exploring the combined effect of multiple oxide inclusions on zirconia toughened alumina

Researchers from three institutions in the South Asian country of Bangladesh investigated the combined effect of using several oxides as sintering aids in the fabrication of zirconia toughened alumina.

The individual effects that titanium dioxide, magnesium oxide, and cerium oxide have on zirconia toughened alumina during sintering are well recorded in the literature. However, "the effect of multiple oxide inclusions has not been investigated yet," the researchers write.

They created two sets of samples containing either 5 wt.% or 15 wt.% of yttria-stabilized zirconia (YSZ). In both cases, there were equal amounts of all the oxide inclusions (5 wt.% each).

Samples were sintered at different temperatures (1,450°C, 1,500°C, 1,600°C, and 1,650°C) for three hours and then cooled in a furnace. Mechanical properties were then analyzed, including density, hardness, fracture toughness, and diametral tensile strength.

The researchers provided an extensive overview of how each parameter—i.e., sintering temperature, sintering aid—affects the results. But in brief,

• The 15 wt.% YSZ sample achieved maximum relative density of 92.91% at 1,450°C and exhibited high fracture toughness (maximum 12.03 MPa*m^{1/2}).



A dish of magnesium oxide powder. Several oxides are routinely used as sintering aids in the fabrication of zirconia toughened alumina, but the effect of including multiple oxides at the same time is not well studied.

• The 5 wt.% YSZ sample achieved maximum relative density of 94.80% at 1,500°C and demonstrated high hardness (maximum 14.15 GPa).

"With high fracture toughness, A15ZMTC [the 15 wt.% YSZ sample] could be used in load bearing applications," the researchers write. In contrast, because the other sample only contains 5 wt.% YSZ, it has a "lower ingredient cost and could be used as cutting tool inserts."

The paper, published in *Journal of the Korean Ceramic Society*, is "Effects of sintering temperature and zirconia content on the mechanical and microstructural properties of MgO, TiO₂ and CeO₂ doped alumina-zirconia (ZTA) ceramic" (DOI: 10.1007/s43207-022-00194-0). ■

Surface weathering transforms ancient Roman glass into natural photonic crystal

Researchers in Italy and the U.S. discovered that an ancient Roman glass fragment called the "wow" glass naturally formed a photonic crystal structure on its surface through environmental weathering.

Photonic crystals are manufactured structures used in many advanced optical devices to control the flow of light. Bragg stacks, a type of photonic crystal, are fabricated by alternating materials with different refractive indices to form multiple layers.

When the researchers analyzed the "wow" glass to understand its almost perfect mirror-like gold reflection, they discovered that dissolution and reprecipitation processes triggered by environmental exposure resulted in the formation of a millimeter-thick film, or patina. The patina featured an alternating arrangement of micrometer-thick silicon and sodium layers of high and low densities, which individually behaved like highreflectivity Bragg stacks.

"It's really remarkable that you have glass that is sitting in the mud for two millennia and you end up with something that is a textbook example of a nanophotonic component," says Fiorenzo Omenetto, Frank C. Doble Professor of Engineering at Tufts University in Massachusetts, in a Tufts news release.

Research News

Nanotech scaffolding supports tissue growth

Pusan National University researchers analyzed the molecular mechanisms to understand why MXene scaffolds help stimulate muscle growth. They found that MXenes promote calcium ion deposition around cells, which triggers the activation of genes that produce iNOS and SGK1 proteins. SGK1 helps promote cell proliferation, survival, and myogenesis while iNOS increases the production of nitric oxide, contributing to myoblast proliferation and muscle fiber fusion. For more information, visit https://www.pusan.ac.kr/eng/CMS/Board/Board.do?mCode=MN104.

Helium-free ultralow-temperature cooling

Due to the relative scarcity of helium in nature, it has become an important challenge within the scientific community to achieve ultralow-temperature refrigeration without using helium. Chinese scientists discovered they could use a triangular-lattice cobaltate material to realize helium-free cooling to a temperature of 94 milli-Kelvin (-273.056°C) with frustrated quantum magnets. For more information, visit http://www.ecns.cn/news/sci-tech.



Close-up of an ancient Roman glass fragment that naturally formed a photonic crystal structure on its surface through environmental weathering.

In future work, the researchers hope to mimic this natural corrosion and reconstruction process in the lab on a significantly faster timescale. Doing so would allow for photonic crystals to be grown instead of manufactured.

The paper, published in *Proceedings of the National Academy of Sciences*, is "Photonic crystals built by time in ancient Roman glass" (DOI: 10.1073/pnas.2311583120).

Geopolymer binders show potential in hightemperature alumina castables

Researchers at the Federal University of São Carlos in Brazil recently designed and characterized three new geopolymer compositions for use as binders in refractory ceramics.

Geopolymers consist of well-polymerized nanoparticles ranging in size from 5 to 40 nm. They offer several benefits as refractory binders, including quick setting, reduced risk of explosions compared to calcium aluminate cement binders, and the ability to be synthesized from industrial waste and byproducts at lower temperatures.

In this study, the researchers focused on geopolymers derived from metakaolin, a dehydroxylated form of the clay mineral kaolinite. They chose this starting material based on promising results from previous studies that found metakaolinbased compositions demonstrate exceptional thermal and mechanical stability.

The researchers synthesized the geopolymers by mixing the metakaolin with three different alkaline silicate-containing liquid reagents based on either NaOH, KOH, or a combination of both.

Characterization of the different binders revealed that geopolymers synthesized using the sodium-based liquid reagent demonstrated faster setting times and higher mechanical strength than the potassium-containing samples. So, the researchers chose the sodium-containing geopolymer for follow-up experiments. They fabricated alumina-based castable refractories using either geopolymer or calcium aluminate cement binders. To ensure a fair comparison, the raw material contents in the matrix were normalized so that each castable featured 12 wt.% of binder.

Initially, the geopolymer-bonded castables exhibited a lower mechanical strength than the cement-bonded castables up to 800°C, likely due to the limited extent of the geopolymerization process. However, after firing at 1,100°C, the geopolymer-bonded castables showed a significant increase in mechanical strength.

The researchers note that refractory compositions are inherently more complex than the ones investigated in this study, as commercialized refractories incorporate both fine and coarse aggregates. Therefore, "the adjustment of the geopolymer binder content, in combination with the presence of coarse components, is expected to play a crucial role in controlling the linear dimensional variation and maximum service temperature of the formulated compositions," they write.

The paper, published in *International Journal of Applied Ceramic Technology*, is "Design, characterization, and incorporation of geopolymer binders in refractory ceramic compositions" (DOI: 10.1111/ijac.14507). ■



Analytical X-ray techniques for chemical and structural characterization of ceramics

(Left) Imaging an oxide battery with a Bruker SKYSCAN 2214 X-ray microsope. (Right) 3D dataset can be reconstructed and then visualized for inspecting internal structures, such as the mesh shown here.

By Nathan Henderson, Tina Hill, David Sampson, and Julia Sedlmair

X-ray techniques are key instrumental methods for chemical and structural analysis of ceramics. This article provides a high-level overview of several analytical X-ray technologies.

Materials testing is essential to qualifying ceramics at various stages of the production cycle—from raw materials verification to characterizing finished formed parts.

In this article, we highlight several key instrumental methods for chemical and structural analysis of ceramics: X-ray fluorescence in both bulk- and microscale applications (XRF and μ XRF, respectively), powder X-ray diffraction (XRD), and X-ray microscopy (XRM).

XRF measurements provide information regarding chemical and elemental composition and can be used in both qualitative and quantitative experiments. Bulk XRF methods are used to test raw feedstocks to verify reagent purity and the desired ratios in intermediate and final products. μ XRF provides similar information within a constrained physical area, allowing for elemental mapping of parts and surfaces. XRD can identify

and quantify crystalline polymorphs by distinguishing between different packing arrangements of atomic and molecular species. Finally, XRM is an imaging technique that explores internal structure and allows for the characterization of features such as cracks and defects.

We will discuss each technique in the following sections, providing a high-level overview of the method as well as relevant examples of the types of data one can expect from an experiment. Additionally, we will describe a case study that uses multiple techniques for a more thorough sample analysis.

X-ray fluorescence

XRF spectrometry plays a crucial role in the ceramics industry for process control and contamination tracing. It enables rapid, nondestructive elemental analysis, ensuring products meet quality standards.

By monitoring elemental composition in real-time, manufacturers can optimize production conditions and detect deviations early in the process. The sensitivity of XRF allows for the identification of contaminants and unknown materials, contributing to quality assurance. The nondestructive nature of XRF makes it a cost-effective and efficient tool for assessing ceramic composition and maintaining product consistency throughout the manufacturing process.

