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President’s update: Industry issues
ACerS President Bill Lee provides the first of three updates to members about key themes of his presidency.
by Bill Lee

Additive manufacturing techniques for fabricating complex ceramic components from preceramic polymers
Properties of preceramic polymers allow use of additive manufacturing to fabricate advanced ceramics through various techniques.
by Paolo Colombo, Johanna Schmidt, Giorgia Franchin, Andrea Zocca, and Jens Günster

Polymer-derived ceramic and ceramic-like coatings: Innovative solutions for real problems
Polymer-derived ceramic coating systems have tunable chemical composition, versatility and ease of processing, and excellent properties, making these materials promising for a variety of applications.
by Gilvan Barroso, Quan Li, Günter Motz, and Rajendra K. Bordia

The QC checklist: An essential tool for managing product quality of ceramics
A quality control checklist clarifies product specifications for mass production and helps ensure the quality of manufactured ceramic products.
by John Niggl

Materials with market value: Global ceramic and glass industry poised to reach $1 trillion
Traditional glass and ceramics comprise 89% of the global market; however, growth will be largest in technical ceramic sectors in the next five years.
by Margareth Gagliardi
Follow all the Ceramics Expo action with Ceramic Tech Today

ACerS is the official media partner of Ceramics Expo—so whether you’re attending the show or watching from afar, stay tuned for full expo coverage. Want us to bring the news to you? Subscribe to the Ceramic Tech Today e-newsletter at www.bit.ly/acersctt.

Follow the expo action at www.ceramics.org/ctt

Low-temperature processing could establish ‘Materials Valley’

What if—instead of redesigning individual materials to make them stronger, lighter, cheaper, and greener—we could rethink a single processing method to improve various different materials? Such a reality may be closer than you think.

Read more at www.ceramics.org/materialsvalley

As seen on Ceramic Tech Today...
President’s update: Industry issues

By Bill Lee

This is the first of three articles for the ACerS Bulletin updating members on key themes of my year as president. This article focuses on industry. An update on young members’ issues will appear in the June/July Bulletin, and an international members update will appear in the October/November international issue.

While my whole career has been spent in academia, all of my research has been geared towards an end application—almost exclusively working with industry—for example, in refractories (Kerneos, Vesuvius, Corus, Tata, Heraeus), electrotechnics (Morgan Advanced Materials), glass (Pilkington), aerospace (Rolls-Royce), nuclear (Sellafield, GE-Hitachi, EdF Energy), and, more recently, in whitewares and coatings (SCG Thailand).

A key aspect of being a ceramic engineer is that we actually make things and that is instantly important to industry. ACerS new Manufacturing Division is thus a crucial development because it encompasses traditional manufacture of high volume whitewares, cements, glasses, and refractories as well as complex multimaterial components for electrical circuits and devices, and films and coatings, along with exciting new processing technologies associated with biomimicry, freeze casting, and, of course, additive manufacture.

The Manufacturing Division has found a natural home for its activities at Ceramics Expo. The Division sponsors short courses of particular interest to manufacturers, as well as the Ceramic Business Leadership Summit (CBLS). The CBLS theme this year is “Marketing for Manufacturers,” a forum that addresses marketing strategies for taking to market all those products ceramic engineers work on.
and glass engineers make. In addition, the Manufacturing Division will hold its annual business meeting at Ceramics Expo, and all are invited. For details, contact Erica Zimmerman, staff liaison for the divisions, at ezimmerman@ceramics.org, or visit www.ceramics.org/acers-community/division-pages/manufacturering-division.

Another key Society development is the rollout this year of the new Corporate Partnerships program with three benefit levels to choose from—appropriately termed Corporate, Sapphire, and Diamond. Companies who partner with ACerS will gain an advantage through greater exposure in the marketplace by leveraging ACerS resources and opportunities. These include Bulletin advertising, meeting registrations, networking sponsorships, discounts on market reports, and more.

“We want to build stronger relationships with our industry partners and offer benefits in three primary areas: marketing and business development; professional development; and technical resources,” says Kevin Thompson, director of membership. He can be reached at kthompson@ceramics.org, or find him at the ACerS booth at Ceramics Expo.

This is the third year for Ceramics Expo—the only trade show in North America for our industry—and ACerS is proud to be a founding partner. We hope you will stop by Booth 308 and visit us. Even better, bring a friend with you who should be a member! Our staff will be there to direct them to the many resources and opportunities our Society offers.

If you are there Tuesday morning, stop by the booth to meet two speakers from the CBLS—Rebecca Geier from TREW Marketing, and Gordon Nameni representing BCC Research. They are expert thought leaders in the area of technical product marketing and business intelligence. Find out more about the Expo at www.ceramicsexpousa.com.

Making quality products requires finding talented people to design, produce, and sell them. The Ceramic and Glass Industry Foundation (CGIF) works to attract, inspire, and train the next generation of ceramic and glass technicians, engineers, and scientists—all of which are vital to our industry. Our industry partners can join us in this effort through sponsorship of key program areas. For example, the Corning Incorporated Foundation recently awarded the CGIF a $50,000 grant to support distribution of our Materials Science Classroom Kits in communities where Corning operates.

In addition, the Sastri Family Foundation just announced a $50,000 donation to support workforce development, especially at the pre-baccalaureate level.

Whether through volunteering, board leadership, or financial gifts, we encourage members to consider how they can support the mission of the CGIF. The CGIF website, www.foundation.ceramics.org, or Marcus Fish, CGIF development director at mfish@ceramics.org, can point interested parties in the right direction.

One final effort to bring to your attention is a new President’s Advocacy Advisory Committee, which is charged with collecting information on regulations, health and safety, government affairs events, and other matters important to manufacturers. The committee looks for activities in other industries that relate to our industry priorities, such as the American Foundry Society Government Affairs Fly-in, June 20–21, in Washington, D.C. The keynote speaker will be Stephen Hayes, writer and FOX News contributor.

The committee publishes its findings on the “Resources for manufacturers” webpage at www.ceramics.org/knowledge-center/resources. Contact Eileen DeGuire, director of communications and marketing, at edeguire@ceramics.org with suggestions for additional content.

As you can see, the Society is making ever increasing efforts to engage with and support our corporate members. I welcome your input on how we can continue to support our industry’s manufacturing activities. Reach me at w.e.lee@imperial.ac.uk.
William Prindle devoted career to glass, ceramics, materials research

ACerS Fellow and Distinguished Life Member William “Bill” Prindle (1926–2016) passed away on Friday, Dec. 29, 2016, in Santa Barbara, Calif.

Prindle spent his career in the fields of glass, ceramics, and materials research and development, working at the following companies: Hazel-Atlas Glass Division of Continental Can Company, American Optical Company, Ferro Corporation, the National Materials Advisory Board (part of the National Research Council of the National Academy of Sciences), and Corning Incorporated. He retired in 1992 from Corning.

Prindle was well-respected among his peers at ACerS. He served as ACerS president 1980–1981, and president of the International Commission on Glass, 1985–1988. Prindle was a member of the National Academy of Engineering and was named Outstanding Ceramist of New England by the New England section in 1974. In 1980 he received the MIT Ceramics Division Alumni Award.

In 1983, Prindle was the John F. McMahon Engineering Lecturer for the Ceramic Association of New York. That year he also received the Phoenix Award as Glass Man of the Year. In 1986 he was awarded Northwest Ohio’s Toledo Glass Award.

Prindle was born on Dec. 19, 1926, in San Francisco to Drs. Harriette N. and Vivian A. Prindle and grew up in Oakland.

During World War II, Prindle enrolled in the V12 Navy program at the University of California, Berkeley. He earned his bachelor’s and master’s degrees in physical metallurgy from the University of California. He also earned an Sc.D. in ceramic engineering from Massachusetts Institute of Technology.

He leaves his wife, Jeanne, son, daughter and son-in-law, brother and sister-in-law, grandson, niece and nephew, and stepchildren and their families.
New Corporate Partnership program continues to expand

In last month’s Bulletin, ACerS announced its new Corporate Partnership program, designed to forge more meaningful partnerships with member companies.

Corporate Partners receive all benefits of the current Corporate Membership program, with valuable new benefits that include advertising, sponsorships, meeting registrations, and more.

To learn more about the new ACerS Corporate Partnership Program, please contact Kevin Thompson, membership director, at 614-794-5894 or kthompson@ceramics.org.

ACerS is pleased to announce the following companies who have joined the new Corporate Partnership program (as of March 8):

Diamond Corporate Partners
- Mo-Sci Corp.
- Saint Gobain
- Morgan Advanced Materials

Sapphire Corporate Partners
- McDaniels Advanced Ceramic Technologies

Corporate Partners
- Allied Mineral Products Inc.
- Applied Research Center
- Astral Material Industrial Co. Ltd.
- Capital Refractories Ltd.
- J. Rettenmaier USA
- Resodyn Acoustic Mixers Inc.
- SELEE Corp.
- Surmet Corp.
- Technology Assessment & Transfer Inc.

Northern Ohio Section holds election

The ACerS Northern Ohio Section recently held an election and following members are serving as officers for 2017:

Chair: Alp Sehirlioglu
   (axs461@case.edu)
Vice chair: Valerie Wiesner
   (valerie.L.wiesner@nasa.gov)
Treasurer: Dennis Fox
   (dennis.s.fox@nasa.gov)
Secretary: Mike Dowell
   (mbdowell@att.net)

Please keep an eye out for updates about local activities as well as volunteering opportunities. Contact the section officers if you would like to get involved.

Names in the news

National Academy of Inventors names ACerS member Fellow

Sarit Bhaduri (University of Toledo) will be inducted as NAI Fellow at a ceremony in Boston on April 6, 2017.

Students and outreach

ACerS GGRN for young ceramic and glass researchers

Are you a current grad student who could benefit from additional networking within the ceramic and glass community? Put yourself on the path toward post-graduate success with ACerS Global Graduate Researcher Network (GGRN)! GGRN is a network that addresses professional and career development needs of graduate-level research students who have a primary interest in ceramics and glass.

GGRN helps graduate students
- Engage with other ACerS members;
- Build a network of contacts within

Presidents’ tribute to Dr. William R. Prindle

Upon hearing of the passing of Bill Prindle, past president of the Society, past president of the International Commission on Glass, and distinguished industrial glass scientist, some of us were reminded of that extended thought from classical English literature, “the death of one of us diminishes all.” A consummate gentleman and mentor to so many, he represented and fostered the enduring values of the Society throughout his professional life. Being a remarkably unpretentious individual, he would not want us to recount here his many accomplishments and contributions to the fields of glass and ceramics; rather, he would encourage us to take up our tasks with renewed energy and commitment to build upon what he helped set in place through his service to the Society, to industry, and to all things glass and ceramics. As long as there is an American Ceramic Society, you will not be forgotten, Bill.

Presidents of the Society

L. David Pye
Paul Becher
Richard Brow
Delbert Day
Robert Eagan
Katherine Faber
Stephen Freiman
Edwin Fuller
David Green
Lyle Holmes
James Houseman
Carol Jantzen
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James Johnson
William Lee
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John Marra
James McCauley
Gary Messing
Dale Niesz
Robert Oxnard
Marina Pascucci
William Payne
David Pye
Dennis Readey
William Rhodes
Kathleen Richardson
Mrityunjay Singh
John Wachtman
George Wicks

Society and Division news (continued)
Students and outreach (continued)

the ceramic and glass community; and

- Access professional development tools.

Visit www.ceramics.org/ggrn to learn what GGRN can do for you, or contact Tricia Freshour, ACerS member engagement manager, tfreshour@ceramics.org.

Grads and undergrads—Further your career by joining the PCSA!

The President’s Council of Student Advisors (PCSA) seeks dedicated and motivated undergraduate and graduate students to help propel ACerS into the future while developing leadership skills. This student-led committee is composed of ceramic- and glass-focused students. Interested students can visit www.ceramics.org/applypcsa to learn more.

Application deadline for the 2017–18 class is April 15, 2017.

Educating public on ceramic science could earn you $250!

Show off your demonstration skills and earn recognition in ACerS Next Top Demo Competition, organized by ACerS President’s Council of Student Advisors. This virtual competition is a way for you to educate the public while promoting the community outreach you and your peers already perform. Get your fellow students together and submit a video conducting a ceramic and/or glass outreach demonstration. Visit www.ceramics.org/pcsademo to submit your videos. Submission deadline is April 28, 2017.


Thursday, April 13, 2017, 11 a.m. ET: One piece of advice students and recent graduates commonly get is to network, network, network. But why? And with whom? This free webinar will focus on the advantages of professional society membership and professional networks, and how to get the most benefit from membership. This webinar is organized by ACerS Global Graduate Researcher Network and ACerS Young Professionals Network. Visit www.ceramics.org/meetings/web-seminars to learn more and register by April 11, 2017.

END

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Dr. Suri A. Sastri of the Sastri Family Foundation has generously provided a $50,000 grant to the Ceramic and Glass Foundation (CGIF) for the purpose of attracting, inspiring, and training the next generation of ceramic and glass professionals.

Sastri is founder, chairman and CEO of Surmet Corporation in Burlington, Mass., Surmet Ceramics Corporation of Buffalo, N.Y., and Surmet Precision Optics of Murrieta, Calif. Surmet Corporation is vertically integrated and combines research and development and specialty manufacturing in a way that laboratory inventions can be brought seamlessly to the production floor. Surmet has a 75,000 sq. ft. manufacturing facility in Buffalo, N.Y.; multiple facilities in Massachusetts, including its headquarters, and a precision fabrication facility in Murrieta, Calif.

Sastri’s thoughtful donation was motivated by his desire to address the need for developing and training young, non-college educated skilled workers to perform well-paying medium- to high-level technician functions in manufacturing industries.

Sastri believes passionately in assisting nonskilled workers with developing the technical skills needed for success. “If a person can learn how to drive and is able to speak and write, he or she is capable of learning many other things as well, including technical work,” says Sastri.

Guided by his entrepreneurial spirit, Sastri founded Surmet Corporation in 1982—an innovative problem solving company addressing the needs of industry. The business was based on a simple premise—“Today’s materials are not suitable for tomorrow’s systems and machines.”

Surmet initially focused on and served the high-tech semiconductor and biomedical industries, and later shifted its focus to specialty manufacturing of advanced polycrystalline transparent ceramics. Best known for its ALON transparent ceramic (also known as transparent aluminum), Surmet is a pioneer in other advanced technologies, including IR optics materials, optical coatings, precision optics fabrication, and lightweight transparent armor design and solutions.