In an XRF experiment, information about the elemental composition of a material is produced through the interactions of a sample and a beam of X-rays. One interaction that occurs is a core electron (K or L shell) is freed by the incident beam, and the vacancy is filled by the transition of an outer shell electron. These transitions result in the generation of fluorescent photons with characteristic energies that can be used to identify distinct elements, much like a fingerprint. X-rays can also be scattered by the material via elastic (Raleigh) or inelastic (Compton) processes without core electron interactions, yielding information about the general matrix.

For ceramics, this technique is used to quantify raw materials and additives; determine ratios of major compounds; screen for impurities; and for specialized tasks, such as determining coating thickness. Following elemental identification, quantification can be achieved through use of a calibration curve or by modeling with fundamental parameters. With respect to precision, repetition studies typically demonstrate standard deviations of less than 0.5 rel.% for major compounds, less than 1 rel.% for minor compounds, and down to the single digit parts per million (ppm, absolute) for trace amounts.

XRF instrumentation can be categorized as either energy dispersive (ED-XRF) or wavelength dispersive (WD-XRF), with some differences in components and detection (Figure 1). ED-XRF acquires wide-range spectra during a measurement. There are few moving parts, and it is often used for fast, routine measurements in quality control environments. Current stateof-the-art 8k detectors differentiate between the most common elements.



Figure 1. Schematic highlighting the difference between ED-XRF (left) and WD-XRF (right). ED-XRF instruments collect wide energy spectra while WD-XRF instruments have additional components in the beam path and higher energy, which allow for increased resolution.



Figure 2. Fluorescence data from a cordierite sample collected with ED-XRF (black spectrum) and WD-XRF (blue spectrum). Major elements are easily identified with both methods though the increased sharpness in the WD-XRF data can help with identifying minor elements.

WD-XRF finds use in applications that require higher resolution and precision. In a WD-XRF instrument, tailored crystals are used to determine X-ray energies by reading the signal with a detector at a specific angle. Collimators can also be used to parallelize the beam and sharpen the observed peaks. The combination of crystal and collimator in the optical path are used to resolve features in the spectrum, which distinguishes WD-XRF instruments from ED-XRF.



Figure 3. A calibration curve for measuring magnesia (MgO) in alumina (Al_2O_3) demonstrating very good linearity. Plotted data is the integrated intensity for the manganese signal in the XRF spectra versus known concentration in the calibration standards. Unknowns with similar composition could be measured against this calibration curve.

Data collected from a sample of cordierite, a refractory silicate, via both ED-XRF and WD-XRF are shown in Figure 2. The major elements such as aluminum and silicon are easily identified with both datasets, though the WD-XRF data has higher resolution for elements such as barium, titanium, potassium, and calcium.

For a simple measurement, sample preparation is straightforward. A loose powder or liquid is poured into a cup and measured directly in air or helium through a thin polymer foil. Powders can also be pressed into stable briquets or fused into glass beads for higher precision.¹ The typical elemental range is fluorine to americium, but, with the right configuration, light elements down to carbon (using ED-XRF) and even beryllium (using WD-XRF) can be measured. XRF can cover six orders of magnitude within one measurement, starting as low as single digit parts per million.

Figure 3 shows an example of a calibration curve for magnesia in alumina using ED-XRF. The magnesium signal for measured standards is integrated and

Analytical X-ray techniques for chemical and structural characterization of ceramics

plotted versus known concentration. This calibration curve can then be used for any unknown samples with the same matrix—the response for the same peak will yield the concentration in the unknown. The standard deviation shows the excellent linearity that can be achieved with an XRF measurement. This approach can also be used for calculating other parameters, such as Al/Si ratios in aluminosilicates.²

In the absence of standards, many commercially available XRF spectrometers also offer a standardless method using fundamental parameters. In this process, a model is calculated based on peak deconvolution, yielding an educated guess for sample composition.

Micro X-ray fluorescence

 μ XRF is an emergent technique that finds increasing use in various scientific disciplines. It excels in providing highresolution elemental composition maps and spatial distributions, especially in the analysis of challenging samples and advanced materials.

This instrumental technique combines the principles of traditional XRF with the use of a small, focused beam of X-rays. This addition enables the measurement of elemental composition at extremely small spot sizes with exceptional spatial precision, down to less than 20 μ m. Sophisticated polycapillary lenses help minimize the loss of X-ray intensity from traditional collimators, which in turn helps maintain high sensitivity to trace elements with detection limits as low as tens to hundreds of ppm for many elements.

A motorized stage with precise sample positioning can be used to produce elemental distribution maps and provide contextual information about areas of interest within a sample. One notable feature is the simplicity of preparing samples, making it suitable for various shapes and sizes. The collected data, presented as energy dispersive spectra for each pixel, enable a thorough examination of elemental distribution maps, providing both qualitative and quantitative insights.

Experiment design includes choice of spot size, measured intensity, and step size. These factors will determine sensitivity and spatial resolution. Further experimental conditions can include options such as various X-ray sources for optimizing specific elements of interest as well as an optional purge with helium gas, which enables the analysis of moist or wet samples. A robust standardless quantification algorithm, based on fundamental parameters, is also beneficial, particularly for the analysis of complex



Figure 4. A thick section of a garnet sample (a) and X-ray elemental distribution map for elements silicon, titanium, calcium, manganese, iron, and potassium (b). For the bottom right crystal, an additional scan was performed using a primary filter to achieve better peak to background for the elemental peaks and minimize spectrum artifacts, such as diffraction peaks. From this measurement, the manganese distribution is displayed as intensity (c) and quantification maps (d), which show the highest intensity (highest concentration of elements) in the core of the grain.

materials where standards may be scarce or unavailable.

While conventional XRF finds widespread use in industrial materials such as oxides or cement, µXRF specializes in complex materials analysis, particularly where mapping and elemental distribution are pertinent. Relevant fields include materials science, microelectronics, forensics, archaeology, art conservation, and more—any application where fast elemental mapping, quantification, and trace analysis are beneficial.

An example dataset from a garnet mineral specimen is shown in Figure 4. Each pixel in the dataset has an associated ED-XRF spectrum; this information can be used to generate colored maps that correspond to distribution of identified elements. Data can be viewed not only as individual elements but also as a function of signal or concentration, allowing for multiple approaches to visualization.

X-ray diffraction

While the previously discussed techniques focus on elemental analysis, XRD is concerned with how the identified elements are connected in three-dimensional motifs. This technique provides structural information about the repeating atomic order found in crystalline materials. Relevant applications include identification of crystalline phases, distinguishing between structural polymorphs (e.g., rutile versus anatase forms of titania), quantification of mixtures, calculation of amorphous/glass content, and understanding sintering processes at elevated temperatures.

XRD studies are significant at multiple points throughout the production cycle of refractories and other ceramics: verifying phase purity of chemical precursors, testing for impurity phases or unconsumed reagents, and optimizing firing conditions for desired final products with correct physical properties.

In a traditional XRD experiment (Figure 5), a powdered sample is prepared as a flat surface and mounted in the center of the diffractometer. A goniometer provides precise control over the angular positions of the X-ray source and detector relative to the sample, down to thousandths of a degree. A diffraction peak is observed as a sharp increase in signal when the Bragg equation $(n\lambda = 2d\sin\theta)$ is fulfilled, which occurs at specific angles (2θ) due to constructive interference of the beam with periodic wavelength, λ . These special angles are related to characteristic distances (*d*) between repeating planes of atoms within a crystalline phase. The combination of peak locations and relative intensities is referred to as a diffraction pattern and can be thought of as the fingerprint for a material.

From a quantification standpoint, mixtures will exhibit convoluted signals for each phase, which can then be quantified with intensity ratios or with modeling from fundamental parameters. For the analysis of formed parts or controlled regions of interest, a spot beam can be generated with the use of specialty mirrors or collimators, though generally beam sizes for diffraction are larger (0.3–1.0 mm) than those used for μ XRF.

Quartz and cristobalite are two distinct polymorphs of silica that are found within the refractory industry. XRD data shown in Figure 6 highlight the differences between these two phases as well as that of amorphous silica glass, which does not have repeating order and thus does not demonstrate diffraction peaks.

Because many ceramic materials are synthesized in furnaces or kilns, temperaturedependent diffraction data is also helpful in understanding reaction mechanisms and formation conditions. If a diffractometer is equipped with a furnace or heater, data can be collected directly at elevated temperatures (in situ). Samples can also be characterized after sintering or processing in a stand-alone furnace (ex situ).

Some experiments involve collecting dozens or hundreds of diffraction patterns, in which case an intensity map can provide a useful way of portraying the data. The intensity map in Figure 7 shows the formation of mullite $(3Al_2O_3 \cdot 2SiO_2)$ from the decomposition of kaolinite $(Al_2Si_2O_5(OH)_4)$ at elevated temperatures. Kaolinite converts to metakaolin around 550°C, transitions through an amorphous intermediate through 800°C, and then to γ -A₂O₃ and mullite at 1,100°C. Higher reaction temperatures and longer durations of heating can further drive the conversion process.



Figure 5. Schematic of a traditional Bragg diffractometer. The X-ray tube (left) and detector (right) are moved together in a coupled manner to increasingly high angles relative to the sample (center). Constructive interference will yield strong diffraction intensity at special angles that are descriptive to a crystalline phase.



Figure 6. Diffraction data for quartz (top scan), cristobalite (middle scan), and silica glass (bottom scan). Though each polymorph is comprised of the same elements (silicon and oxygen), different arrangements of the atoms produce different fingerprint patterns. Quartz adopts a hexagonal structure (top structure), cristobalite forms a tetragonal structure (bottom structure), while silica glass has no long-range order and does not demonstrate diffraction.



Figure 7. Intensity map for nonambient XRD data collected in situ with a heating furnace. The x-axis is 2θ , as is tradition, and the y-axis is temperature. Diffraction intensity is plotted here as a function of brightness (black is low intensity, white/pink is high intensity, blue colors are intermediate intensities).

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X-ray microscopy

The final technology in this review is XRM, an imaging technique centered on two principles: contrast in X-ray transmission based on density, and geometric image magnification based on distance to a sensor. XRM is related to microcomputed tomography but extends these capabilities through the use of sophisticated software algorithms for statistical analysis and visualization as well as the potential for higher resolution.

Within the ceramics industry, XRM finds use in any application where structural imaging is desired, particularly for investigation of internal features. Samples are frequently characterized in their native state without the need for cutting, polishing, or sputter coating. Relevant uses include internal defects; void structures in porous or foamed ceramics; orientation of fibers and meshes; structural integrity of green and sintered parts formed via injection molding or 3D printing; and layer thickness in conductive oxides, such as batteries or fuel cells.

A schematic of a typical instrument is shown in Figure 8. An intense X-ray beam is generated at the source and optionally conditioned through various filters. The sample is mounted on a precision stage that allows for fine control over rotation angle; height; and distance between source, sample, and detector. As the X-ray beam passes through the sample, 2D radiographs are collected that provide information about differences in material density. Moving the sample closer to the source and further from the detector provides a magnified image from a smaller physical volume within the sample (geometric magnification).

A full experiment will collect a stack of images with variable rotation angle and height. This data can then be processed into a 3D body that will be inspected for cracks, defects, porosity, and a multitude of other physical features. Perhaps most significantly, XRM is a nondestructive technique that allows for investigations of internal structures that might not be accessible through optical or electron microscopy. Data collected from a sandstone core are shown in Figure 9. The consolidation and structure of the silica grains is clearly seen; however, the colored images provide an additional level of clarity and visualization. In the left reconstruction, the pores are displayed as an intensity gradient based on size. Similarly, the dense mineral grains are shown on the right, again plotted as function of size. These types of studies can be furthered with statistical analysis for calculations of total pore volume, histograms of grain sizes, and more.

Case study: Injection molded ceramics

Two injection molded ceramic components were analyzed with multiple techniques to demonstrate how supporting technologies can provide a deeper level of material characterization.

The first sample—a white cylindrical fitting with a lustrous surface—was analyzed with µXRF at multiple points along the head and body using a Bruker M4 TORNADO. Elemental analysis reveals a consistent composition across the sample with zirconium as the major identified element. Smaller amounts of yttrium, hafnium, and silicon are also identified.

Hafnium is frequently found in zirconium-containing compounds due to difficulty in separating these two elements, so its presence here is unsurprising. Yttrium and silicon content are perhaps more interesting. Pure zirconia adopts a monoclinic structure at room temperature; however, many industrial applications use tetragonal or cubic stabilized forms of zirconia that can be obtained with substitutions of cations such as Y³⁺. The amount of dopant directly influences the stabilized form.³

Diffraction experiments provide insights into which crystalline forms are present. XRD data (Figure 10) were collected using a Bruker D8 DISCOVER diffractometer using a copper microfocus source and an EIGER2 R 500K area detector. The most intense diffraction signal is matched to the major phase, tetragonal ZrO₂. Closer inspection of overlapping peaks reveals the presence of the cubic structure, and smaller peaks around the baseline are identified as the monoclinic form. In some specified applications, a small amount of monoclinic zirconia is



Figure 8. Schematic of an XRM experiment. The X-ray beam passes through the sample, which is placed at a specific distance from the source and detector to optimize for viewing region or magnification. The detector collects a 2D image of the sample where the beam is attenuated by more dense regions of the sample, providing contrast in the radiograph. The sample is rotated along the central axis, which provides a 3D image set that can then be reconstructed and analyzed in greater detail.



Figure 9. XRM data from a sandstone core with average size plotted as a function of intensity gradient for pores (left) and dense grains (right). This plot demonstrates a clever extension of the technique by visualizing the void space rather than the sample itself.

targeted to provide increased toughness through a stress-induced transformation. This mixture of phases is referred to as partially stabilized zirconia.

No additional peaks are observed in the diffraction data, which rules out any crystalline phases containing silicon, such as quartz or zircon. The silicon detected in the XRF data—possibly added to tailor mechanical surface behavior or optical properties, such as the refractive index⁴—is then implied to be amorphous.

A small threaded nozzle—off-white in color and with a matte finish—was characterized with joint XRD and XRM studies. The diffraction data confirm that the sample is composed of corundum (Al_2O_3 , alpha phase). A closer inspection at the peak shapes indicates much sharper peaks than the previous zirconia sample. Sharper reflections are an indication of larger crystallites within the sample, which is consistent with corundum behavior with sintering. Spotty diffraction rings (Debye rings) in the 2D data set also indicate the existence of large crystal grains.

An XRM dataset was collected with a Bruker SKYSCAN 2214 equipped with high resolution components, including tungsten filament and CMOS detector. Two primary features are observed in the image slice shown in Figure 11: a small crack on the inner wall and graininess within the sintered oxide body. The speckled appearance is not an artifact but is the result of the large grains that were observed previously in the XRD data. The internal crack is measured with maximum dimensions of 1,014 x 126 x 239 µm (length x width x depth). The diameter of the inner channel is 492 µm at the top opening and about 2,040 µm throughout the main body with some small variations. Visualization as a function of density also reveals a subtle variance between the tip of the nozzle, the wider body, and the threaded base. The tip and base are nearly identical densities and roughly 3% higher than the wider middle region.

A video of this sample reconstruction is available at www.youtube.com/ watch?v=t33ewufEfSs. It demonstrates the types of visualizations possible with a fully rendered 3D dataset.



Figure 10. (insets) Elemental analysis of a ceramic fitting. Zirconium (Zr) is identified as the major element with yttrium (Y) and hafnium (Hf) also observed. The spectra from body and head overlay nicely together, indicating a similar overall composition throughout the sample. (main) Diffraction data for the zirconia sample showing the tetragonal main phase with moderate amounts of cubic and some minor/trace monoclinic phases. The stabilization into tetragonal and cubic forms is due to the substitution of yttrium for zirconium. The detection of monoclinic ZrO_2 classifies this material as partially stabilized zirconia rather than fully stabilized.



Figure 11. Selected images from an 3D XRM dataset for (a) the alumina nozzle showing (b) a small internal crack on the inner wall of the channel and (c) some observable differences in density between the end, body, and screw regions of the sample.

Concluding remarks

Each of the highlighted X-ray technologies reveals critically important information in materials characterization: elemental analysis with XRF and μ XRF, phase analysis with XRD, and structural analysis with XRM. When used in conjunction, these analytical methods can provide a more complete understanding of a project. Additional educational videos and resources are available at www.youtube. com/bruker.

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'There is always another way to destroy refractories!' Root cause analysis of a steel ladle argon system breakout

By Tom Vert

Determining the root cause of a refractory failure issue is essential for liability and safeguarding reasons. A proper root cause analysis must consider all potential sources of failure, from materials to installation to operational factors.