This grant to CGIF represents Sastri’s deep commitment to the CGIF’s mission of ensuring the industry is able to attract and train the highest quality talent available to work with engineered systems and products that utilize ceramic and glass materials.

Marcus Fish, director of development of the CGIF, says, “Dr. Sastri’s generous donation will be used to help us attract, inspire, and train the next generation of ceramic and glass professionals, which certainly includes technicians—a vital part of the industry.”

“This donation is the latest example of Dr. Sastri’s commitment not only to the CGIF, but to the entire community”, says Charlie Spahr, executive director of The American Ceramic Society. “Both he and his company serve as outstanding models of the creative leadership needed to optimize workforce development and organizational excellence.”

For more information about the work of the CGIF, visit foundation.ceramics.org. 
Awards and deadlines

Nominations open for ECD Mueller, Bridge Building, and Global Young Investigator awards

The Engineering Ceramics Division (ECD) invites nominations for the 2018 James I. Mueller, Bridge Building, and Global Young Investigator awards. Deadline for submitting nominations for these awards is July 1, 2017. For details about each award visit www.bit.ly/2lZwVne.

The Mueller Award recognizes accomplishments of individuals who have made similar contributions to ECD and/or work in areas of engineering ceramics resulting in significant industrial, national, or academic impact. The award consists of a memorial plaque, certificate, and $1,000 honorarium. For questions email Andrew Gyekenyesi, Andrew.L.Gyekenyesi@nasa.gov.

The Bridge Building Award recognizes individuals outside the United States who have made outstanding contributions to engineering ceramics. The award consists of a glass piece, certificate, and $1,000 honorarium. For questions contact Jingyang Wang at jywang@imr.ac.cn.

The Global Young Investigator Award recognizes an outstanding scientist conducting research in academia, industry, or at a government-funded laboratory. Candidates must be ACerS members 35 years of age or younger. The award consists of $1,000, a glass piece, and certificate. For questions contact Manabu Fukushima at manabu-fukushima@aist.go.jp.

Nominations close May 15 for three awards

Glass & Optical Materials: Alfred R. Cooper Scholars Award recognizes undergraduate students who have demonstrated excellence in research, engineering, and/or study in glass science or technology.

Electronics: Edward C. Henry Award recognizes an outstanding paper reporting original work in the Journal of the American Ceramic Society or the Bulletin during the previous calendar year on a subject related to electronic ceramics.

Electronics: Lewis C. Hoffman Scholarship recognizes academic interest and excellence among undergraduate students in the area of ceramics/materials science and engineering.

Visit www.ceramics.org/awards for award criteria and nomination forms. Contact Erica Zimmerman at ezimmerman@ceramics.org with any questions.

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NEW
Team to combine in situ microscopy and modeling for deep dive into flash sintering

A collaboration of researchers from Purdue University and beyond is using a $3 million grant to take a close look at flash sintering in a massive effort to broaden applications of the technique. Using a combination of in situ and modeling techniques, the team aims to characterize the nano- and microscale events that happen during flash sintering in a variety of ceramic materials.

Haiyan Wang, Basil S. Turner Professor of Engineering in Purdue’s School of Materials Engineering, will lead the project, which also includes Edwin García and Xinghang Zhang from Purdue University; Amiya Mukherjee, distinguished professor of materials science and engineering at the University of California, Davis; Thomas Tsakalakos, distinguished professor of materials science and engineering at Rutgers University; and C. Stephen Hellberg, Noam Bernstein, and Steven Erwin, physicists at the Naval Research Laboratory.

“Our scope is to understand why within a matter of seconds and at such a low temperature you can facilitate sintering, which conventionally needs a much longer time at higher temperature,” Wang says in a Purdue press release.

“Despite successful demonstrations of flash sintering, it remains poorly understood at the atomic scale.”

To get at those atomic scale details, the scientists will probe mechanical properties of ceramic materials during different sintering conditions. Using in situ methods to simulate what happens ex situ, the scientists will carefully dissect how an electrical field and heat affect a material’s microstructure during flash sintering.

Although Wang says there are various possibilities to explain how flash sintering works—such as Joule heating, ion transport, and dielectric breakdown—we do not yet understand the fundamental mechanism or mechanisms of flash sintering.

In particular, some hypotheses suggest that grain boundary effects are key to flash sintering, so the team will precisely probe grain boundary dynamics during flash sintering using conventional TEM, in situ TEM, and in situ XTEM microscopy. Using these microscopy tools, the team will watch what happens in the ceramics’ crystal structure during sintering, using real-time video to capture the small scale of sintering.

“The first step is to understand the mechanism through detailed grain boundary studies,” Wang says. “The second step is to use that understanding to design ceramic materials to meet functionality needs, and to use flash sintering to sinter those materials.”

That is where the modeling comes in. The scientists will use their newfound understanding of the process to develop simulations that will help other scientists pinpoint flash sintering conditions for a particular material. “This is a strong part of the proposal—we are going to use both in situ experiments and modeling simulations to create a sort of feedback loop,” Wang says.

She explains that understanding how and why the technique works will help researchers apply flash sintering to other materials that are more difficult to process. Those materials may require a higher power supply, longer processing times, or higher temperatures during flash sintering—and Wang and her team want to understand why and how to help facilitate flash sintering in those materials, she says, to broaden applications of flash sintering.

“We can’t understand everything, but we hope that the combined efforts with collaborators can help the community understand a better way to flash sintering,” Wang says.

Hear more about the project from Wang and her Purdue team in a short video available at youtu.be/O6BQLIetpKc.

Simple technique effortlessly converts bulk materials into oxide nanowires

Researchers at Georgia Institute of Technology (Atlanta, Ga.) have developed a technique that may put ceramic separators at the forefront of the next generation of safer, improved batteries. The team devised a simple method to transform bulk alloy materials into oxide nanowires at room temperature and pressure, without the use of catalysts, toxic chemicals, or expensive processes.

The technique is so simple and inexpensive that the authors think it could propel incorporation of oxide nanowire materials into a variety of technologies,
Georgia Tech professor Gleb Yushin and a team of scientists have devised a technique to produce oxide nanowires from bulk materials.

including batteries, lightweight structural composites, advanced sensors, and electronic devices.

“This technique could open the door for a range of synthesis opportunities to produce low-cost 1-D nanomaterials in large quantities,” Georgia Tech materials science and engineering professor Gleb Yushin says in a Georgia Tech press release. “You can essentially put the bulk materials into a bucket, fill it with a suitable solvent, and collect nanowires after a few hours, which is way simpler than how many of these structures are produced today.”

The team accidently discovered that dissolving a bimetallic

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Fish scales inspire ceramic-plated protective gloves that are puncture-resistant yet flexible

Alligator gar are a kind of prehistoric-looking megafauna that are covered in extremely tough scales—which have some interesting engineering principles to teach scientists about being both flexible and tough.

By studying how gar scales deform, interact, and fracture, scientists at McGill University in Canada have uncovered mechanisms to translate that flexible strength into principles to engineer puncture-resistant gloves that can maintain dexterity while protecting workers with superior appendage protection.

The team developed a flexible armor made of overlapping ceramic tiles. According to the school’s press release, “By using computer modeling, they were able to determine the optimal size, shape, arrangement, and overlap to make protective gloves that are much more resistant to piercing than those currently in use.”

While one may be tempted to think bigger is better when it comes to armor plates, the team’s puncture tests show that small, 0.6-mm-thick, high-purity alumina plates affixed to a flexible substrate were up to three times more puncture-resistant than longer ribbons of alumina.

That is because the flexural span is smaller in the smaller sized tiles, resulting in lower flexural stress, which delays fracture of the tiles.

Plus, larger scales “produce stiffer responses, since large scales deform a larger volume of the backing material,” the authors write in the paper.

And while large scales always failed due to fracture, small scales had higher puncture resistance, although they required greater overlap of the tiles because they tended to tilt.

But there is a trade-off between flexibility and toughness—while greater tile overlap increased puncture resistance, it also decreased flexibility. Overall, the authors conclude, small scales with reasonable overlap can offer the best protection for workers’ fingers.

“Fish scales surprised us,” postdoctoral researcher and lead author Roberto Martini says in the press release. “It may sound counter intuitive, but we discovered that smaller scales are actually more difficult to pierce than the larger ones, something we can now fully explain using engineering analysis. We also learned that they are the toughest collagen-based material known.”

And, when it comes to fabricating protective gloves, other materials could be used as well. The authors suggest that alumina tiles affixed to carbon fiber mats could offer superior penetration resistance to morphing structures, while glass tiles affixed to cotton substrates could offer the possibility of transparent protection.
Hear and see more from the researchers themselves in the short video available at youtu.be/t78zi_e9gA.

The paper, published in *Bioinspiration & Biomimetics*, is “Stretch-and-release fabrication, testing and optimization of a flexible ceramic armor inspired from fish scales” (DOI: 10.1088/1748-3190/11/6/066001).

**Method quickly infiltrates ceramic foams with molten metal to create stable cermet composites**

Cermets join together some of the best of the materials worlds—ceramics and metals—giving this class of materials the high temperature resistance of ceramics yet the ductility and machinability of metals, among other properties.

And thanks to a new ceramic-metal joining technique developed at Texas A&M University (College Station, Texas), cermets might become even more useful in the hunt for new materials to solve some of the most pressing energy technology challenges.

The Texas A&M team has developed a current-activated, pressure-assisted infiltration (CAPAI) method that can quickly and efficiently combine ceramics and metals into stable, high-performance composites.

Usually, cermets are created by sintering together powders of metals and ceramics at high temperatures—but this technique causes the materials to react with each other, often ruining the properties of the resulting composite.

However, CAPAI is different.

The method instead applies an electric current and pressure to combine molten metal into a ceramic foam, bypassing the problems encountered when heating mixed powders.

“The electric current and the pressure together provided simultaneous heating and pressure that actively drove the molten metals into the ceramic preform,” ACerS member Miladin Radovic, associate professor and associate department head in the Department of Materials Science and Engineering at Texas A&M University.
A&M and senior author of the paper describing the work, says in a university press release. “The fast and controllable heating rate, which was as high as 700 degrees Celsius, offered an easy and efficient way to avoid reactions between ceramics and molten metal.”

ACerS member Liangfa Hu is first author on the paper, published in Scientific Reports.

The Texas team’s experiments with molten aluminum and titanium aluminum carbide (TiAlC) ceramic foams show that the technique can produce a lightweight, strong, and stable cermet.

The team reports its TiAlC/Al composite is 10 times stronger than aluminum alloys at room temperature. And at 400°C, the composite is 14 times stronger and less likely to degrade with heat than aluminum alloys.

And the technique is fast—in the paper, the team reports that just 30 seconds of processing infiltrated molten aluminum into 97% of the open pores in the ceramic foam.

Plus, composite structures generated via CAPAl are tunable, the team says, by simply adjusting the porosity of the starting ceramic foam.

“Both aluminum and titanium aluminum carbides challenged the conventional methods for producing desirable composite materials because they react to each other at temperature that is well beyond that needed to combine them in the composite material,” says Radovic. “The CAPAI method allowed processing novel ceramic-metal composites which could not otherwise be obtained using powder metallurgy and conventional infiltration techniques.”

Besides energy applications, cermets incorporating aluminum could be particularly well-suited for aerospace and transportation applications, where they can save considerable weight.

The open-access paper, published in Scientific Reports, is “High-performance metal/carbide composites with far-from-equilibrium compositions and controlled microstructures” (DOI: 10.1038/srep35523).

Nanorod-connected quantum dots create two-way LEDs that could integrate smart displays into our future

A team at the University of Illinois at Urbana–Champaign (Urbana, Ill.), Electronics and Telecommunications Research Institute (Daejeon, Korea), and Dow Electronic Materials (Marlborough, Mass.) has taken a big step in this direction with the development of two-way LEDs that can both emit and harvest light.

Built from quantum dots connected by semiconductor nanorods, these two-way LEDs hold a lot of promise to develop integrated, responsive, and smart touchless display screens that can autonomously detect input, communicate with other screens, and so much more.

“These LEDs are the beginning of enabling displays to do something completely different, moving well beyond just displaying information to be much more interactive devices,” Moonsub Shim, materials science and engineering professor at the University of Illinois and leader of the study, says in a university press release. “That can become the basis for new and interesting designs for a lot of electronics.”

The LEDs can absorb and emit light via a thin film of asymmetrically organized quantum dots connected by nanorods, each composed of three semiconductor materials. The nanorod collects electrons, and the quantum dots’ shells gather positive charges—which the quantum dots can use together to generate light.

And that entire charged particle process is reversible, too—meaning that the quantum dot–nanorod structures can also collect, in addition to generate, light energy.

“The way it responds to light is like a solar cell. So not only can we enhance interaction between users and devices or displays, now we can actually use the displays to harvest light,” Shim says in the release. “So imagine your cellphone just sitting there collecting the ambient light and charging. That’s a possibility without having to integrate separate solar cells. We still have a lot of development to do before a display can be completely self-powered, but we think that we can boost the power-harvesting properties without compromising LED performance, so that a significant amount of the display’s power is coming from the array itself.”

See more about this interesting research in the short Science video available at youtu.be/EjAWpsNUSAQ.

The paper, published in Science, is “Double-heterojunction nanorod light-responsive LEDs for display applications” (DOI: 10.1126/science.aal2038).
As the industry continually moves toward better-resolution display screens, glass researchers work to improve the science behind the manufacturing process.

John Mauro, senior research manager of glass research at Corning Incorporated and ACerS Fellow, and Qiuju Zheng, associate professor at Qilu University of Technology in China, are pioneering research in glass relaxation behavior. In a new paper, Mauro and Zheng show that the glass “relaxation variability can be reduced dramatically by increasing the fragility of the system.”

A glass’s thermal history is one of the contributors to its properties. Glass substrates are heated during the manufacturing of flat panel display screens to deposit thin-film transistors. This alters and complicates the thermal history of the glass sheet. As the glass relaxes during the process, some of its volume shrinks slightly. If fluctuations in the relaxation behavior are not managed and accurately controlled, pixels in the screen will not align properly, resulting in a sort of “pixel chaos”—in other words, a display that does not work.