This article will show how root cause analysis can be used to investigate and resolve refractory failure issues, using the example of a steel ladle argon system breakout.

Breakouts are when molten metal leaks and/or pours out from the refractory-lined ladle during steel production. When breakouts occur, all personnel in a steel shop have a stake in knowing what caused the breakout to avoid future occurrences. For example, people working in operations, installation, and refractory supply will want to ensure that their practices, handiwork, and products, respectively, did not cause the breakout, and if they did, what changes need to be made to error-proof the system.

Determining the cause(s) of a breakout can help personnel and companies avoid liability. With so many stakeholders, diplomatic skills are a must for someone conducting a breakout investigation. But even if everyone performed their job perfectly, breakouts will inevitably occur at some point during production due to the wide range of possible failure modes. So, identifying the root cause(s) behind a breakout will allow personnel to put measures in place to avoid future failures.

This article describes the fundamentals to conducting a proper root cause analysis. Such an analysis will give all personnel confidence in the results and drive the prevention phase of the investigation.

Background: The mechanics of a steel ladle argon system breakout

When molten steel is placed in a refractory-lined ladle to undergo refinement before casting, stirring the molten mixture is necessary to ensure optimal control of temperature and chemistry during critical grade manufacturing. But depending on the stir system used, there is a risk that the molten mixture will breakout from the ladle.

There are two main stir systems commercially available: indirect stirring (through electromagnetic forces) and direct stirring (through refractory argon plugs). While the former option does not come with the risk of molten steel breakout, the latter option is more common because it allows for much more vigorous and controllable stirring, as well as avoiding the major capital cost of installing an electromagnetic system.

In a direct stirring system (Figure 1), argon is injected through a piping system into the bottom of the steel ladle. The argon plugs are made of a permeable refractory that allows the gas to flow at the rate necessary for good stirring. Over time, the plugs will wear down and must be replaced with new ones, typically after 10–20 uses. Sometimes, the wear is accelerated and/or the plugs are not replaced at the right moment. In that case, the 20–350 tons of molten steel may break out from the ladle and escape, resulting in damages to major equipment (Figure 2).

To determine the root cause(s) of a molten steel breakout, the first step is to ensure all refractories are preserved before demolition so that a thorough analysis can be conducted. Ruling out potential failure modes can be just as useful as identifying the right one because direct observation of certain breakout pathways is not always available. For example, molten steel can flow out of the ladle with such force that the argon plug itself and/or the sleeve is washed out, so they are not available for review.

Figure 3 shows the seven main failure modes through which molten steel escapes the ladle during a breakout event. Failure modes 1, 2, and 3 usually can be determined by the physical evidence of deteriorated refractories and/or steel skulls left over from the breakout. In contrast, failure modes 4, 5, 6, and 7 can be harder to find, and so require a review of the following key evidence:

- Last laser and/or visual analysis of the hot face of the ladle argon plug at the lay down stand.
- Information on oxygen lancing history (e.g., frequency, pressures, times).
- Stirring history of the plugs (e.g., # of heats, length of stirring, long stirring, flow rates, pressures).
- Installation history of the plugs (e.g., who changed them, installation practices, proximity to the failure).

There are 57 factors that are recognized as potential root causes for breakout failures, classified generally as material failures, installation practices, and operating/processing practices, and usually, some combination of these. An investigator must be open minded and review every potential failure to determine what is the root cause and then find a way to eliminate it.

The seven failure modes of molten steel breakout

During root cause analysis, an investigator will consider each of the following failure modes and determine which mode, or more accurately, which combination of modes led to the breakout of molten steel.

Mode 1: Failure of block support

Failure cause: The supporting refractory material around the block either wears too quickly, cracks, and/or spalls, creating an easy pathway through which molten steel can flow. The steel may take a few heat cycles to break through due to freezing near the ladle shell, but if true integrity is lost, then it will make its way down, creep under and/or lift the block, and break out.

Potential refractory cause(s)

- a. Failure of the refractory material due to poor quality from the supplier.
- b. Failure of refractory material due to over aged and/or improper storage (e.g., stored in high humidity area).



Figure 1. Typical argon stirring system layout.

c. Low quality material chosen for an application with higher slag and/or temperature resistance.

Potential installation cause(s)

- d. Ram or plastic not installed dense enough and/or with air pockets due to poor ramming equipment and/or technique.
- e. Castable not installed and/or dried out properly with too much water and/or poor material or ambient temperature control, leading to poor density and/or minimal bonding strength.

Potential process cause(s)

- f. Surrounding material damaged due to improper dig out on block and/or plug changes.
- g. Extremely aggressive slags eating into the surrounding material and causing extreme unexpected wear.
- h. Extreme oxygen lancing in the wrong spot eating into the surrounding material and causing extreme unexpected wear.

Mode 2: Failure of refractory block (assuming a precast block is used)

<u>Failure cause:</u> The main refractory block either wears too quickly, cracks, and/or spalls, creating an easy pathway through which molten steel can flow. The steel may take a few heat cycles to break through due to freezing near the ladle



Figure 2. An illustration showing one pathway that molten steel can take during a breakout event.

Tom Ver

credit:

'There is always another way to destroy refractories!' Root cause analysis of a . . .



Figure 3. Seven main failure modes through which molten steel escapes in a direct stirring system: 1) plastic refractory joint, 2) refractory surround block, 3) joint between block and sleeve, 4) sleeve itself (and supporting plastic), 5) joint between the sleeve and plug, 6) argon plug itself (and supporting plastic), and 7) argon plug itself and piping system.

shell, but if true integrity is lost, then it will make its way down and break out.

Potential refractory cause(s)

- a. Failure of refractory material due to poor quality from supplier.
- b. Failure of refractory material due to over aged and/or improper storage (e.g., getting soaked in water in storage).
- c. Low quality material chosen for an application with higher slag and/or temperature resistance.
- d. Improper refractory shape (i.e., square blocks always crack in service).

Potential installation cause(s)

- e. Block is not installed level and secure leading to stress and then cracks.
- f. Supporting refractory is not installed and/or dried out properly with too much water and/or poor material or ambient temperature control, leading to poor density and/or minimal bonding strength and then a moving and/or cracking block (see Mode 1 for more info).

Potential process cause(s)

- g. Block is damaged due to improper dig out on block and/ or plug changes.
- h. Extremely aggressive slags eating into the block and causing extreme unexpected wear.
- i. Extreme oxygen lancing in the wrong spot eating into the block material and causing extreme unexpected wear.

Mode 3: Failure of joint between block and sleeve

<u>Failure cause</u>: The joint between the main refractory block and the sleeve joint becomes compromised, creating an easy pathway through which molten steel can flow. The steel may take as little as one heat cycle to break through, at which point it will make its way down through the natural path and break out.

Potential refractory cause(s)

- a. Failure of refractory material due to poor quality from supplier.
- b. Failure of refractory material mortar due to improper mixing and/or over aged and/or improper storage (e.g., getting frozen).
- c. Low quality material chosen for an application with higher slag and/or mechanical strength requirement.

Potential installation cause(s)

- d. Sleeve is not installed properly due to bad mortaring (too much mortar and too thick a joint), leading to a loose installation and potential cracking and/or joint and/or sleeve movement.
- e. Sleeve is not installed properly due to bad mortaring (too little mortar and too thin a joint), leading to a tight installation and potential cracking/stress and/or joint.

Potential process cause(s)

- f. Block is damaged and/or worn low (high wear and/or run too long), leading to direct access to the lower joint area.
- g. Improper cleanout of slag/steel at hot face of plug/sleeve/ block, leading to sleeve not sitting in correct location and open and/or offset joint (note that this condition can lead to Mode 3d failure, large joint).

Mode 4: Failure of refractory sleeve (assuming precast sleeve is used)

<u>Failure cause</u>: The main refractory sleeve either wears too quickly, cracks, and/or spalls, creating an easy pathway through which molten steel can flow. The steel may take a few heat cycles to break through due to freezing near the ladle shell, but if true integrity is lost, then it will make its way down and break out.

Potential refractory cause(s)

- a. Failure of refractory material due to poor quality from supplier.
- b. Failure of refractory material due to over aged and/or improper storage (e.g., getting soaked in water in storage).
- c. Low quality material chosen for an application with higher slag and/or temperature resistance.
- d. Improper refractory shape (i.e., too thin a sleeve [< 30 mm] can lead to cracks in service).

Potential installation cause(s)

- e. Sleeve is not installed level and secure, leading to stress and then cracks.
- f. Supporting refractory is not installed and/or dried out properly with too much water and/or poor material or ambient temperature control, leading to a moving and/or cracking sleeve (see Mode 3 for more info).