Think of it like a marching band director (production manager) trying to organize band members (pixels) into their proper place in a creative formation for the halftime show. If they are not lined up in their correct spot when the show begins, the visual effect is lost on the audience. As the show plays out, band members know exactly where to step, based on yard lines on the football field. If the football field dimensions varied, the line markings would vary, and mayhem would result as band members missed their marks and crashed into each other.

Manufacturers are bedeviled not so much by shrinkage, but by the unpredictable nature of shrinkage. As Mauro and Zheng strive to understand what controls fluctuations in glass relaxation behavior, they can predict where the fluctuations originated—which could lead to better control of thermal history during manufacturing or to new compositions that are more stable and predictable with respect to relaxation behavior.

In an American Institute of Physics press release about the work, Mauro explains that the knowledge he and Zheng have gained through their research is already having positive effects within the glass manufacturing industry. The researchers suggest their study could bridge the gap between the physics of glass relaxation and the chemistry behind it.

“Our research will lead to improved glass composition designs to help enable higher resolution displays for next-generation display technology,” Mauro predicts in an email.

Additive manufacturing techniques for fabricating complex ceramic components from preceramic polymers

By Paolo Colombo, Johanna Schmidt, Giorgia Franchin, Andrea Zocca, and Jens Günster

Properties of preceramic polymers allow use of additive manufacturing to fabricate advanced ceramics through various techniques.

Additive manufacturing of polymeric materials has a long history. During the 1980s and 1990s, stereolithography, fused deposition modeling, and selective laser sintering were initially developed based on the successful use of polymeric feedstocks. The physical properties of polymeric materials make them particularly suitable for various additive manufacturing technologies. For instance, polymeric materials can easily be converted from a solid to a liquid or paste by dissolution or low-temperature melting. Therefore, manufacturing techniques can fuse polymeric filaments or powders in a layer-by-layer buildup of parts. Additional methods can trigger the reverse phase transition back to a solid either by a change in temperature of the material or by evaporation of solvents.

Photopolymerization also can selectively cross-link polymeric materials to generate solid structures from a liquid bath, or, through localized spraying of a solvent, 3-D printing can bind particles by partial dissolution. Because of low surface tension and strong cohesive interaction, polymeric materials in the form of liquids, powders, or filaments easily can be consolidated to form a strong part in a layer-wise fashion using a variety of additive manufacturing processes. By modifying composition, molecular architecture, and molecular weight, properties of polymeric materials can be adapted perfectly to specific processing requirements of each additive manufacturing technology.
The particular attraction of preceramic polymers lies in the possibility of combining properties of a polymeric feedstock—very favorable for high-resolution additive buildup of parts—with the capability of transforming them into a ceramic. Preceramic polymers are a special class of inorganic polymers that can convert with a high yield into ceramic materials, or polymer-derived ceramics (PDCs), via high-temperature treatment in inert or oxidative atmospheres. The polymerto-ceramic conversion occurs with gas release and shrinkage at 400°C–800°C.

The most frequently used preceramic polymers contain silicon atoms in the backbone (e.g., polysiloxanes, polysilazanes, and polycarbosilanes), yielding SiOxC, SiCN, or SiC ceramics after pyrolysis. However, aluminum- and boron-containing polymers also are possible. In addition, preceramic polymers can be mixed with various fillers (either reactive or inert) to produce numerous advanced ceramic phases.1

This unique spectrum of characteristics has recently stimulated a variety of approaches for the use of preceramic polymers, either pure or mixed with fillers, as feedstocks in virtually all additive manufacturing technologies, both direct and indirect.2 Preceramic polymers can allow fabrication of high-resolution, high-performance, and complex ceramic parts with an ease not encountered when processing powder-based systems.

When mixed with fillers, preceramic polymers can act simply as nonsacrificial binders, providing good green body strength and an interconnecting ceramic matrix upon pyrolysis, or they can react during high-temperature treatment to produce ceramic phases of a targeted composition. Table 1 lists additive manufacturing technologies that were tested successfully with preceramic polymers or could be used with them (see later), together with their main characteristics. Table 2 reports the availability, cost, and main physical state of various preceramic polymers.

### Powder-bed-based technologies: 3-D printing and selective laser treatment

Powder-based indirect additive manufacturing technologies share the approach of depositing thin layers of powder one on top of the previous one, followed by selectively inscribing corresponding layer information with a laser (selective laser treat-
Additive manufacturing techniques for fabricating complex ceramic components...

Figure 1. SiOC coffee cup pyrolyzed at 1,200°C. Inset shows detail of the as-printed object before pyrolysis.

<table>
<thead>
<tr>
<th>Preceramic Polymer</th>
<th>Availability</th>
<th>Cost</th>
<th>Most Common Physical State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysiloxane</td>
<td>Commercially available (in large amounts)</td>
<td>Low</td>
<td>Powder or liquid</td>
</tr>
<tr>
<td>Polycarbosilane</td>
<td>Commercially available (limited availability)</td>
<td>High</td>
<td>Liquid or powder</td>
</tr>
<tr>
<td>Polysilazane</td>
<td>Commercially available (in large amounts)</td>
<td>Low–medium</td>
<td>Liquid</td>
</tr>
<tr>
<td>Other (e.g., polyborosilazane, or borazine)</td>
<td>Custom laboratory synthesis (very limited availability)</td>
<td>Very high</td>
<td>Liquid</td>
</tr>
</tbody>
</table>

Table 2. Availability, cost, and physical state of preceramic polymers

Additive manufacturing techniques for fabricating complex ceramic components...

ments include sintering, melting, or curing of powder) or by ink-jetting a liquid binder into powder (3-D printing). One major difference between powder-based additive manufacturing of a polymeric and a ceramic powder is that a polymeric powder is dissolved easily by solvents or melted by a laser, whereas a ceramic powder generally is bound by printing a binder and/or mixing the powder with additives. In addition, 3-D printing of a ceramic powder generates parts that are green bodies, which, therefore, require debinding and sintering steps to achieve the superior physicochemical properties of a ceramic material.

An intuitive approach for improving the properties of 3-D printed green bodies is postinfiltration of parts with a liquid preceramic polymer to fill the porosity between ceramic particles. This route can infiltrate 3-D-printed green bodies with liquid polysiloxane, which, afterward, can also be infiltrated with liquid silicon to generate SiSiC lattice structures or ceramic-matrix composite components.

However, preceramic polymer powders also are used directly as raw material for additive manufacturing. In particular, high ceramic yield polysiloxane powders are available commercially at low cost and in large amounts. Such materials are used in a selective laser-curing additive manufacturing process with SiC powder as filler. The same material can also be 3-D-printed in complex-shaped structures, such as porous lattices, which are successively converted to a SiOC ceramic upon heat treatment in an inert atmosphere.

A major advantage of using a polymeric powder instead of a ceramic is that polymers are readily soluble in several common organic solvents. Therefore, a wide range of low-viscosity solvents are used as printing liquids. In the printing process, particle surfaces are dissolved by the jetted solvent and, after vaporization, strong connecting necks form between particles. This mechanism also enhances densification of the printed powder compared with that of the surrounding powder bed (the printed part has a relative density of 80%, whereas the powder bed has a relative density of 45%). For example, Figure 1 shows a 3-D-printed coffee cup produced from a siloxane powder pyrolyzed at 1,200°C.

3-D printing of a polysiloxane allows for further exploitation of its polymeric nature. For example, mixing a catalyst into the printing liquid enables cross-linking of the polymeric part in a successive heat treatment. Two dissimilar printing heads even can print some areas with catalyst and others without catalyst, resulting in a part that partially cross-links and partially melts—for example, a shell structure that melts and infiltrates its inner cross-linked core structure. Following this concept, the cross-linked structure provides geometric boundary conditions, whereas the material without cross-linker melts to a shape determined by self-organization through interplay of external forces (e.g., surface tension, viscous forces, and gravitation). Therefore, 3-D printing can shape a roughly precise geometry that does not require high resolution and that self-organizes into its final shape.

Siloxane resins can also be mixed with inert or reactive fillers for 3-D printing. When heat-treated in air, the polymer leaves a SiO2 residue that can react with inorganic fillers to provide the desired silicate ceramic phases. In addition, this approach can use either inert or reactive fillers to 3-D print apatite–wollastonite bioglass–ceramic scaffolds.

Further work at The Federal Institute for Materials Research and Testing (BAM) (Berlin, Germany) also shows that it is possible to directly dissolve a siloxane in a printing solvent (such as isopropyl alcohol) and use it as a printing binder, which adds SiO2 to the final composition of the ceramic (data not yet published). BAM uses this approach to locally dope specific areas of the component with SiO2 or to establish compositional gradients.

Inkjet printing

Inkjet printing is a direct additive manufacturing technology that delivers...
droplets on a building platform. It is used to fabricate 3-D components, although with some limitations in overall 3-D architecture. Preceramic polymers, also loaded with SiC particles, can fabricate low-viscosity inks suitable for this additive manufacturing technology.10,11

Laminated object manufacturing
In laminated object manufacturing, a cross section of a manufactured object is defined on a sheet of material by cutting the contour with a knife or a laser, and the sheet then is stacked on top of previous ones. Preceramic polymers can function as nonsacrificial lamination aids to stack sheets produced by tape casting or other techniques.12,13 For instance, a preceramic paper can be infiltrated with polysiloxane and inert or reactive fillers to produce laminates.14 Laminated object manufacturing also can shape tape-cast sheets containing polysiloxanes, polysilanes, SiC, silicon, and catalysts. The main advantage of this approach is the ability to laminate tapes with no additional adhesive.15

Direct ink writing
Preceramic polymers also can be used in inks for direct ink writing technologies. An ink should fulfill some specific rheological requirements to enable fabrication of components with

Figure 2. (a) Hadystonite (Ca2ZnSi2O7) bioceramic scaffold. Inset shows microporosity in a strut. (b) SiOC ceramic-matrix composite scaffold. Inset shows carbon fiber pullout.
Additive manufacturing techniques for fabricating complex ceramic components . . .

large overhangs and spanning features. Namely, ink should flow through the deposition nozzle at high shear stresses and then quickly set at low stress (i.e., once out from the nozzle) to achieve shape retention (e.g., no sagging of overhangs or spanning features).

The ink, therefore, should behave as a non-Newtonian fluid, displaying shear thinning behavior with a yield stress. This behavior can be achieved with chemical additives that form a reversible gel—such as poly(ethylene glycol), carboxymethyl cellulose, or poly(acrylic acid)—or particles that form suitable reversible aggregates—such as fumed silica, Laponite (BYK Additives & Instruments, Wesel, Germany), or other clays. In some cases, rapid evaporation of the liquid in which the solid part of the ink is dispersed or dissolved is enough to increase viscosity of the printed filament and limit deformation after exiting the nozzle.16 nozzle diameter controls printing resolution (commonly 60 µm–2 mm), and printer heads can be based on a syringe or an extruder, the latter allowing use of inks with a wider range of viscosity values and better control of fluid mixing and delivery.

Pure preceramic polymers with cross-linked particles of the same siloxane resin can be added to adjust rheology of the ink,17 whereas introducing various fillers can modify the composition, phase assemblage, and properties of resulting structures. In particular, bioceramic scaffolds are obtained by mixing oxide precursors (e.g., carbonates or hydroxides) or oxide particles with a silicone resin and firing in air to fabricate single-phase18 or multiphase19 ceramic components with suitable properties for bone tissue engineering applications. Use of preceramic polymer in the formulation thus helps control ink rheology and develops the desired crystalline phases—silica produced during firing reacts in air with the oxide particles present. Decomposition of fillers also creates secondary porosity in the struts, which is beneficial for cell adhesion and for infiltration with additional materials, such as growth factor or biopolymers.

Further, adding glass particles with the same oxide composition as the silicone-based ink and crystallizing into the same phases (wollastonite and diopside) increases the strength of scaffolds because of viscous flow of glass, which helps obtain denser and defect-free struts.19 Addition of other types of fillers—such as graphene oxide, which spontaneously converts to graphene during pyrolysis—also enables functional properties, such as electrical conductivity, to printed parts.17

Ceramic-matrix composite structures also can be produced from a silicone resin by adding short carbon fibers with a diameter of 7.5 µm and an average length of ~100 µm. The shear stress generated by extrusion leads to very good alignment of fibers along the main axis of printed filaments. Further, adding SiC powder to the formulation can reduce formation of cracks in the ceramic matrix perpendicular to fibers because of constrained shrinkage during pyrolysis.20 Figure 2 shows examples of a bioceramic and ceramic-matrix composite scaffold.

Fused deposition modeling

Fused deposition modeling is based on the possibility of melting a polymer filament and taking advantage of increased viscosity during cooling to obtain solid structures capable of retaining a given shape. Therefore, it seems natural to consider this the most appropriate technique for direct additive manufacturing of preceramic polymers. However, we find no such scientific reports published so far, despite the ever expanding range of commercially available polymeric filaments.

One reason probably is related to the fact that solid preceramic polymers, with a melting temperature of ~70°C–90°C (for polysiloxanes) to ~230°C–250°C (for polycarbosilanes), have a glass transition temperature well above room temperature (>50°C). Therefore, filaments made from these materials are rigid and cannot be made into a spool that could easily be fed to the printing head. Experiments conducted at the
University of Padova (Padova, Italy) demonstrate that addition of plastifying agents allows fabrication of preceramic filaments, also loaded with calcium carbonate particles. Researchers there apply these agents to print bioceramic components using fused deposition modeling (data not yet published). However, much more study of suitable additives is needed before they are able to obtain an appropriate and stable preceramic feedstock to use with this additive manufacturing technology.

**Stereolithography, digital light processing, and two-photon stereolithography**

These indirect additive manufacturing techniques convert a liquid photocurable polymeric resin to a solid in a layer-by-layer fashion. However, stereolithography aims a laser beam across the print area, whereas digital light processing uses a digital projector screen to flash a single image of each layer across the entire platform at once. Therefore, the two technologies have differences in printing time, resolution, and surface quality. Often, support structures need to be added and later removed when fabricating components with complex architectures.

From a materials point of view, preceramic polymers need to be liquid or dissolvable in low-volatility solvents and possess photocurable moieties in a sufficient amount to provide adequate curing. In any case, subsequent thermal treatment or additional exposure to radiation can increase the density of cross-links. Very few photocurable preceramic polymers are commercially available, and existing ones have a very limited ceramic yield. Also, a suitable photoactive initiator (to rapidly activate the cross-linking reaction) and absorber (to limit the penetration depth of light and, thereby, control resolution along the z-axis) need to be added to the preceramic polymer.

There are three potential approaches.

- The first option is chemical modification of commercially available, high-ceramic-yield preceramic polymers by grafting photocurable moieties (e.g., acrylic or vinyl groups). For instance, (trimethoxysilyl)propylmethacrylate is reacted with a silicone resin, taking advantage of its Si-OH reactive groups and resulting in a preceramic polymer that can be shaped into complex structures with very good surface quality and a sufficiently high ceramic yield.

- The second option is physical blending of a high-ceramic-yield preceramic polymer with a photocurable polymer, which typically has very limited ceramic yield because of its molecular architecture and composition. The challenge in this case is to find the correct type and combination of polymers and solvent to enable fabrication of the component and to retain shape during pyrolysis. This is a very versatile approach that allows for manipulation of the ceramic yield and pyrolysis shrinkage in a wide range of values.

- The third option is to build up a preceramic polymeric structure via copolymerization, starting from monomeric/low-molecular-weight photocurable precursors. For instance, (mercaptopropyl)methylsiloxane mixed with vinylmethoxysiloxane yields low-density SiOC components with high strength and excellent stability at high temperatures in air.

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Additive manufacturing techniques for fabricating complex ceramic components . . .

Two-photon photopolymerization in conjunction with photosensitive preceramic polymers enables fabrication of 3-D structures with a resolution of a few hundred nanometers or better. However, the difficulty of detaching components from the build platform makes it challenging to obtain self-standing components and so far has limited the pyrolysis temperature to 600°C. Introduction of nanopowders reduces distortions generated by the resulting constrained shrinkage during pyrolysis, but a low-shrinkage preceramic polymer has been used with success. In all cases, addition of inert or reactive powders to the preceramic polymer solutions can produce ceramics of various compositions and properties, on the condition that they interfere in a well-controlled manner with propagation of light into the liquid preceramic, depending on their amount, size, and optical characteristics. Figure 3 shows examples of a complex, highly porous diamond structure produced at various length scales by stereolithography and two-photon photopolymerization.

Advanced additive manufacturing with preceramic polymers

The research discussed above demonstrates that preceramic polymers offer the potential to produce relatively easily ceramic components in a wide range of compositions using a variety of additive manufacturing technologies. However, when discussing additive manufacturing in combination with preceramic polymers, we should consider that they provide convenient technical solutions and process improvements and also enable new advanced manufacturing strategies capable of overcoming some of the problems that are intrinsic to additive manufacturing in general.

In additive manufacturing, addition of incremental portions of material build up a 3-D object. The method adds material layer by layer, followed by local consolidation, as filaments, individual droplets, particles, etc. Successively smaller incremental portions of the material yield higher volumetric resolution of the building process. On the other hand, smaller portions increase time of the build-up process. Therefore, a high volumetric definition generally reduces rapidity of the build-up. Apart from volumetric resolution and process speed, material properties are an additional major concern in additive manufacturing. To fulfill these criteria, we need to further improve additive manufacturing technologies or devise new technologies, with parallel intensive R&D activities for the development of appropriate feedstocks.

Intrinsically, additive manufacturing can realize a minimum feature size with appreciable resolution. Self-organization processes can help increase process speed and obtain a precise definition of the outer contour of parts. Artifacts, such as kinks or steps, from the material deposition process can be smoothed out. However, using this strategy, we can also build entire structural elements with almost ultimate high precision even without a high-resolution additive manufacturing process, which favors build-up speed. Figure 4 shows an example of a core–shell lattice structure produced by 3-D printing of a siloxane powder, which was then heated to low temperature and allowed to self-organize into its final geometry.

Moreover, we can exploit large shrinkage (up to 70% linear, depending on molecular architecture and ceramic yield of the polymer) during the polymer-to-ceramic conversion to achieve higher resolution with respect to the particular additive manufacturing process. Further, the possibility of strongly diluting the preceramic polymer in suitable solvents could enable extrusion (direct ink writing) through small capillaries (diameter <50 μm) to produce very fine ceramic structures.

Finally, development of unique ceramic phases (such as SiOC or SiCN) containing graphenelike carbon nanoscale inclusions also may provide the possibility of manufacturing components with functional properties useful in various engineering applications. Further, addition of fibers to a preceramic polymer feedstock could enable manufacturing of composite ceramic components with enhanced mechanical characteristics.

About the authors

Johanna Schmidt is a Ph.D. student, Giorgia Franchin is postdoctoral researcher, and Paolo Colombo is professor in the Department of Industrial Engineering at the University of Padova (Padova, Italy). Colombo also is adjunct professor in the Department of Materials Science and Engineering at Pennsylvania State University (University Park, Pa.). Andrea Zocca is a postdoctoral researcher and Jens Günster is head of the Ceramic Processing and Biomaterials Division at The Federal Institute for Materials Research and Testing (BAM) (Berlin, Germany). Günster also is professor at the Institute of Non-Metallic Materials at Technical University Clausthal (Clausthal, Germany). Contact Colombo at paolo.colombo@unipd.it.
References


Advanced materials for 3-D printing

By Andrew McWilliams

The total global market for 3-D printing materials was $475.4 million in 2015 and is expected to rise to $576.6 million in 2016 and more than $1.5 billion in 2021, at a compound annual growth (CAGR) of 21.5%. The industry is very concentrated—just four companies, Arcam, ExOne, 3D Systems, and Stratasys, control an estimated 75% of the market.

As an indication of the growth of the 3-D printing materials market, BCC Research identified at least 90 U.S. patents pertaining directly to materials used in 3-D printing through a keyword search of the U.S. Patent and Trademark Office database. Photopolymers accounted for 58% of the patents; thermoplastics and polymers accounted for 19 patents; and metals accounted for 16 patents.

Photopolymers accounted for the largest share of the market (59.8%) in 2015, but they comprise the slowest growing segment, with a projected CAGR of 16.3% (Table 1). As a result, this segment’s market share should decline to roughly 47% by 2021. Meanwhile, thermoplastics will remain the second-largest segment, with 25%–26% of the market across the entire period. Ceramics, metals, and other materials account for the rest of the market.

The medical and dental sector is the largest end-user of 3-D printing materials, accounting for more than 50% of total global consumption in 2015 and 29% in 2021 (Table 2). Automotive products are the second largest end-users of 3-D printing materials in 2015, when they accounted for approximately 22% of the market. Consumer products accounted for 16% of the market in 2015. However, consumer products are growing much faster than automotive end uses and, as a result, should become the second largest segment with almost 20% of the market by 2021. Aerospace comes in third, with 18% of the market in 2015 and 20% in 2021.

The market for 3-D printed ceramic materials is still in the early stages of development, and thus, is currently small. The total value of ceramic materials consumed in 3-D printing was approximately $2.8 million in 2015. This market is expected to grow at a CAGR of 16.9%, reaching $3.3 million in 2016 and $7.2 million in 2021.

Alumina was the most widely used ceramic 3-D printing material in 2015, accounting for nearly 54% of total consumption. Zirconia accounted for almost 36% of consumption. Other ceramics, including hydroxyapatite (7.1%), are less widely used at present. Alumina- and zirconia-based ceramic materials are expected to continue to dominate the market through 2021.

Consumer products was the largest end-use sector of 3-D printing ceramic materials in 2015, accounting for nearly 60% of total consumption. Zirconia accounted for almost 36% of consumption. Other ceramics, including hydroxyapatite (7.1%), are less widely used at present. Alumina- and zirconia-based ceramic materials are expected to continue to dominate the market through 2021.

Aerospace’s share is expected to decline from 6% in 2016 to about 4% in 2021, while the medical and dental sectors are expected to increase to over 22%.

About the author
Andrew McWilliams is project analyst for BCC Research. Contact McWilliams at analysts@bccresearch.com.

Resource

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Table 1. Global 3-D printing market by material through 2021 ($ millions)

<table>
<thead>
<tr>
<th>Material</th>
<th>2015</th>
<th>2016</th>
<th>2021</th>
<th>CAGR% 2016–2021</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photopolymers</td>
<td>284.4</td>
<td>334.6</td>
<td>711.8</td>
<td>16.3</td>
</tr>
<tr>
<td>Thermoplastics</td>
<td>120.1</td>
<td>149.0</td>
<td>392.3</td>
<td>21.4</td>
</tr>
<tr>
<td>Ceramics, metals, and other materials</td>
<td>70.9</td>
<td>93.0</td>
<td>423.5</td>
<td>35.4</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>475.4</strong></td>
<td><strong>576.6</strong></td>
<td><strong>1,527.6</strong></td>
<td><strong>21.5</strong></td>
</tr>
</tbody>
</table>

Table 2. Global 3-D printing market by end-use sector through 2021 (%)

<table>
<thead>
<tr>
<th>End-use sector</th>
<th>2015</th>
<th>2016</th>
<th>2021</th>
<th>CAGR% 2016–2021</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medical and dental</td>
<td>25.3</td>
<td>26.2</td>
<td>28.8</td>
<td>23.9</td>
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<tr>
<td>Automotive</td>
<td>21.6</td>
<td>20.5</td>
<td>15.7</td>
<td>15.3</td>
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<tr>
<td>Aerospace</td>
<td>17.8</td>
<td>18.2</td>
<td>20.1</td>
<td>23.9</td>
</tr>
<tr>
<td>Consumer products</td>
<td>15.8</td>
<td>16.8</td>
<td>20.1</td>
<td>25.9</td>
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<tr>
<td>Other</td>
<td>19.5</td>
<td>18.3</td>
<td>15.3</td>
<td>17.2</td>
</tr>
</tbody>
</table>

Table 3. Global 3-D printed ceramic material market share by end use sector through 2021 (%)

<table>
<thead>
<tr>
<th>Sector</th>
<th>2015</th>
<th>2016</th>
<th>2021</th>
<th>CAGR% 2016–2021</th>
</tr>
</thead>
<tbody>
<tr>
<td>Consumer products</td>
<td>64.3</td>
<td>63.6</td>
<td>55.6</td>
<td>13.8</td>
</tr>
<tr>
<td>Medical and dental</td>
<td>17.9</td>
<td>18.2</td>
<td>22.2</td>
<td>21.7</td>
</tr>
<tr>
<td>Aerospace</td>
<td>3.6</td>
<td>6.1</td>
<td>4.2</td>
<td>8.4</td>
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<tr>
<td>Other</td>
<td>14.2</td>
<td>12.1</td>
<td>18.0</td>
<td>26.6</td>
</tr>
</tbody>
</table>
MATERIALS WITH MARKET VALUE:
Global ceramic and glass industry poised to reach $1 trillion
Welcome to the *ACerS 2017 Bulletin Business Supplement*!

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Editor, *American Ceramic Society Bulletin*
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Traditional glass and ceramics comprise 89% of the global market; however, growth will be largest in technical ceramic sectors in the next five years.

The global ceramic and glass industry is assessed at $717.7 billion in 2016 and is expected to grow at an overall compounded annual growth rate (CAGR) of 6.2%. The industry is global—Figure 1 maps main producers or manufacturers of various categories of ceramics and glass by the location of each company’s headquarters.

Cements dominate the industry with a 42.7% share of the total, but there are other categories of products that, combined with cements, form the bulk of the market at more than 80% of the total—namely, structural clay products, electroceramics, container glass, refractories, and flat glass for construction and transportation (Figure 2).

Glass and traditional ceramics represent a combined 89% of the global market. However, technical ceramics will be associated with the fastest market growth during the next five years. Projected to rise at a CAGR greater than 7%, electroceramics, medical ceramics, structural ceramics, and ceramics for extreme environments will be the main contributors to this overall healthy expansion. These products will also be joined by structural clay products in terms of outstanding growth and will drive the global ceramic and glass industry to a nearly $1 trillion market by 2021.
The scope of this analysis is informed by the definition of ceramics and glass adopted here: ceramics are natural or synthetic inorganic, nonmetallic, polycrystalline materials, whereas glass is made of inorganic, non-metallic materials with an amorphous structure. Glass-ceramics—materials with properties in between—are also included in this market analysis, but to simplify data reporting, they are grouped with ceramics.

Traditional versus advanced or technical products

Ceramics and glass are differentiated according to two main categories based on end-use: advanced/technical and traditional products (Figure 3). Traditional ceramics and glass include products that have been used since ancient times for construction, decoration, furnishing, food and beverages, transportation, and industrial applications. Most market classification systems include refractory ceramics as “traditional” ceramics, even though modern refractory technology is highly sophisticated. Advanced ceramics and glass comprise products used in nontraditional industries. Many of these products were introduced after World War II to meet the requirements of fast-growing industry sectors, such as electronics, optoelectronics, energy, and healthcare.

In recent years, the term “technical” or “engineered” is increasingly used instead of “advanced” to designate these products. In fact, “advanced” is most often used to indicate recently developed and innovative manufactured products. For example, solar-control glass is a type of flat glass and therefore falls within the traditional ceramic/glass category, but it is also considered an advanced product because it is obtained by applying very thin films to glass that modify its refractive index and reflect infrared radiation. Another example of a traditional but advanced ceramic is tile that incorporates photovoltaic cells.

To obtain a more detailed overview of the market, gain valuable insights, and predict future trends, ceramic and glass products in this analysis sort into three groups: traditional ceramics, technical ceramics, and glass.

It is also noteworthy that ceramic and glass forming technologies have evolved to the point that myriad product configurations (i.e., shapes and sizes) are commercially available.

### Table 1. Classification of traditional ceramics by product type

<table>
<thead>
<tr>
<th>Product type</th>
<th>Main products</th>
<th>End-use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractories</td>
<td>Refractory bricks, tiles, blocks, linings, crucibles, spouts, ladles, fibers</td>
<td>Industrial applications</td>
</tr>
<tr>
<td>Structural clay products</td>
<td>Tiles, bricks, drainage/soil pipes, and chimney pipes/linings</td>
<td>Construction and furnishing/</td>
</tr>
<tr>
<td></td>
<td></td>
<td>decoration</td>
</tr>
<tr>
<td>Whitewares</td>
<td>Fine tableware/cookware, china, sanitary ware, decorative articles,</td>
<td>Food/beverage, construction,</td>
</tr>
<tr>
<td></td>
<td>and porcelain coatings</td>
<td>and furnishing/decoration</td>
</tr>
<tr>
<td>Earthenware</td>
<td>Tableware, cookware, vases, pots, figurines, and decorative objects</td>
<td>Food/beverage and furnishing/</td>
</tr>
<tr>
<td></td>
<td></td>
<td>decoration</td>
</tr>
<tr>
<td>Abrasives</td>
<td>Abrasive powders, grains, beads, and wheels</td>
<td>Industrial applications</td>
</tr>
<tr>
<td>Cements</td>
<td>Portland cement, mortars, and concrete bricks/blocks</td>
<td>Construction</td>
</tr>
</tbody>
</table>

Figure 1. Main producers or manufacturers of types of ceramics and glass by headquarter location.