Potential process cause(s)

- g. Sleeve is damaged due to improper dig out on plug changes.
- h. Extremely aggressive slags eating into the sleeve causing extreme unexpected wear.
- i. Extreme oxygen lancing in the wrong spot eating into the sleeve material and causing extreme unexpected wear.

Mode 5: Failure of joint between sleeve and plug (for systems with a sleeve)

<u>Failure cause</u>: The joint between the main refractory sleeve and the plug joint becomes compromised, creating an easy pathway through which molten steel can flow. The steel may take as little as one heat cycle to break through, at which point it will make its way down through the natural path and break out.

Potential refractory cause(s)

- a. Failure of refractory material due to poor quality from supplier.
- b. Failure of refractory material mortar due to improper mixing and/or over aged and/or improper storage (e.g., getting frozen).
- c. Low quality material chosen for an application with higher slag and/or mechanical strength requirement.

Potential installation cause(s)

- d. Plug is not installed properly due to bad mortaring (too much mortar and too thick a joint), leading to a loose installation and potential cracking and/or joint and/or plug movement.
- e. Plug is not installed properly due to bad mortaring (too little mortar and too thin a joint), leading to a tight installation and potential cracking/stress and/or joint opening.

Potential process cause(s)

- f. Sleeve is damaged and/or worn low (high wear and/or used too long), leading to direct access to the lower joint area.
- g. Improper cleanout of slag/steel at hot face of plug/sleeve, leading to plug not sitting in correct location and open and/of offset joint (note that this condition can lead to Mode 5d failure, large joint).

Mode 6: Failure of refractory plug

<u>Failure cause</u>: The main refractory plug either wears too quickly, cracks, and/or spalls, creating an easy pathway through which liquid steel can flow. The steel may take a few heat cycles to break through due to freezing near the ladle shell, but if true integrity is lost, then it will make its way down and break out.

Potential refractory cause(s)

- a. Failure of refractory material due to poor quality from supplier.
- b. Failure of refractory material due to over aged and/or improper storage (e.g., getting magnesia plug soaked in water).
- c. Low quality material chosen for an application with higher slag and/or temperature resistance (e.g., low alumina plug for low price).
- d. Improper refractory type (i.e., porous vs slit vs combination plug).
- e. No argon plug wear indicator (either shape and/or radiant color), making it hard to read.

Potential installation cause(s)

f. Argon plug is not installed level and secure, leading to stress and then cracks.

g. Supporting refractory joint is not installed properly, leading to a moving and/or cracking plug (see Mode 5 for more info).

Potential process cause(s)

- h. Plug is damaged due to improper dig out on the plug change, in either plug or sleeve area.
- i. Extremely aggressive slags eating into the plug and causing extreme unexpected wear.
- j. Extreme oxygen lancing in the wrong spot eating into the plug material and causing extreme unexpected wear.
- k. Thick slag and/or steel layer covering plug, making it hard to read.
- l. Oxygen contaminates the argon system and burns the plug out from back side internally.

Mode 7: Failure of argon plug support system

Failure cause: The mechanical support system located behind the plug (including the refractory plastic) becomes loose, leading to plug and/or sleeve movement, including joint openings, that creates an easy pathway through which molten steel can flow. The steel may take a few heat cycles to break through due to freezing near the ladle shell, but if true integrity is lost, then it will make its way down and break out.

Potential refractory cause(s)

- a. Failure of refractory material due to poor quality from supplier.
- b. Failure of refractory material due to over aged and/or improper storage (e.g., getting soaked in water).

Potential installation cause(s)

- c. Supporting refractory is not installed and compacted enough, leading to loss of density and looseness in the system.
- d. Supporting mechanical system is not installed and/or secured properly leading to movement of supporting plastic and/or plug/sleeve moving and/or cracking with path for steel to follow. (Note that head pressure of entire heat can quickly pressurize any looseness and the heat will be lost).

Potential process cause(s)

e. Mechanical system or argon hoses are ripped off /damaged/ bent, leading to loss of supporting mechanical system.

Conclusions

Root cause analysis of a steel ladle argon system breakout is an exhaustive process that incorporates a detailed review of all relevant material, installation, and/or processing anomalies that result in loss of the molten steel. An open mind, a detailed process, and a determination not to be swayed by theory but only by facts are all required if the root cause is to be found. Only in this way can a proper engineering solution be tailored to mitigate the possibility of future breakout events.

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Schematic diagram showing the link between real microstructures and discrete element modeling. Images reproduced with permission from Reference 1 and www.vesuvius.com. Descriptive captions provided by Damien André.

Discrete element modeling deepens understanding of microcracking phenomena in refractory materials

By Harikeshava Ranganathan, Damien André, Marc Huger, Ratana Soth, and Christoph Wöhrmeyer

A new discrete element method provides a deeper understanding of the relationship between a refractory's microstructure and its macroscopic thermomechanical properties—paving the way to use microcrack engineering for commercial refractory production.

Though defects are often associated with weakening mechanical properties, the purposeful introduction of microcracks into refractory materials can improve their thermal shock resistance.

Refractories are heterogeneous materials, consisting of numerous aggregates within a brittle matrix.^{1,2} Microcracking occurs during synthesis when the refractory is cooled from its sintering temperature due to the heterogeneity and anisotropy of thermal expansion coefficients of each constituent.^{3,4} The presence of numerous microcracks within the microstructure can promote a significant nonlinear macroscopic mechanical response, which improves the material's resistance to thermal shock. ^{1,3,4}

Improved thermal shock resistance is a desirable property for refractories in steel making, cement making, glass processing, and other high-temperature industries. However, the relationship between a refractory's microstructure and its macroscopic thermomechanical properties is complex, and deeper understanding of this relationship is needed to enable the use of microcrack engineering for commercial production.

As part of the European Union-funded CESAREF project (www.cesaref.eu), the authors developed a novel discrete element method (DEM) to deepen understanding of the refractory microstructure-property relationship. The development, testing, and prospects for this tool are described in the following sections.

Background: Numerical methods for modeling the refractory microstructure–property relationship

Numerical modeling is a vast field with different numerical approaches. Many researchers have used the finite element method (FEM), which breaks down complex systems into smaller elements for analysis, to comprehend the mechanics of bulk materials for high-temperature applications.⁵ However, FEM's limitations include its computational time-consuming nature due to dynamic meshing and its difficulty in analyzing fractures without considering preexisting crack location, path, and growth at the microstructure level.

The extended finite element method (XFEM) was introduced as an improvement on FEM due to its ability to describe discontinuities without mesh refining.⁶ However, this approach, unlike FEM, does not allow researchers to capture nucleation of multiple microcracks. Additionally, it is difficult to depict the opening and closing of microcracks at the microstructure level.

Phase-field modeling (PFM) was introduced as another method to investigate multiple crack nucleation, propagation, and branching behaviors at the microstructure level. While PFM shares some similar concepts with FEM, it relies on different criterion for the simulation. For this reason, PFM can accurately replicate crack morphology of experimental tests, but model discrepancies may lead to unrealistic crack growth in simulations due to difficulties in capturing the complete microstructure characteristics.⁷

These limitations with the above continuum approaches led researchers to start using DEM for refractory applications. Initially, DEM was used to investigate the free flow of granular particles from a silo or hopper.⁸ Later, DEM was adopted for performing thermomechanical simulations on a cohesive medium.^{8,9} Today, DEM is seen as an advanced numerical technique that can be used to perform multiphysics, multiscale, and quasi-brittle analysis for cohesive mediums.^{2,10,11}

Unlike FEM, XFEM, and PFM, which represent systems as a single continuum, DEM represents bodies as discrete particles. These particles interact with their neighbors according to contact interaction laws,^{8,9} which state that microscale interactions result in emergent properties that can be measured on the macroscale as an apparent property.¹¹⁻¹³ As such, DEM offers significant potential for modeling microstructures with numerous discontinuities, such as inclusions, cracks, debonding, and porosity, as seen in many refractory microstructures.

Previously, researchers used DEM with contact models between spherical discrete elements for investigating the relationship between the refractory microstructure and the macroscopic thermomechanical properties.¹⁴⁻¹⁶ The current study instead uses polyhedral discrete elements, as described in



Figure 1. The real microstructure1 (a) and DEM model (b) of aluminum titanate, which was used as the reference material in this study.

Reference 14, to investigate this relationship. Similar to Reference 14, the phases in the model are assumed to be chemically inert, and the presences of interphases are negligible in the model microstructure.