Figure 2. Total ceramic and glass industry market share by product type, 2016.
available, ranging from powders and microspheres to beads, objects with complex geometric shapes, films, coatings, panels, and multilayer components, produced either as monoliths or ceramic composites.

The market analysis includes all of these configurations, except powders used as raw materials in ceramic processing. As an example, the market assessment covers abrasives in powder form, but does not include barium titanate powder for producing ceramic capacitors. In other words, the ceramic and glass industry is evaluated from a product or end-use standpoint, rather than from a raw materials standpoint. In addition, market figures represent sales of ceramic and glass products at the manufacturer level.

**Market for traditional ceramics**

Traditional ceramics include refractories, structural clay products, whiteware, earthenware (i.e., pottery), abrasives, and cements (Table 1).

**Refractories**

Refractories are used as liners, molds, crucibles, ladles, and other high-temperature items that find application primarily in the metallurgical sector (for both ferrous and nonferrous metals) and also in other industrial sectors, such as power generation and glass, ceramics, and cement manufacturing. The metallurgical sector currently accounts for approximately 80% of the refractory market.

The refractory market (Figure 4) comprises three main segments based on product type: bricks and stackable shapes, which include bricks (standard or unconventional shapes), blocks, tiles, cylinders, and other articles that are typically clay-based; monoliths, which are unshaped products formed on site; and other shapes, such as precast liners, crucibles, ladles, valves, nozzles, diffusers, boards, and fibers.

Bricks and stackable shapes, which represent the most traditional products, currently account for the largest share of the market, with global revenues of $19.1 billion in 2016, or 57.7% of the total refractory market (Figure 5). Reflecting the overall moderate growth of the iron and steel industry and other sectors where they are used, the
market for these refractory products is forecast to grow at a 3.7% CAGR through 2021.

Monolithic refractories, which generated global revenues of $8.2 billion in 2016 (or 24.8% of the total), are experiencing faster growth worldwide due to several key advantages, such as lower cost, faster installation, and reduced downtime for repair. The market for these products is projected to have a CAGR of 4.2% over the next five years.

Other shapes, which had sales of $5.8 billion in 2016 (17.5% of the total), include a group of products in which demand is driven by the two previously mentioned markets.

Table 2. Classification of advanced/technical ceramics by product type

<table>
<thead>
<tr>
<th>Product type</th>
<th>Main products</th>
<th>End-use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Medical ceramics</td>
<td>Medical implants, dental implants and prostheses, orthodontic products, biomedical coatings, part for implantable electronic devices, surgical instruments, drug delivery devices, tissue engineering scaffolds, pumps</td>
<td>Life sciences</td>
</tr>
<tr>
<td>Electroceramics</td>
<td>Capacitors, inductors, fixed and variable resistors, circuit protection devices, piezoelectric devices, antennas, substrates and films for circuit devices, ceramic packages, low- and high-temperature co-fired ceramics, sensing elements, permanent magnets, spark plugs, electrical insulators, ceramic arc tubes, hermetic insulating packaging</td>
<td>Electronics and electrical applications, defense and security, sensors and instrumentation, energy</td>
</tr>
<tr>
<td>Optoceramics</td>
<td>Transparent conductive coatings, substrates and films for photonic integrated circuits, optical filters, parts for solid-state lasers, components for solid-state lighting devices, optical coatings, optical switches, scintillators, non-linear optical components, components for military systems</td>
<td>Optical applications, optoelectronics, defense and security, sensors and instrumentation</td>
</tr>
<tr>
<td>Structural ceramics and ceramics for extreme environments</td>
<td>Cutting tools, bearings, pump seals, valves, nozzles, friction products, wear-resistant coatings, catalysts, catalyst carriers, filtration media, high- and ultra-high temperature components, armor, parts for nuclear reactors</td>
<td>Mechanical applications, chemical applications, environmental applications, defense and security, aerospace and space exploration, sensors and instrumentation</td>
</tr>
<tr>
<td>Ceramics for energy transfer, storage and conversion</td>
<td>Components for solar energy storage, thermoelectric generators, superconducting devices, batteries, and fuel cells</td>
<td>Energy</td>
</tr>
<tr>
<td>Other ceramics</td>
<td>Cosmetic products, antibacterial agents, food packaging, additives for lubricants, paint and ink additives</td>
<td>Consumer products, chemical applications</td>
</tr>
</tbody>
</table>

Their growth prospects reflect this, with a 4.1% CAGR through 2021. The 4.1% CAGR matches the overall growth rate of the global refractory industry, which is projected to have a CAGR of 4.2% over the next five years.

**Structural clay products**

Structural clay products include many types of tiles (e.g., floor, wall, decorative, and roof), construction bricks (i.e., non-refractory bricks), and other shapes, such as drainage, sewer, and chimney pipes and linings. Tiles represent by far the largest share of the structural clay product market (Figure 6), with 73.7% of the total in 2016 (Figure 7), corresponding to global revenues of $85.6 billion. Improvements in the housing market and growing demand for tile products in developing countries are projected to spur healthy growth during the next five years, leading this segment to expand at an 8.8% CAGR through 2021.

Construction bricks, which generated global revenues of $29.7 billion in 2016 (or 25.6% of the total), are experiencing greater competition from alternative, more environmentally friendly materials, such as structurally insulating panels and hardwood. Therefore, a 5.2% CAGR is projected for this segment during the forecast period.

At $0.8 billion in 2016 (or 0.7% of the total), other shapes currently represent a very small market with moderate growth prospects (4.6% CAGR over the next five years). Overall, the structural clay products market generated global revenues of $116.1 billion in 2016 and is forecast to rise at a 7.9% CAGR through 2021.

**Other traditional ceramics**

The market for all remaining other traditional ceramics (OTC) is very large (Figure 8), reaching $374.6 billion in 2016. Cements account for the largest share by far, at 81.8% of the total (Figure 9). However, the cement industry has not yet fully recovered from the 2007–2009 global downturn. A lack of new investments in infrastructure and increasing price pressure from Chinese products is keeping revenues subdued; consequently, moderate growth for this market will continue, at least in the short term.

Within the OTC market, the fastest growth is forecast for whitewares. Driven by increasing sales of sanitaryware in developing countries and growth in the number of restrooms per household in Western countries, the market for whitewares is projected to expand at a CAGR of 8.3% during the next five years, reaching $44.4 billion in 2021. Although smaller, abrasives and earthenware also represented a relevant

Figure 6. Structural clay products market, 2016–2021.

Figure 7. Structural clay products market share by type, 2016.
share of the 2016 market at 7.7% and 2.6%, respectively. Moderate growth is projected for these mature markets through 2021.

**Market for technical ceramics**

Technical ceramics (Table 2) are classified based on functionality (e.g., biocompatibility, electrical properties, optical properties, mechanical strength, and high-temperature resistance) according to the following types: medical ceramics; electroceramics; optoceramics; structural ceramics and ceramics for extreme environments; ceramics for energy transfer, storage, and conversion; and other ceramics.

**Medical ceramics**

The medical ceramics market (Figure 10) is estimated to have reached $12.8 billion in 2016. The largest share of the market (Figure 11) is represented by medical implants, at 45.3% of the total. In recent years, ceramic parts and coatings for hip, knee, joint, cranio-maxillofacial, and spinal implants have grown at a healthy rate, enabling this segment to surpass dental ceramics, which, until recently, represented the largest application for medical ceramics. The market for medical implants is driven by an increasing number of orthopedic procedures, primarily due to a rapidly expanding elderly population worldwide, and by the growing availability of these procedures in developing countries. These trends are expected to continue during the next five years, resulting in a CAGR of 7.2% through 2021.

Dental ceramics generated estimated revenues of $4.9 billion in 2016 (or 38.3% of the total). Ceramic prostheses and implants (e.g., crowns, bridges, and all-ceramic root implants) represent the largest share of this market, although in recent years orthodontic products such as braces have increasingly adopted the use of ceramic materials to create “invisible” devices. Because they can match the natural color of the tooth, ceramic materials provide aesthetically better results compared to traditional metal products.
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Further, with respect to dental implants, ceramic materials offer better osseointegration than titanium and are being engineered to prevent infection and deterioration, particularly through the use of nanomaterials. These factors are expected to drive robust market growth for dental ceramics through 2021 and lead to global revenues of $6.8 billion by 2021.

Within the medical sector, the fastest market growth is forecast for components used in implantable electronic devices, with a CAGR of 8.4% through 2021, and other products (13.2% CAGR). Sales of feedthroughs and circuit devices for pacemakers, defibrillators, neurostimulators, and cochlear implants, as well as tissue engineering scaffolds, medical pumps, and piezoelectric devices for medical tools and instruments, will all contribute strongly to growth of the medical ceramics market, projected to reach $18.4 billion in 2021, corresponding to a CAGR of 7.5% for the five-year forecast period.

Electroceramics

Electroceramics are products in which the ceramic is utilized for its electrical properties, typically insulating properties and capacity to store electrical energy (dielectric properties). Although ceramics are traditionally considered to be insulators, their composition can be tailored also to exhibit semiconducting, conducting, piezoelectric, or magnetic properties. As such, ceramics find numerous applications in electronic and electrical applications, either as components of circuits (e.g., capacitors, inductors, and resistors) or as circuit devices (e.g., low-temperature cofired ceramics or LTCCs). These components and devices also are used to manufacture intelligent systems for defense and security and many types of sensors, whereas circuit boards and modules containing these components are becoming ubiquitous. Superconductors and solid electrolytes are also types of electroceramics, but in this study they are included in the energy category because their end-use is primarily for energy transfer and storage.

Ceramic devices used as electrical insulators, such as hermetic packaging, spark plugs, ceramic arc tubes, and protective parts (e.g., beads and tubing) for bare wires and power lines, currently represent the largest share of the electroceramics market (Figure 12), with global revenues estimated at $12.3 billion in 2016, corresponding to 28.6% of the total (Figure 13). These devices are primarily used in slow-growing sectors, such as automotive, aerospace, and electricity distribution. Thus, a moderate CAGR of 5.5% is forecast for this segment during the next five years.

The second-largest category of electroceramics is passive components, whose market is valued at $11.0 billion in 2016 (or 25.6% of the total). Ceramic capacitors represent the bulk of the passive component market, with estimated revenues of $8.4 billion in 2016. Other passive components include fixed and variable resistors, inductors, and circuit protection devices.

The market for passive components follows the general semiconductor market. Sales of semiconductors and related components have experienced healthy growth during 2009–2015 with a CAGR of 7.5%. However, this is an inherently cyclical market that was already exhibiting signs of a slowdown in 2016. In addition, price pressures continue to persist for passive components. In fact, the average unit selling price has dropped at an annual rate of approximately 3% during the past 10 years. As a result,
a CAGR of 5.7% is projected for ceramic passive components through 2021.

Piezoelectric ceramics (excluding piezoceramics for medical use) generated global revenues of $9.6 billion in 2016 (22.3% of the total electroceramics market).

These devices are becoming increasingly popular for use as filters, resonators, transducers, acoustic elements, actuators, and components for pressure sensors. Easy to manufacture in various shapes and sizes, piezoelectric ceramics contribute significantly to the miniaturization of electromechanical features and, consequently, are gaining greater penetration in consumer electronics, robotics, automotive, sensors and instrumentation, and energy harvesting. As a result, a CAGR of 14.7% is projected for these devices through 2021.

Other electroceramics, which consist primarily of magnets and circuit devices for high-reliability applications (e.g., low- and high-temperature cofired ceramics, and ceramic electronic substrates) also are expected to experience moderate growth and expand at a CAGR of 6.3% from $10.1 billion in 2016 (23.5% of the total).

Overall, the electroceramics market is forecast to grow at a healthy 8.1% CAGR during the next five years and generate global revenues of $63.4 billion by 2021.

Optoceramics

Optoceramics are products that exploit different optical properties offered by various types of ceramic and glass-ceramic materials. Coatings represent the largest share of the optoceramics market (Figure 14), in particular transparent conductive coatings (TCOs), which generated global revenues of $4.2 billion in 2016, corresponding to 56.8% of the total optoceramics market (Figure 15). TCOs currently are based primarily on indium-tin oxide (ITO), which is by far the most popular, followed by aluminum-doped zinc oxide (AZO) and fluorine-doped tin oxide (FTO). They find their main application in glass for displays and solar cells. However, other materials, such as carbon nanotube films, transparent organics, and nanosilver films, are emerging as lower-cost alternatives and are expected to gain a larger share of this market during the next five years. As a result, a modest 3.5% CAGR is forecast for TCO coatings through 2021.

The second-largest segment of the optoceramics market is represented by optical coatings, in particular antireflective (i.e., antiglare) coatings, which are estimated to account for 36.5% of the total in 2016, with global revenues of $2.7 billion. Optical coatings are becoming increasingly popular in various consumer (e.g., eyewear) and industrial applications (e.g., displays, instrumentation, and solar cells). The market for optical coatings is forecast to expand at a 7.6% CAGR through 2021.

Optoceramics for other applications, such as photonic integrated circuits, lasers, solid-state lighting, scintillators, optical filters, domes, and lenses for military systems, are currently in early stages of commercialization, but their use is expected to rapidly increase during the forecast period due to the opening of new frontiers in optoelectronics, defense, and sensors and instrumentation. The market for these products, which is estimated to be valued at no more than $500 million in 2016, is forecast to expand at a 17.1% CAGR through 2021. Currently valued at $7.4 billion, the total market for optoceram-
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Structural ceramics and ceramics for extreme environments

The market for structural ceramics and ceramics for extreme environments (STEE) is estimated at $14.3 billion in 2016 (Figure 16). Catalysts and catalyst carriers (i.e., substrates and media that support the catalyst) represent the largest share of this market at 37.1% of the total in 2016 (Figure 17), with revenues of $5.3 billion. These products are primarily used in petroleum refining, chemical processing, and automotive emissions control. Increasingly strict environmental regulations will be the main driver for growth during the next five years, with the market forecast to expand at a 7.2% CAGR.

Filtration media include both filters and membranes. Ceramic filtration media are achieving increasing market penetration. Although more expensive than polymeric media, ceramic media are favored for treatment of high-temperature and/or corrosive fluids and also offer the advantage of being less affected by fouling and can be more easily regenerated with steam and heat treatments. The higher initial cost is compensated by a longer lifetime and reduced downtime. With the market valued at $3.7 billion in 2016 (25.9% of the total), ceramic filtration media are projected to grow at a 9.8% CAGR through 2021.

Wear- and corrosion-resistant parts and coatings include products such as ceramic cutting tools, bearings, pump seals, nozzles, valves, and brakes. They are used in fairly mature industry sectors, and therefore moderate growth is expected during the forecast period. Sales of these products are forecast to expand at a 6.6% CAGR through 2021.

Other STEE ceramics include products used in the defense, aerospace, and energy sectors, such as armor, aircraft engine parts, gas turbine elements, and protective casings for spent nuclear rods. The market for these ceramics reached $2.4 billion in 2016, corresponding to a 16.8% share of the total. The aerospace industry is in the process of substantially increasing its consumption of ceramic-based parts, driving the market to an 8.4% CAGR during the next five years.

Table 3. Classification of glass by product type

<table>
<thead>
<tr>
<th>Product type</th>
<th>Main products</th>
<th>End-use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Traditional glass</td>
<td>Flat glass, container glass, pressed and blown glass, lighting fixture glass, mirrors, decorative glass, glass fibers, eyewear</td>
<td>Construction, transportation, furnishing and decoration, food and beverages</td>
</tr>
<tr>
<td>Technical glass</td>
<td>Display glass, glass for solar and thermal panels, optical waveguides, optical filters, precision lenses and mirrors, glass sealants for fuel cells, optical components for microscopes and other instruments, night vision systems, passivation glass for electronic devices, medical implants, dental restoration, tissue engineering scaffolds, microfluidic chips, drug carriers, periodontic products, glass microsphere for cancer therapy, anti-inflammatory agents, containers for pharmaceutical packaging</td>
<td>Electronics, optoelectronics, life sciences, energy, defense and security, aerospace and space exploration, sensors and instrumentation, consumer products</td>
</tr>
</tbody>
</table>

Figure 16. Structural ceramics and ceramics for extreme environments ceramics market, 2016–2021.

Figure 17. Structural ceramics and ceramics for extreme environments ceramics market share by type, 2016.

Figure 18. Ceramics for energy and other uses market, 2016–2021.

Figure 19. Ceramics for energy and other uses market share by type, 2016.
As a result, the STEE ceramics market is projected to experience robust growth overall, with a CAGR of 8.0% through 2021.

**Ceramics for energy and other uses**

Ceramics for energy and other uses (CEOT) represent a small market with global estimated sales of $1.2 billion in 2016 (Figure 18). Ceramics for energy include components and coatings for devices that convert, transfer, or store energy. Examples of these devices are fuel cells, batteries, solar panels, solar collectors, superconducting magnets, and thermoelectric generators. Ceramics for other uses include products that do not fall within any of the previous categories. They can be classified as consumer products (e.g., platelet additives for cosmetics) and chemistry/food products (e.g., microspheres for paints and coatings, antibacterial balls for water tanks, coatings for food packaging, and additives for lubricants).

Components for energy devices represent the largest share of the CEOT market, at 75% of the total (Figure 19). Superconductive wires account for more than 50% of revenues. Utilization of ceramics for fabrication of energy devices is expected to increase quite rapidly during the next five years as production technologies improve and manufacturing costs decrease, resulting in a 9.6% CAGR for the global CEOT market through 2021.

**Glass market**

Traditional glass (Table 3) includes products such as flat glass for construction and transportation (e.g., windows, facades, doors, windshields, security glass, control glass, and smart glass); container glass (e.g., bottles for beverages and perfumes); pressed and blown glass (i.e., tableware glass); glass fibers (used primarily as reinforcing agents); and other glass for household use and consumer products (e.g., mirrors and glass for furniture, glass for lighting fixtures, decorative and art glass, and eyewear).

The traditional glass market generated global sales of $94.6 billion in 2016 and is forecast to expand at a 4.6% CAGR through 2021, reflecting the overall slow to moderate growth of these mature sectors.
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(Figure 20). The largest share is associated with container glass, which reached revenues of $39.4 billion in 2016, corresponding to 41.6% (Figure 21). Other relevant industry segments are flat glass for construction (25.7%), flat glass for transportation (15.3%), and glass fibers (8.1%).

Healthier growth is forecast for the technical glass market, which is projected to rise at a 6.1% CAGR during the next five years, from $20.6 billion in 2016 (Figure 22). Glass for electronics, which is primarily used to produce displays, represents the largest segment of this market (Figure 23), with a 46.1% share of the total, corresponding to revenues of $9.5 billion in 2016. However, industry growth will be primarily driven by rapid growth in the energy (solar cell fabrication) and life sciences sectors. Within the life sciences sector, container glass for pharmaceutical use currently represents the largest application in terms of revenues. However, glass is finding new applications within rapidly expanding niches, such as microfluidic devices, bioglass, drug delivery devices, and antibacterial products.

Summary and conclusions

The combined ceramic and glass industry is projected to reach a nearly $1 trillion value by 2021. While all sectors explored in this analysis are projected to experience growth, traditional ceramics are expected to contribute most to the industry’s growing market value, largely due to cements (Figure 24). However, technical ceramics represent the fastest growing segment of the market, with burgeoning applications in electroceramics, especially piezoelectrics (Figure 25). In addition, glasses contribute a steady and significant portion of the total market.

About the author

Margareth Gagliardi is a market research analyst and consultant in advanced materials and emerging technologies. For more information, contact her at margarethg@earthlink.net.

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Figure 24. Total ceramic and glass industry market value by product type, 2016–2021.

Figure 25. Ceramic and glass industry CAGR, 2016–2021.
ACerS Fellow Ivar Reimanis on Denali’s Summit, June 2016. Credit: Reimanis
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9–11 ACerS Structural Clay Products Division and Southwest Section Meeting in conjunction with the National Brick Research Center Meeting – Fort Worth, Texas; www.ceramics.org/rcd

21–26 12th Pacific Rim Conference on Ceramic and Glass Technology, including Glass & Optical Materials Division Meeting – Hilton Waikoloa Village, Waikoloa, Hawaii; www.ceramics.org/pacrim12

June 2017
14–16 BIT’s 6th Annual World Congress of Advanced Materials 2017 – Xi’an, China; www.bitcongress.com/wcam2017

26–28 8th Advances in Cements-Based Materials (Cements 2017) – Georgia Tech, Atlanta, Ga.; www.ceramics.org


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September 2017

October 2017

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Polymer-derived ceramic and ceramic-like coatings: Innovative solutions for real problems

By Gilvan Barroso, Quan Li, Günter Motz, and Rajendra K. Bordia

Polymer-derived ceramic coating systems have tunable chemical composition, versatility and ease of processing, and excellent properties, making these materials promising for a variety of applications.

Polymer-derived ceramic (PDC) technology focuses on the conversion of metalorganic compounds, also known as preceramic polymers, to ceramic materials. Preceramic polymers, which are either liquids or meltable/soluble solids, are subjected—after or during shaping processes—to chemical and thermal treatments, which induce cross-linking of the polymers into thermoset materials. Further thermal treatment converts the thermoset polymer to an amorphous ceramic and, at higher temperatures, to a crystalline ceramic.

In comparison with traditional powder technology to prepare ceramic materials, the PDC route has advantages of homogeneity of chemical composition at the molecular level and lower processing temperatures. Moreover, shaping in the polymeric state before conversion to ceramic reduces processing cost and time and extends the lifespan of shaping machines.

Because of the availability of a broad spectrum of polymer and ceramic shaping technologies, such as casting, tape casting, fiber drawing, molding, and pressing, the PDC route enables realization of a variety of ceramics, including bulk parts, cellular materials, fibers, and coatings. PDC is especially attractive for coating applications, because it enables use of wet deposition techniques, typical of organic coatings, to prepare layers with properties of ceramic materials, such as high-temperature resistance and hardness.

Preceramic polymers
Preceramic polymers are mostly silicon-based compounds with a combination of additional elements (e.g., boron, nitrogen, carbon, and oxygen) in the main chain and side groups, including hydrogen, alkyl, vinyl, and aryl. Composition of the backbone and side groups determines behavior of the material in the polymeric state and properties of the resulting ceramic. Researchers can adjust the
resulting material’s rheology, reactivity, temperature resistance, and many other properties by manipulating the chemistry of preceramic polymers.

To be suitable for PDC coatings, precursors must be either a liquid or soluble solid with an appropriate rheology to allow deposition of the coatings in liquid phase. Moreover, the technique also requires a latent reactivity to enable conversion of the liquid or soluble polymer to a thermoset material and a sufficient ceramic yield (mass yield after conversion to ceramic). Figure 1 shows preceramic polymers most commonly used for coating applications.

**Fillers**

The greatest challenge of PDC is extensive shrinkage of preceramic polymers during conversion to ceramics. This shrinkage is caused by mass loss (up to 50%) and by densification (~1 g/cm³ as polymer, and up to 3–4 g/cm³ as ceramic). Because of stresses caused by the volume change, the thickness of pure PDC coatings is limited to a few micrometers.

Addition of passive or active filler particles to the precursors can counter shrinkage. Passive fillers, such as ZrO₂, TiO₂, SiC, and BN, reduce only the volume fraction of the shrinking phase (precursor), whereas active fillers, such as Al, Ti, TiSi₂, ZrSi₂, and TiB₂, react with gaseous products or with the atmosphere to form phases with a higher volume than that of the initial material.² However, the same material may behave like a passive or an active filler, depending on thermal treatment conditions. In addition, glass and sacrificial fillers (usually polymeric particles, such as polystyrene or polyethylene) can modify microstructure of the coatings and increase coating thickness.

Fillers also may modify properties of the final coating, including thermal expansion (e.g., ZrO₂), thermal and electrical conductivity (e.g., metals, graphite, ZrO₂), and hardness (e.g., SiC, c-BN). We can obtain new functionalities that are not possible with pure PDC coatings by introducing suitable fillers into the system, such as self-lubrication (e.g., h-BN, graphite) or electromagnetic radiation shielding (e.g., SiC, Cr₂O₃). In some cases, fillers constitute the largest volume fraction of the coating, and the precursor acts only as a binder with high-temperature stability.

**Capsule summary**

**POLYMER POTENTIAL**

Compared to traditional powder-based ceramics, polymer-derived ceramics have several advantages—including homogeneous molecular composition, lower processing temperatures, and ease of shaping—that enable these materials to realize a variety of ceramics.

**MATERIALS THAT APPLY THEMSELVES**

Polymer-derived ceramics have outstanding protective properties that enable realization of bulk parts, cellular materials, fibers, and coatings for various applications, including electronics, gas and diffusion barriers, thermal barriers, environmental barriers, wear protection, and biological coatings.

**THE FUTURE IS BRIGHT**

Polymer-derived ceramic coatings will continue to expand their already diverse applications through chemical modification of precursors to obtain novel coatings. These modifications may enable new catalytic properties and adjustment of surface energy, opening applications for these materials in, for example, corrosion protection, nonstick coatings, and self-lubrication.

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**Figure 1. Basic chemical structure of the typical preceramic polymers used for the processing of PDC coatings.**

Credit: Barroso et al.
Polymer-derived ceramic and ceramic-like coatings: Innovative solutions for real problems

Deposition techniques

PDC coatings are usually deposited using typical lacquer techniques, such as tape casting or dip, spin, or spray coating. These methods have the advantages of simplicity and low cost in comparison with conventional ceramic coating deposition techniques, such as PVD, CVD, and thermal spraying. Moreover, coatings may be deposited at room temperature without the requirement of reduced pressure or special sample preparation, such as surface activation.

Fundamental requirements of various deposition methods are adequate wettability with the substrate and a suitable surface roughness to improve coating adhesion. The surface also must be adequately clean and free from grease, dust, rust, or other materials, which could result in weak adhesion, defects, or failure of the coating. Each method has unique requirements and advantages. Therefore, selection of the most suitable technique depends on properties of the coating solution/suspension, substrate geometry, and desired coating thickness.

Moreover, for industrial applications, factors such as processing costs, material waste, safety, ability to automate, and reproducibility also must be considered. Figure 2 summarizes basic aspects of each deposition technique, including equipment and processing complexity (considering control of processing parameters and equipment maintenance), amount of waste, ease of automation to obtain good reproducibility, and suitable substrate geometry.

Curing (or cross-linking) and conversion to ceramics

During transformation to ceramic, preceramic precursors experience a series of physical–chemical processes, including curing, conversion to amorphous ceramics, reaction with fillers, and crystallization. Curing of precursors is a crucial process for fabrication of PDCs, because curing increases ceramic yield by reducing loss of low-molecular-weight components. In addition, cross-linking converts low-molecular-weight preceramic precursor to an infusible thermoset polymer that retains its shape during subsequent pyrolysis and heat treatment.

In most cases, curing is thermally induced at 100°C–400°C, depending on polymer composition and structure. Cross-linking agents are added to decrease curing temperature and avoid release of oligomers. During curing, chemical reactions, such as condensation and addition reactions, of functional groups (e.g., Si–H, Si–OH, or Si–vinyl) lead to formation of cross-linked thermoset polymer. Cross-linking can incorporate reactive gases from the curing atmosphere into the polymer. Therefore, oxide-based PDCs usually are cured in oxygen (or air).

For non-oxide PDCs, preceramic precursors are cured in inert atmospheres. In addition to thermal curing, radiation (including e-beam, gamma-beam, laser, and UV) and reactive atmospheres can cure preceramic precursors, usually for special applications. For example, researchers use reaction with a humid, catalyzed atmosphere or UV irradiation to cure preceramic coatings on substrates with low-temperature stability, such as organic polymers.