Numerical procedure

<u>Reference model material: Polycrystalline aluminum titanate</u>

Polycrystalline aluminum titanate (Figure 1a) was chosen as the reference material because the numerous microcracks within its microstructure lead to a very low thermal expansion and high thermal shock resistance.¹

These microcracks result from high anisotropic thermal expansion coefficients of the individual grains, which generate internal stresses within the microstructure during the cooling stage right after sintering.^{1,4} The resulting microcracked microstructure, after complete cooling, promotes a significant quasi-brittle behavior in tension. The DEM model aimed to qualitatively reproduce this tensile behavior (microcracks nucleation and their influences on the macroscopic mechanical properties), which is typical in many industrial refractory materials.¹ The simulation is performed with GranOO (www.granoo.org), an opensource discrete element workbench. The input data used in this DEM simulation, which represent local properties of each aluminum titanate grain at 1,200°C, are summarized in Table 1.

The DEM numerical sample is a box with dimensions of $100 \ \mu\text{m} \times 100 \ \mu\text{m}$ × $100 \ \mu\text{m}$ to mimic the bulk cohesive medium. Each crystal in the numerical sample is assigned a random orientation, which is depicted by the crystal having different colors (Figure 1b), and they are built by assembling about 40 polyhedral discrete elements of random sizes. The polyhedral discrete elements are assigned the physical, mechanical, and thermal properties given in Table 1. The model is imposed with the elastic brittle law and local failure criteria.

Table 1. Input data used in the DEM simulation, assumed to be representative of local properties of each aluminum titanate grain at 1,200°C.¹

*Experimental parameters used in the simulation. **Numerical parameters used in the simulation.

Parameter	Notation	Value	Unit
Young's modulus*	Ε	170	MPa
Poisson's ratio*	Э	0.28	-
Coefficient of thermal expansion along \vec{a}^*	α	–1.975×10 ^{−6}	K ⁻¹
Coefficient of thermal expansion along \vec{b}^*	α _b	9.9351×10⁻ ⁶	K ⁻¹
Coefficient of thermal expansion along \overline{c}^*	α	17.264×10 ⁻⁶	K ⁻¹
Maximum tensile strength**	σ_{ft}	350	MPa
Maximum compressive strength**	σ_{fc}	3500	MPa
Number of crystals**	Ν	500	_
Number of DE**	N _{DF}	≈20k	_

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Seeds for Voronoi tessellation

Polyhedral discrete elements

Figure 2. The Voronoi tessellation process: a) 2D sketch and b) 3D view with discrete elements.

Lattice spring model and Voronoi tessellation

The DEM introduces discrete element interactions into the simulation through so-called contact models. In literature, many contact models exist: dual spring model,¹⁶ flat-joint,¹² and cohesive beam,¹³ to name a few. Among them, the lattice spring model (LSM) is an advanced contact model because of its ability to deal directly with continuous mechanical properties, such as stress and strain. In this aspect, fastidious calibration steps can be avoided with LSM, and material thermomechanical properties, such as Young's modulus (*E*), Poisson's ratio (ϑ), and coefficient of thermal expansion (α), can be directly introduced in the model.

However, this introduction is possible only if the interaction surfaces between the discrete elements are equivalent to a continuum medium without voids. So, to obtain a domain equivalent to a continuum medium, a plane-sweeping algorithm called a Voronoi tessellation is processed on the dedicated domain.

In a Voronoi tessellation, several points scattered on a plane are subdivided into exactly *n* cells that enclose a portion of the plane closest to each point. To generate scattered points for the tessellation, transitory spherical discrete elements (in a predefined range of size) are filled in the domain, as shown in Figure 2a. The centroids of the transitory spherical discrete elements are used as input for the Voronoi tessellation to generate polyhedral elements. These polyhedral discrete elements are connected using contacts (yellow line in Figure 2a) generated by a Delaunay tessellation. So, the process to generate the DEM model (with LSM) involves dual tessellation. For more details about the fundamental aspects of the LSM contact model, readers can refer to Reference 9. The current study uses LSM as the contact model in the DEM simulation. Additionally, this simulation can handle anisotropic thermal expansion thanks to the inclusion of periodic boundary conditions within the simulation.

Periodic boundary conditions

Periodic boundary conditions, or PBCs, are a wellknown concept in the field of homogenization modeling. Homogenization is a numerical technique that can perform multiscale analyzes from the micro- to macroscale by taking advantage of the potential periodicity of the microstructure.

Past researchers have incorporated PBCs into DEM models to introduce an infinite cohesive media using a finite periodic cell (green cell in Figure 3a) to replicate the microstructure.¹² In this way, the PBC eliminates the boundary surfaces. This study incorporates PBCs for the same reason.

Introducing crystals in numerical sample

Each crystal, containing a significant number of discrete elements within the numerical model, should have its own randomly assigned crystal orientation. Again, a Voronoi tessellation is used to define the full crystal geometry. After obtaining the geometry, the Voronoi tessellation is applied as a mask on the periodic polyhedral numerical domain, which was previously obtained. This process allows each aluminum titanate crystal to be defined as a cluster of discrete elements (Figure 4). Then, a numerical sample with N grains are generated using the Voronoi tessellation to define the grain boundaries for the polycrystalline numerical sample. The crystals are represented by different colors.



Figure 3. Voronoi tessellation process for periodic boundary conditions: a) 2D sketch and b) 3D view with discrete elements.

Thermomechanical simulations

The thermomechanical simulation is segregated into two steps. The first step is the cooling process, where the sample is cooled down from 1,200°C to 900°C. During this cooling step, some microcracks are initiated and propagated due to the anisotropic thermal expansion of the crystals. After the cooling stage, the numerical sample with microcracks is obtained. The second step is to perform a uniaxial tensile test on the obtained numerical sample to monitor the macro-



Figure 4. 2D sketch of the numerical polycrystalline representative volume element (RVE), accounting for periodic boundary conditions obtained by Voronoi tessellation.

scopic materials' mechanical response in terms of strain versus stress evolution (Figure 5).

Discussion

As seen in Figure 5, the microcracked numerical sample exhibits a significant nonlinear mechanical response under tension when cooled from 1,200°C to 900°C. When cooled even further, to 600°C (Figure 6a), the sample shows a similar nonlinear mechanical response under tension. On the other hand, in the case of the numerical sample with no microcrack, it exhibits a brittle mechanical response under tensile test (see the 1,200°C curve in Figure 6a).

This difference in the mechanical response supports the claim that the microcracks network strongly influences the thermomechanical properties of the (aluminum titanate) refractory materials. Additionally, the stress-strain curves depict a strong variation from brittle fracture to quasi-brittle behavior depending on the number of preexistent microcracks.¹

Similar mechanical responses were observed when microcracked aluminum titanate samples that were cooled down from 1,400°C to 850°C and 20°C were then loaded under tensile test (Figure 6b). The microstructure with no microcracks exhibited a brittle response (Figure 6b at 850°C) and the microstructure with a huge microcracks network exhibited a large nonlinear mechanical response (Figure 6b at 20°C).



Figure 5. Mechanical response of the numerical sample under uniaxial tensile stress.

Conclusion and future directions

To clarify the relationship between microstructure and macroscopic properties in refractory materials, a DEM model was developed and tested using aluminum titanate as a reference. This simulation successfully captured the microcracking phenomena during cooling and then during tensile loading, as well as the macroscopic stress-strain law, demonstrating the potential of DEM models to deepen understanding of the refractory microstructure-property relationship.

In the future, this novel tool could be used to help visualize the evolution of Young's modulus, Poisson's ratio, and the coefficient of thermal expansion of aluminum titanate materi-



Figure 6. Evolution of the nonlinearity in the stress–strain curve in tension on polycrystalline aluminum titanate materials at different temperatures after a given cooling stage. a) DEM simulation results at 1,200°C, 900°C, and 600°C (after cooling from 1,200°C). b) Experimental results at 850°C and 20°C (after cooling from 1,400°C).

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als versus temperature. First, however, the GranOO platform used in this study should be upgraded so it can capture phenomena such as crack healing mechanisms and crack trajectory mapping. These new data will help the refractory industry to improve on the design of their materials.

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Zachariasen and the Manhattan Project



By Mario Affatigato

Numerous ceramists played hidden but key roles in the Manhattan Project. This article remembers the work of one such scientist, William Houlder Zachariasen.

July 17, 1915	
A PETITION TO THE PRESIDENT OF THE UNITED STATES	
Discoveries of which the people of the United States are not aware may affect	

the welfare of this mation in the mear future. The liberation of atomic power which has been achieved places atomic tombs in the hands of the Army. It places in your hands, as Commander-in-Ohlef, the fateful decision whether or not to sanction the use of such bombs in the present phase of the war against Japan.