Cross-linked polymer is converted to amorphous ceramic at 400°C–1,000°C. This pyrolysis step is accompanied by evolution of organic groups (e.g., hydrogen and hydrocarbon), leading to significant weight loss. Amorphous PDCs eventually crystallize if they continue to be subjected to high temperatures. Crystallization temperature, phase composition, and phase distribution are highly dependent on molecular structure and composition of precursors and processing conditions (temperature...
and atmosphere). Crystallization temperature of PDCs–SiC is around 1,100°C.6 PDCs–SiCN can be stable up to 1,400°C, and PDCs–SiBCN can be stable up to 1,700°C.7,8

Annealing in air or oxygen introduces oxygen into PDCs, which leads to formation of SiO$_2$. For SiCN ceramics, annealing in argon favors formation of SiC, while annealing in nitrogen or ammonia favors formation of Si$_3$N$_4$.8 To avoid thermal degradation of substrates, some researchers propose alternative pyrolysis techniques, such as laser pyrolysis, to enable preparation of ceramic coatings on substrates with low melting temperature or reduced thermal stability.9,10

Applications

Adjustable chemical composition, versatility and ease of processing, and excellent properties of PDC systems have drawn attention of research institutes and companies for a variety of applications. Preceramic polymers are attractive for coating applications because of their strong adhesion to polymers, metals, and ceramics, which is attributed to the formation of covalent bonds between precursors and coated surfaces.

Further, these compounds, in polymeric and ceramic states, possess outstanding protective properties that are necessary for environmental barrier applications. One well-developed application is spin-on, low-dielectric-glass layers for electronic applications. Compared with carbon-based organic coatings, higher density makes PDC and ceramic-like coatings good candidates for gas and diffusion barrier applications (e.g., food packaging). Finally, addition of fillers expands the range of these coatings to applications that include thermal barrier, high-temperature-environmental-barrier, wear-protection, and bioactive coatings.

Protective coatings

Corrosion of metals leads to significant costs to industry and infrastructure—NACE International estimates that corrosion costs $2.5 trillion worldwide, which is equivalent to 3.4% of the global gross domestic product (GDP) in 2013.11 In addition, corrosion is responsible for accidents with severe consequences to the environment and human health. Therefore, there is a continuous demand for protective coatings. In this context, PDC coatings stand out, because they combine strong adhesion with thermal resistance and chemical stability.

Researchers have demonstrated protective properties of PDC coatings on substrates, such as copper, nickel-based and titanium alloys, and various types of steel. Recently, polysilazane and polysiloxane also have been used to fabricate protective coatings that demonstrate promising results. Figure 3 illustrates the oxidation and corrosion protective properties of pure silazane-based coatings. However, in extremely harsh environments, thin coatings are not sufficient to prevent damage. Thus, thick PDC coatings have been developed using active and passive fillers.

Günthner et al.13 developed a silazane-based environmental barrier coating system with zirconia and glass fillers for mild steel substrates. The researchers obtained coatings thicker than 100 µm for a targeted application in heat exchangers of waste incineration plants (Figure 4). Waste incineration plants are among the most aggressive environments because of the presence of strongly corrosive compounds, abrasive particles, and temperatures higher than 500°C. These conditions lead to growth of a layer of corrosion and oxidation products with a

Figure 3. Silazane-based protective coatings on metallic substrates: (a) copper after oxidation at 500°C for 1 h (upper region uncoated); (b) stainless steel 304 after oxidation at 1,000°C for 1 h (upper region uncoated); and (c) carbon steel 1006 uncoated (above) and coated (below) after corrosion test with 0.1 mol•L$^{−1}$ H$_2$SO$_4$ solution. Reprinted from Coan et al.,12 with permission from Elsevier.
Polymer-derived ceramic and ceramic-like coatings: Innovative solutions for real problems

During the past decade, researchers have developed specific coatings for steels and nickel-based superalloys. The coated systems have excellent oxidation protection at 800°C under static and cyclic conditions (Figure 5). They also have developed a SiOC-based coating system with active fillers for extremely aggressive chemical environments (>95% sulfuric acid at 104°C–107°C). Figure 6 shows coated stainless steel 316 substrates have much better corrosion resistance than an uncoated system and even better than Alloy 20, a specialty alloy specifically developed for acidic environments. Further, corrosion protection improves as thickness of the coating increases. With a coating thickness of approximately 80 µm (quad coating), there is almost no weight loss even after exposure to hot concentrated sulfuric acid for 30 days.

Researchers also developed environmental barrier coatings for nonmetallic substrates. Because of the need for weight reduction to increase system efficiency, especially in aerospace applications, ceramic-matrix composites are being developed. However, these materials suffer from low oxidation and water vapor corrosion resistance, which limits their applications.

Liu and co-workers reported yttrium silicate environmental barrier coatings fabricated by reaction between polysiloxanes and yttrium oxide powders. The developed environmental barrier coating provides good protection for C/SiC composites up to 1,400°C in water-vapor environments. In addition, Gadow and Kern developed silazane coatings for protection of carbon fibers against oxidation and chemical attack of molten silicon in the fabrication of carbon-fiber-reinforced ceramic-matrix composites.

Figure 4. Silazane-based environmental barrier coating with zirconia and glass fillers.

Figure 5. SEM image in backscatter compositional mode shows oxidation of 316 stainless steel (a) after 10 cycles at 800°C in air and (b) after 100-h hold at 800°C in air; and coated 316 stainless steel (c) after 10 cycles at 800°C in air with a heating and cooling rate of 10°C·min⁻¹ and (d) after a 100-h hold at 800°C in air with a heating and cooling rate of 5°C·min⁻¹. Reprinted from Wang et al., with permission from Elsevier.
Coatings for application in electronics

One of the largest applications of PDC coatings is in electronic systems (Figure 7). Vapor-phase deposition techniques have been standard in the electronic industry for a long time. However, increased packing density and miniaturization of electronic components leads to difficulties in the coverage of structures. In contrast, deposition of PDC coatings in liquid phase, usually by spin-coating, enables complete coverage of electronic structures and filling of gaps as small as 10 nm by the polymers. Silicon-based precursors, especially silazanes, then are converted quickly and easily to SiO₂ by treatment in oxidative atmospheres to obtain dielectric layers.

Another important application in the electronic industry is protection of electronic devices—such as LEDs, thin-film transistors, and solar cells—from oxygen and moisture. The high reactivity of some precursors enables conversion of polymeric layers to ceramics, even at low temperatures, enabling preparation of ceramic-like coatings onto substrates with low thermal stability, such as organic polymers. Indeed, polymer-derived ceramic-like coatings have been developed into gas and moisture barriers for electronic devices.

Further, a unique PDC-based coating has been developed for space applications. Photovoltaic modules operating in the vacuum of space suffer from insufficient heat dissipation, because the only possible heat exchange mechanism is thermal radiation. Therefore, surfaces with high emissivity are required to enhance heat transfer by radiation. Silazane coatings have been developed that combine flexibility and barrier properties with high emissivity. Finally, to improve the hardness of electronic-grade silicon wafers, researchers have developed polycarbosilane-derived SiC coatings.

Other applications

Perhydropolysilazane (PHPS) can be used to fabricate a dense coating with adjustable hydrophilic and hydrophobic properties. The coating exhibits hydrophobic properties when annealed at...
Polymer-derived ceramic and ceramic-like coatings: Innovative solutions for real problems

Silazanes also can be used as additives in organic coatings, resulting in enhanced adhesion, reduced wettability, and improved corrosion protection. The mechanical stability combined with adjustable surface energy of silazane coatings also led to development of antigraffiti coatings. Rather than preventing application of graffiti paints, these coatings offer an easy-to-clean surface, enabling removal of graffiti paint without color change or damage to the original paint (Figure 9).

Addition of fillers to preceramic polymers enables development of coatings for many other applications. For instance, adding silver nanoparticles to silazane-derived coatings gives the coatings antibacterial properties. Further, addition of high amounts of zirconia and adjusted amounts of active filler enables development of PDC-based thermal barrier coatings with very low thermal conductivity that can be applied to the inside and outside of pipes, such as automotive exhaust systems.

In another application, diffusion barrier properties of silazane-based coatings with h-BN reduce diffusion of carbon from industrial graphite dies used in hot pressing of Si$_3$N$_4$. Carbon diffusion is responsible for loss of sintering additives and insufficient sintering on the outer region of hot-pressed Si$_3$N$_4$ parts.

Future of PDCs

The greatest drawback of the PDC route to prepare ceramic coatings is related to limited coating thickness caused by shrinkage during pyrolysis, which leads to cracking. Hence, there is a continuous effort to develop coatings thicker than 100 µm in a single coating/pyrolysis cycle.

In addition, pyrolysis temperature is a limiting factor for PDC coatings on metallic substrates. In general, thermal expansion of metals is considerably different from ceramics, which leads to stresses in the coatings during thermal cycling. However, if we use suitable fillers, we can adjust thermal expansion and microstructure to obtain strain-tolerant coatings. Further, bondcoats can increase the compatibility of substrates and coatings by enabling a more gradual transition from metallic substrate to ceramic coating and can simultaneously protect the metal surface against oxidation.

Another potential avenue is further development of ceramization techniques to prepare thick ceramic layers on substrates with low temperature resistance. Ceramic coatings on such substrates, especially aluminum, have...
great potential in protection against abrasion, wear, and corrosion. Recently, laser pyrolysis has progressed by enabling selective ceramicization of layers and surface patterning.

Chemical modification of precursors is a promising approach to obtain novel coatings. Inclusion of catalytic active elements in the molecular structure of precursors combined with control of microstructure may lead to ceramic coatings for catalytic applications with improved activity because of the homogeneous distribution of catalytic sites. Moreover, we can use chemical modification of precursors to adjust the surface energy for varied applications, such as corrosion protection, nonstick coatings, and self-lubrication.

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References


The QC checklist: An essential tool for managing product quality of ceramics

By John Niggl

A quality control checklist clarifies product specifications for mass production and helps ensure the quality of manufactured ceramic products.

How might ceramics manufacturers be affected without the benefit of having a quality-control checklist for their products?

Ceramic knives, dishware, tile, and even disk brakes—common everyday products—would receive less oversight during production. Without the clarity that a quality control checklist provides, product inspection would be much less effective in finding quality issues and determining if ceramic products meet requirements. Put simply: Professionals in the ceramics industry would find it much harder to reliably manufacture their products.

When designers and product developers want to ensure that suppliers adhere to product dimensions and other specifications for mass production, the QC checklist helps them clarify these requirements. When manufacturers want their QC teams to follow a certain procedure when checking a product, they use a checklist as an outline of inspection criteria. And when a supplier or inspector wants to advise changes to a product or the standard used for evaluating a product, these changes are typically reflected in a checklist.

Let us take a closer look at the vital role QC checklists play in ensuring ceramic products are made to meet expectations.

What is a quality control checklist?

Sometimes called an “inspection criteria sheet,” a QC checklist is a written guide that outlines requirements for manufacturing a product and the criteria for its inspection at the factory. Checklists typically include product specifications, such as dimensions, color, and appearance, as well as packaging, function, and special requirements.

The complete document can vary from several pages in length for a relatively simple consumer product to 10 or more pages for complex products. An effective checklist should be detailed enough to address all manufacturer’s concerns about the product. But it also needs to be concise and organized so that suppliers and product inspectors can quickly find the information they need. Experienced QC professionals often use of tables and other visual elements, such as photographs or diagrams, when developing a prod-
ADDED VALUE

Quality control checklists help ensure that suppliers adhere to product specifications for mass production, guide manufacturers in product inspection procedures, and advise suppliers to product changes or evaluation standards.

MAKING A LIST

QC checklists outline requirements for manufacturing a product and criteria for its inspection at the factory, including product requirements, packaging requirements, on-site tests and checks, and defect classification.

LET’S WORK TOGETHER

Manufacturers, suppliers, and inspectors must work together to ensure consensus and application of a QC checklist—because quality is built into a product, not added in after the fact.

How do QC checklists limit quality defects and other problems with manufacturing ceramics?

Experienced manufacturers and importers know their supplier must clearly understand all facets of their product before beginning mass production, whether working with ceramics or other materials. They also realize the need for any QC staff to have clear criteria and instructions for inspecting the product.

An effective QC checklist clarifies expectations and addresses product requirements and inspection criteria by

- Outlining quality standards and product requirements the supplier is expected to meet; and
- Providing objective criteria for inspecting the product to ensure it meets customers’ expectations.

Imagine manufacturing ceramic distribution boxes for transferring molten metal. The product functions as a mold used in air and vacuum casting for steel. It is vital that factory staff manufacturing the product are familiar with dimensional requirements. It also is important that inspectors who check the product know how to measure it and its tolerances. Like many industrial products, a distribution box with a dimension measuring more than 0.1 mm out of tolerance may be unusable.

Manufacturers can minimize the risk of errors in manufacturing or inspection by clearly stating dimensions, measuring methods, and tolerances in a QC checklist. The conse-
The QC checklist: An essential tool for managing product quality of ceramics

Figure 2. Comparing an approved sample to a mass-produced product.

consequence of omitting these or other important considerations from a checklist could be unsellable finished goods or an unreliable inspection report.

Four important sections to include in a QC checklist

Most product QC checklists contain four important sections. Although we can include some smaller sections, such as desired sample size to be pulled during product inspection, a typical checklist contains:

- Product requirements;
- Packaging requirements;
- On-site tests and checks; and
- Defect classification.

It may seem initially that some of these points are important only for the product inspector. But, as many QC professionals can attest, quality is built into a product. It is important for suppliers to know the standard that will be used to evaluate the product, so they can take this into account when selecting raw materials and components, producing the product, and packaging it for shipping.

Product requirements

Manufacturers often find product requirements are the most obvious point to include in their QC checklist. After all, quality defects and issues related to the product itself are more likely to cause customer dissatisfaction and returns than problems related to packaging, for example. QC checklists should include requirements for product material, construction, weight, dimensions, color, markings, and labeling.

Material composition can be a major concern for manufacturers of certain ceramic products. The ceramic material used in thermocouple protection tubes, for example, often contains a certain percentage of alumina (Al₂O₃) used for its thermal conductive properties. Tubes subjected to higher temperatures generally must contain a higher content of alumina. A deficiency in this constituent could lead to product failure in service. Therefore, manufacturers must address material and construction in their QC checklist and to ensure their supplier understands requirements before starting mass production.