We, the undersigned scientists, have been working in the field of atomic power. Until recently we have had to fear that the United States might be attacked by stords book during this war and bath her only defense might lie in a counterattack by the same means. Today, with the defeat of Germany, this danger is averted and we feel impelled to say what follows:

The war has to be brought speedily to a successful conclusion and attacks by attacks obabs may very well be an effective method of warfare. We feel, however, that such attacks on Japan could not be justified, at least not unless the terms which will be imposed after the war on Japan were made public in detail and Japan were given an opportunity to surrender.

If such public announcement gave assurance to the Japanese that they could look forward to a life devoted to peaceful pursuits in their homeland and if Japan still refused to surrender our nation might them, in certain circumstances find itself forced to resort to the use of atomic bombs. Such a step, however, ought not to be made at any time without seriously considering the moral responsibilities winch are involved.

The development of stamic power will provide the nations with new means of destruction. The atomic bombs at our disposal represent only the first step in this direction, and there is almost no limit to the destructive power which will become evailable in the course of their future development. Thus a nation which ests the precedent or using these newly liberated forces of nature for purposes of destruction may have to bear the responsibility of opening the door to an era of devestation on an unimaginable scale.

If after this war a situation is allowed to develop in the world which permits rival powers to be in uncontrolled possession of these new means of destruction, the dities of the United States as well as the cities of other nations will be in continuous danger of audoen annihilation. All the resources of the United States, moral and material, any have to be sobilized to pervent the advent of such a world statuation. Itse prevention is at present the soleam responsibility of the United States--singled out by virtue of her lead in the field of atomic power.

The added material strength which this lead gives to the United States brings with it the obligation of restraint and if we were to violate this obligation our moral position would be weakened in the eyes of the world and in our own eyes. It would then be more difficult for us to live up to our responsibility of bringing the unlosened forces of destruction under control.

In view of the foregoing, we, the undersigned, respectfully petition: first, that you exercise your power as Commander-In-CM26f, to rule that the United States shall not resort to the use of atomic bombs in this war unless the terms which will be imposed upon Japan have been made public in detail and Japan knowing these terms has refused to aurrender; second, that in such ar event the question whether or not to use atomic bombs be decided by you in the light of the considerations presented in this petition as well as all the other moril responsibilities end are involved.

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Figure 1. Scan of the Szilard Petition, which asked President Harry S. Truman to inform Japan of the terms of surrender before using atomic weapons. The popular movie "Oppenheimer" has provided a new generation of the U.S. public with a powerful recount of the events surrounding the Manhattan Project and the end of the Second World War.

In September 2023, Lisa McDonald–in a *Ceramic Tech Today* article–highlighted the role of Massachusetts Institute of Technology ceramists in the Manhattan Project,¹ based on the work of Whittemore and McCreight. In this article, we seek to remember the work of William Houlder Zachariasen, a multifaceted physicist who made a seminal contribution to glass science and played an important role in the Manhattan Project.

Zachariasen was born in Langesund, Norway, in 1906. The town, near Oslo, gave Zachariasen (known as "Willie" to many) access to the fjord and the many islands there. This location is especially relevant because these islands had many mines rich in rare earths, sparking an early interest in mineralogy for Zachariasen. He studied at the University of Oslo under the guidance of the great geochemist Victor Moritz Goldschmidt,^{2,3} focusing on the X-ray characterization of minerals. Incredibly, Goldschmidt owned one of the islands and had a picnic there with Einstein in 1920!

After publishing his first paper in 1925, Zachariasen published 19 more papers before receiving his Ph.D. in 1928 at the age of 22. He followed this accelerated pace with a postdoctoral position in the lab of Nobel laureate Sir Lawrence Bragg, an expert on X-rays and crystal structure. During this one-year postdoctoral work, Zachariasen focused on silicates, perhaps impacting his later insights on glass structure.

After the postdoctoral fellowship, Zachariasen returned to the University of Oslo. Within a year (and upon Bragg's recommendation), University of Chicago professor Arthur Compton offered Zachariasen a physics professorship at UChicago, which he accepted. He would stay at UChicago for 44 years.

Zachariasen was 24 years old when he left Norway in 1930. The early years in Chicago were tough. He had little money for research. Going to conferences, he would sleep on trains—coming and going on the same day—to save the hotel room cost. Using his prior work on silicates, he published his first (and only) paper on glass, "The atomic arrangement in glass" (1932). Yet this publication arguably became the most influential paper in the history of glass science. As Alfred R. Cooper wrote in his introductory paper to the 1980 Borate Glass Conference,⁴

"We dedicate this session on glass structure to Frederik William Holder Zachariasen because his single contribution to glass literature, 'The atomic arrangement in glass,' may be the most influential paper on glass structure in this century."

Yet Zachariasen had no further interest in glass. Later in life, he had to be reminded that he published in this subject.

By 1943, Zachariasen had joined the Manhattan Project after becoming a U.S. citizen in 1941. Why was he needed? Fermi, working on the nuclear pile at UChicago, had demonstrated the chain reaction of uranium. Zachariasen was already involved in UChicago's Metallurgical Laboratory. In the words of Robert A. Penneman,³

"Plans were being rushed for the pilot plant at Oak Ridge, Tennessee, and the production reactors at Hanford, Washington. This meant that the new element, plutonium, would be made in large quantity using neutrons from a nuclear reactor. Before this, plutonium could be made only in microgram quantities by tedious cyclotron irradiation."

But plutonium metal had to be separated from uranium. Under Glenn Seaborg's leadership, 60 chemists were put on this challenge. Zachariasen, with his expertise on rare earths, was to provide the X-ray analysis and "... deciphering singlehandedly the composition of countless samples that were prepared by the chemists."³

Seaborg wrote that on June 21, 1944, a 10-microgram sample that was thought to be neptunium dioxide (NpO_2) was sent to Zachariasen. By 11 a.m. on June 22, his X-ray analysis had confirmed that it was NpO₂. In his report, Zachariasen wrote:³

"The radius of Np^{*4} is thus 0.0158 Å larger than that of Pu^{*4} , 0.016 Å smaller than that of U^{*4} , and nearly identical with that of Ce^{*4}. I believe that a new set of 'rare earth' elements has made its appearance. I believe that the persistent valence is four, so that thorium is to be regarded as the prototype just as lanthanum is the prototype of the regular rare earth elements."

In a later interview, Zachariasen noted how hard the work was:

"We had a very exciting time struggling with all these patterns over the various plutonium compounds, identifying what the chemists had made and, hence, getting information about the chemistry of plutonium that was essential ... I remember working like hell on New Year's Day and all holidays: often I worked late for many, many hours to get the work done. I had a wonderful time..."

Zachariasen was also a signatory (see middle column in Figure 1) to the Szilard Petition. The petition, drafted in July 1945, asked President Harry S. Truman to inform Japan of the terms of surrender before using atomic weapons. After much discussion (with Oppenheimer opposing it), the petition was brought to soon-to-be-named Secretary of State James F. Byrnes. He also was not sympathetic, and, therefore, President Truman never saw the petition.

Late in 1945, Zachariasen was appointed chair of the physics department at UChicago, and he also published a book titled "The Theory of X-Ray Diffraction in Crystals." He was chair from 1945 to 1950, until an untimely heart attack, and then again from 1955–1959. Under his leadership, he brought Enrico Fermi, Edward Teller, Robert F. Christy, Walter H. Zinn, Maria



Goeppert-Mayer, Gregor Wentzel, and other distinguished physicists to UChicago as professors of physics (Figure 2).

During his time at UChicago and after, Zachariasen led a 37-year effort to elucidate the structure and chemistry of transuranic elements (metals and compounds). In 1948 alone, he published 26 papers. After retiring in 1970, Zachariasen consulted with friends at Los Alamos National Laboratory after moving to Santa Fe, N.M. He died on Dec. 24, 1979, aged 73.

Zachariasen's contributions are memorialized in a variety of ways. The UChicago physics department holds one of its most significant lecture series in his name. But perhaps the most notable commentary on Zachariasen's work was given by Linus Pauling (Nobel Laureate in Chemistry, 1954), who wrote:

"I have known Professor Zachariasen for nearly fifty years. His principal field of work has been the determination of the structure of crystals of inorganic substances by use of the X-ray diffraction technique. This is a field in which I have also done a large amount of work, and I believe that I am in a position to form a sound opinion about his ability and his contributions. It is my opinion that he has been and is the world leader in this field. I feel that he is to be classed among the outstanding scientists of the twentieth century, and at the top of the field in inorganic crystal structures."

About the author

Mario Affatigato is the Fran Allison and Francis Halpin Professor of Physics at Coe College in Cedar Rapids, Iowa. Contact Affatigato at maffatig@coe.edu.

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18–19 Thermal Management Workshop – NC State University, Raleigh, N.C.; https://www.mae.ncsu. edu/event/american-carbon-societythermal-management-conference

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30–May 1 → Ceramics Expo 2024 – Suburban Collection Showplace, Novi, Mich.; https://ceramics.org/event/ ceramics-expo-2024

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16–19 → The 5th International Symposium on New Frontier of Advanced Silicon-Based Ceramics and Composites (ISASC-2024) – Seogwipo KAL Hotel, Jeju, Korea; https://www.isasc2024.org

17–19 ACerS 2024 Structural Clay Products Division & Southwest Section Meeting in conjunction with the National Brick Research Center Meeting – Sheraton Oklahoma City Downtown Hotel, Oklahoma City, Okla.; https://ceramics.org/clay2024

19–21 14th Advances in Cement-Based Materials – Missouri University of Science and Technology, Rolla, Mo.; https://ceramics.org/cements2024

23–27 → American Conference on Neutron Scattering (ACNS 2024) – Crowne Plaza Knoxville Downtown University, Knoxville, Tenn.; https:// ceramics.org/event/americanconference-on-neutron-scatteringacns-2024

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18–22 → 14th International Conference on Ceramic Materials and Components for Energy and Environmental Systems – Budapest Congress Center, Budapest, Hungary; https://akcongress.com/cmcee14

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4–9 16th Pacific Rim Conference on Ceramic and Glass Technology and the Glass & Optical Materials Division Meeting – Hyatt Regency Vancouver, Vancouver, Canada; https://ceramics.org/pacrim16

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• deciphering the discipline

A regular column offering the student perspective of the next generation of ceramic and scientists, organized by the ACerS Presidents Council of Student Advisors.



Our increasingly digital world requires the development of new electronic devices that process data faster, resist overheating, and are economical to manufacture. To that end, materials scientists must develop higher performance dielectric and ferroelectric materials, which serve as the backbone of data processing and memory storage components within electronic systems.

High-entropy materials have enabled access to a broader compositional selection space and improved functionalities for electroceramics.¹ "Entropy" refers to the number of configurations in which different chemical species may be arranged within a material's structure. High-entropy materials possess numerous potential configurations within a single-phase structure. The configurational complexity promotes extended solid solubility and phase stability, while the diverse chemistry gives rise to unique and tunable properties.

As a member of the Maria Group at Penn State, I use an entropy-inspired design approach to develop novel oxide electroceramics. Specifically, I study the interplay between configurational entropy and electrical properties in the $A_6B_2O_{17}$ (A = Zr, Hf; B = Nb, Ta) disordered oxide family across length scales, from bulk ceramics to thin films.

These oxides, modeled in Figure 1, present a unique opportunity for entropy engineering. They host multiple constituent cations on a complex sublattice with three types of sites (6-, 7-, and 8-fold oxygen coordinations), which allows for many possible structural and chemical configurations. Moreover, 7-fold coordination sites are closely associated with ferroelectric behavior in HfO₂, a structural relative to $A_6B_2O_{17}$.² Despite this potential, the electronic properties of $A_6B_2O_{17}$ phases have hitherto remained unstudied.

To elucidate the structure-property relationships in $A_6B_2O_{17}$ phases, we first improved our understanding of the material's structure by assessing the degree of disorder on the cation sublattice. We did so by leveraging in situ and ex situ X-ray diffraction to study the $A_6B_2O_{17}$ phase formation behavior in bulk ceramics at high temperatures (up to 1,300°C), as minimum stabilization temperatures are dependent on the degree of cation disorder.³

Our observations support the cation-disordered model of the $A_6B_2O_{17}$ phases and demonstrate extended solid solubility consistent with high-entropy effects,⁴ making this system interesting for further exploring the interplay between entropy and properties.

Turning to electronic properties, we measured high dielectric permittivities converging to approximately 60 while retaining low loss values in the 10^{-3} range in the bulk regime for ternary $A_6B_2O_{17}$ phases. Similar values were obtained for thin films produced via sputter deposition from dense bulk ceramic targets.

These measurements, which will be published soon within a journal article, suggest contributions to polarizability arising from long-range interactions and hint at potential ferroelectric responses. We are now exploring the structure and property effects derived from additional cation species.



Figure 1. The compositional complexity, structure, and site disorder of $A_{b}B_{2}O_{17}$ disordered oxides make these materials attractive as potential high-entropy electroceramics. Adapted from Reference 4.

Our results confirm the potential of $A_6B_2O_{17}$ disordered oxides as promising electroceramics. More broadly, they illustrate the viability of using entropy-inspired design to develop new functional materials for electroceramic and other applications.

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Jackson Spurling is a Ph.D. candidate in the Department of Materials Science and Engineering at The Pennsylvania State University, working in Jon-Paul Maria's group. His research focuses on high-entropy and disordered oxides for electroceramic applications. Outside of the lab, Jackson is an avid fan of Penn State Nittany Lions Football and enjoys hiking in the Appalachian Mountains of Central Pennsylvania.

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K 39.0983 otassium	20 Ca ² Calcium	21 Sc ² 9 2 44.955912 Scandium	22 Ti 47.867 Titanium	23 28 28 50.9415 Vanadium	24 28 Cr ² 13 51.9961 Chromium	25 28 Mn ² 54.938045 Manganese	26 Fe ² 55.845 Iron	27 28 CO 28 58.933195 Cobalt	28 28 Ni ⁸ 58.6934 Nickel	29 28 Cu 18 63.546 Copper	30 2 8 8 8 2 1 2 1 2 1 2 1 2 1 2 1 2 1 2 1	31 8 69,723 Gallium	32 Ge ² 72.64 Germanium	33 28 35 As 5 74.9216 Arsenic	34 2 8 78.96 Selenium	35 8 1 8 1 8 1 8 1 8 1 8 1 1 1 1 1 1 1 1 1 1	36 2 83 83 83 83 83 83 83 83 83 83 83 83 83
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CS ² 132.9054 Cesium	56 2 Ba ¹⁸ 18 18 2 137.327 Barium	57 2 La 18 138.90547 Lanthanum	72 Hff 15 10 2 178.48 Hafnium	73 7 3 7	74 28 8 28 18 18 18 12 2 18 3.84 Tungsten	75 8 Re 2 185.207 Rhenium	76 2 8 05 32 190.23 0smium	77 2 8 18 19 15 19 2217 19 2217 17 17 10 10 10 10	78 2 Pt 18 195.084 Platinum	79 2 8 8 18 18 18 18 18 18 18 18 18 18 18 18	80 Hg ² 80 80 8 8 18 18 18 18 18 18	81 28 204.3833 Thallium	82 Pb ² 18 207.2 Lead	83 8 Bi 35 208.9904 Bismuth	84 8 4 8 4 8 4 8 4 8 4 8 4 1 5	85 At ² 8 ¹⁸ ¹⁸ ¹⁸ ¹⁸ ¹⁸ ¹⁸ ¹⁸ 	86 Rn ² 15 15 15 15 15 8 15 15 15 15 15 15 15 15 15 15 15 15 15
(223)	88 2 Raa (226) Radium	89 28 Acc 18 22 (227) Actinium	104 2 Rf 35 32 (267) Rutherfordium	105 Db (268) Dubnium	106 Sgg (271) Seaborgium	107 Bh (272) Bohrium	108 2 HS 32 (270) Hassium	109 2 8 8 18 32 32 32 5 2 2 2 5 2 8 18 32 32 5 2 2 2 2 2 32 5 2 2 32 5 5 2 32 32 5 5 5 32 32 5 5 5 5	110 2 DS 15 15 15 15 15 15 15 15 17 17 17 17 17 17 17 17 17 17	111 28 Rgg 22 (280) Roentgenium	112 Copernicium ² ⁸ ⁸ ⁸ ⁵ ²⁰ ²⁰ ²⁰ ²⁰ ²⁰ ²⁰ ²⁰ ²⁰	113 Nh (284) Nihonium	114 Fi (289) Fierovium	115 Mcc (288) Moscovium	116 Lv (293) Livermorium	117 TS (294) Tennessine	118 2 0g 3 (254) 0ganesson



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