For many ceramics manufacturers, verifying color and dimensions often is vital. Dimensional tolerances and measuring methods should be included directly in the QC checklist, if not in a supplemental table or drawing. Inspectors often use a Pantone swatch to verify product color—if there are particular color requirements, the checklist should include a Pantone code for reference.

Markings and labeling can be a very important consideration for certain products, and it is an aspect of inspection that manufacturers sometimes neglect to consider. For example, the U.S. Food and Drug Administration¹ and some European governments² limit use of certain toxic metals in ceramicware. Legislation compels manufacturers to meet certain guidelines for use of the term “lead-free” and similar claims in product labels. Ceramics manufacturers may be prohibited from distributing their products if they do not meet labeling requirements mandated in the markets they sell.

In addition to stating clear product requirements in a QC checklist, manufacturers may benefit from establishing an approved “golden” sample.³ Before mass production begins, manufacturers can ask suppliers to send a product sample and then have them revise the sample as needed until one perfectly meets the manufacturing requirements. With this approved sample in hand, the supplier has a model to follow for mass production, and QC staff have a model for comparison during inspection (Figure 2).

Packaging requirements

Packaging a ceramic product using the proper method and materials can be a critical part of the manufacturing process. Although often discarded after the product reaches consumers, packaging protects the product during transit and can greatly influence consumers’ perception of its quality, because it often is the first part of the product they see.

A QC checklist that adequately addresses packaging requirements typically contains all of the following:

- Packaging weight and dimensions;
- Carton labeling requirements;
- Carton material;
- Packing and assortment method; and
- Retail packaging graphics and labeling.

The weight and size of packaging can greatly impact shipping. Suppose a manufacturer plans to ship 1,500 porcelain sinks in a single, 40-ft shipping container. The manufacturer requires the factory to package each sink in a carton that is 0.5-m wide. If the factory mistakenly uses packaging that is 0.55-m wide, the whole order may not fit in one container as planned. What may seem like a minor discrepancy could cause shipping delays and significantly increase costs.

Carton labeling can affect salability of a product in the same way as labeling on the product itself. But cartons tend to have more labeling and markings, and distributors often have their own standards they impose on suppliers. For example, Amazon.com requires sellers to use shipment labels measuring 3-1/3 in. × 4 in., along with many other requirements.⁴ Ensuring the right barcodes are printed on a product is very important for tracking goods throughout the supply chain.
Manufacturers should explicitly state carton material and packing method in QC checklists (Figure 3). Glass and porcelain, for example, tend to be delicate products that must be packed with materials that protect against damage during shipping and handling. Some manufacturers require factory workers to add small, silica desiccant packets to shipper cartons to limit the amount of moisture inside. Others may want to specify details, such as glue or staples used for binding or double- or single-ply cardboard cartons. Inadequate packaging strength can lead to damaged goods when multiple cartons are packed on top of each other, crushing those near the bottom.

Points related to retail packaging often are similar to those for outer carton packaging. But, retail packaging requirements typically will include any artwork and a breakdown of assortment. For example, suppliers often ship ceramic dinnerware and stoneware for cooking in sets of three, five, or more pieces. The QC checklist may specify what quantities of various pieces or components the factory should pack in each shipper carton, retail carton, polybag, etc.

**On-site product tests and checks**

Although many manufacturers carefully specify detailed requirements for their product and its packaging in a checklist, far fewer adequately address on-site testing. These are tests QC staff can perform at the factory to identify any issues with product functionality, safety, and performance. Neglecting on-site testing can lead to serious issues, often putting consumers at risk.

A QC checklist includes three key points regarding on-site testing:
- Procedures and testing criteria for any on-site testing;
- Required equipment for tests; and
- Who will provide the required equipment.

Many manufacturers assume there are uniform and widely accepted testing standards and procedures for their products. This is true in some cases. The procedure for crosshatch adhesion testing of enamel-coated cookware, for example, is simple and generally does not vary depending on the item. But, there are other tests common for the same type of product, such as the hotplate shock test, that vary depending on the item and its unique quality standards. A procedure may call for each sample to be tested on the surface of a hotplate heated to 280°C, whereas another manufacturer of a similar product may want the hotplate surface heated to 320°C. Regardless of whether a manufacturer suspects the QC team and supplier are familiar with the testing method, it is always wise to include this information in the QC checklist to avoid errors.
Failure to clarify equipment needed for on-site testing can result in inspectors’ inability to conduct the test or to conduct it accurately. In the earlier example of hotplate shock testing, the inspector likely needs a temperature gun to reliably measure surface temperature of the hotplate. Another common test for enamel-coated products is an impact test to measure strength of the enamel coating using a steel ball with specific weight requirements. Without having a working temperature gun and the proper steel ball on hand during inspection, these tests will not provide reliable outcomes.

The last main point about testing concerns what party will be responsible for making the testing equipment available at the inspection site. It may seem like a minor detail—but leaving this point out of the checklist often leads to a situation where the inspector mistakenly thinks the factory will provide the needed equipment and vice versa. Going back again to the enamel-coated product, a coating thickness gauge is needed to accurately measure enamel thickness on-site. But there is no guarantee that either factory or QC staff will know to provide the gauge unless notified before inspection. The best place to clarify these details is the QC checklist.

Classifying quality defects

One of the least understood aspects of creating an effective QC checklist for a product is how to define and classify quality defects. Most QC professionals rely on an international standard known as acceptable quality limits (AQL) for conducting product inspection. Inspectors and manufacturers apply the AQL standard to a sampling method and to reporting various types of defects during inspection. The ultimate result of an inspection is largely governed by this standard.

Quality defects are typically sorted into one of three categories (Figure 4):

- “Minor” defects—those found in relatively small quantities that typically do not affect the salability of a product and are not normally noticed by customers;
- “Major” defects—those that do not pose a threat to user safety, but do not match product specifications or the golden sample; and
- “Critical” defects—those that present a safety hazard to the user, might cause property damage, or otherwise harm the end user.

Depending on tolerance for particular quality issues—the acceptable quality limit—manufacturers can determine the maximum number of minor, major, and critical defects allowed in a sample of goods using the AQL standard.

Without delving too deeply into determining a specific tolerance, which tends to vary from one manufacturer to another, individual manufacturers should recognize the importance of clarifying which defects should be reported as minor, major, and critical in the QC checklist (Figure 5). For example, manufacturers might consider crazing, or fine cracks on the surface of the material, to be a minor defect, whereas crazing beyond a certain length might constitute a major defect. Pinholes, dents, chips, scratches, and discolorations are other examples of defects commonly found in certain types of ceramics. But each manufacturer must decide which defects, and in what frequency, it is willing to accept in finished goods. Inspectors will

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<tr>
<th>8.2. Individual product</th>
<th>Critical</th>
<th>Major</th>
<th>Minor</th>
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<tbody>
<tr>
<td>1. Use of any unverified paint, marker, or other substrate to cover an imperfection.</td>
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<td>X</td>
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<td>2. Crazing under glaze</td>
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<td>XL</td>
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<td>Any visual crazing under glaze with less severity than above.</td>
<td>X</td>
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<td>3. Pinhole</td>
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<td>A surface: Any pinhole &gt;1 mm, or more than 7 pinholes ≤1 mm; B surface: Any pinhole &gt;1.5 mm, or more than 7 pinholes ≤1.5 mm at 1 side.</td>
<td>A surface: Any pinhole &gt;1 mm, or more than 5 pinholes ≤1 mm; B surface: Any pinhole &gt;1.5 mm, or more than 5 pinholes ≤1.5 mm at 1 side.</td>
<td>A surface: Any pinhole &gt;1 mm, or more than 3 pinholes ≤1 mm; B surface: Any pinhole &gt;1 mm, or more than 5 pinholes ≤1 mm at 1 side.</td>
<td>A surface: Any pinhole &gt;1 mm, or more than 3 pinholes ≤1 mm; B surface: Any pinhole &gt;1 mm, or more than 5 pinholes ≤1 mm at 1 side.</td>
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Figure 5. Example of defect specifications from a product checklist.
look for this standard in the QC checklist to guide them in how to report results.

**Collaboration is the best approach to creating a QC checklist**

Having an effective QC checklist will go a long way in helping a manufacturer maintain the right standards for its products. But outlining requirements in the checklist is only part of the equation. It is important that manufacturers, suppliers, and inspectors understand and agree with the expectations before the manufacturer can be confident that the QC checklist will be followed. Collaboration and consensus on the requirements in the checklist is best reached as early as possible—well before mass production begins, if not during product development. Again, quality is built into a product, not added in after the fact.

In addition, suppliers need the opportunity to provide feedback on manufacturers’ requirements. If a manufacturer has unreasonable expectations or a requirement the supplier cannot reasonably meet, it typically is less costly in time and money to find out earlier, rather than be surprised later.

Remember the earlier example of thermocouple protection tubes? Can you imagine a supplier manufacturing the product with only 80% aluminum oxide because the manufacturer did not clarify a requirement of 90%? At worst, the supplier might lie about the material composition, and the manufacturer might not know until receiving the finished goods. At best, suppliers would directly tell the manufacturer about the misunderstanding when they finally see the checklist, but they likely would need to discard any tubes already produced and restart production. By letting suppliers review the manufacturer’s checklist beforehand, they have the opportunity to ask questions and manage expectations.

Just as it is important to work with a supplier to develop a checklist, input from any QC staff who will ultimately inspect the product can be invaluable. Most professional inspectors specialize in a limited number of product categories. An inspector may be able to advise what quality issues tend to affect the product type, what testing should be performed during inspection, and more. Even for experienced manufacturers that have worked with a particular product for many years, having an open discussion with the QC team about checklist requirements ensures there is a mutual understanding about how the product should be inspected.

Often a forgotten aspect of QC checklist development, collaboration helps manufacturers avoid costly mistakes and surprises. No individual checklist is a one-size-fits-all solution. Product requirements, packaging, on-site testing, and quality defects can differ vastly between ceramic products. And approaching the process of setting product standards alone, or forgoing a QC checklist entirely, is a mistake most manufacturers cannot afford to make.

**About the author**

John Niggl is marketing and communications manager at InTouch Services Ltd. (Shenzhen, China). For more information about InTouch, visit www.intouch-quality.com. Contact Niggl at john.niggl@intouchquality.com.

**References**

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April 24, 2017 | Cleveland, Ohio

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Monday, April 24

9 – 10:15 a.m. | Business intelligence—How to dissect a market opportunity
Gordon Nameni*, management consultant, senior editor, BCC Research LLC

10:30 – 11:45 a.m. | Growth in the Glass Age—Managing product introductions
Kevin T. Gahagan, senior manager, technology strategy, Corning Glass Technologies, Corning Incorporated

11:45 a.m. – 1 p.m. | Lunch
Céline Guermeur, director, exploratory markets and technologies, Corning Incorporated

1– 2:30 p.m. | Smart marketing for engineers
Rebecca Geier*, CEO and co-founder, TREW Marketing

2:30 – 3:30 p.m. | Case study: Marketing new technology—Additive manufacturing for ceramic materials
Johannes Homa, CEO and co-founder, Lithoz

3 – 3:30 p.m. | Case study: How to address multidirectional industry segments through strategic marketing
Alexander Frenzl, business field manager, glass, ceramics and building materials, NETZSCH-Gerätebau GmbH

4 – 5 p.m. | Develop your marketing action plan
Rebecca Geier*, CEO and co-founder, TREW Marketing

7 – 9 p.m. | CBLS dinner and speaker
Parsing out Palissy: Recent findings on ceramic glazes in Renaissance France
Colleen Snyder, associate conservator of objects, The Cleveland Museum of Art

*Gordon Nemini and Rebecca Geier will be at ACerS booth #308 at Ceramics Expo to talk to you about your business!

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www.ceramics.org | American Ceramic Society Bulletin, Vol. 96, No. 3
This year marks the first time that ACerS Structural Clay Products Division, ACerS Southwest Section, and the National Brick Research Center have joined their meetings to serve the needs of the structural clay industry.

**SCHEDULE**

**Tuesday, May 9**
- Registration open: Afternoon
- Hospitality suite: Evening

**Wednesday, May 10**
- Registration open: Morning
- Plant tours of Acme Brick (Denton) and Meridian Brick (Mineral Wells): All day
- Lunch sponsored by Acme Brick: Afternoon
- Suppliers mixer reception: Evening
- Hospitality suite: Evening

**Thursday, May 11**
- Technical session 1: Morning
- Lunch for all (includes SWACerS business meeting): Afternoon
- Technical session 2: Afternoon
- Banquet (short reception preceding): Evening
- Hospitality suite: Evening

**Friday, May 12**
- NBRC member meeting: Morning

The full-day technical program includes, but is not limited to:
- Measuring the crystalline silica content of raw materials – **John Sanders**, National Brick Research Council, Clemson University
- Rheometer measurements on brickmaking clays and shales – **Mike Walker**, National Brick Research Council, Clemson University
- Today’s roll mills are not what you remember – **Xavi del Molino**, Verdes, S.A.
- Lesson 3 on kiln and kiln maintenance – **Joern Boeke**, Refratechnik Ceramics GmbH
- The expanding use of glass in healthcare – **Delbert E. Day**, Graduate Center for Materials Research, Missouri University of Science & Technology

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SCHEDULE OF EVENTS
Visit ceramics.org/pacrim12 for program and hotel information, full schedule, and to register today!

SUNDAY, MAY 21
Evening welcome reception

MONDAY, MAY 22
Morning plenary session
Publishing workshop
Afternoon concurrent technical sessions

TUESDAY, MAY 23
Morning and afternoon concurrent technical sessions
Evening poster session
GLASS & OPTICAL MATERIALS DIVISION ANNUAL MEETING (GOMD 2017)

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Fundamentals of the glassy state
Glasses in healthcare—fundamentals and application
Optical and electronic materials and devices—fundamentals and applications
Glass technology and crosscutting topics
Professor Jacques Lucas honorary symposium
Professor Takayuki Komatsu Kinen honorary symposium

GLASS CORROSION SHORT COURSE

ceramics.org/glasscorrosion

May 20, 2017  |  8:00 a.m. – 4:00 p.m.
Six experts team-teach corrosion mechanisms and kinetics—a key concern for industrial and environmental applications—as it relates to bioglasses, and natural, archaeological, nuclear, and commercial glasses. Experimental, analytical, and modeling approaches will be covered.

COURSE OUTLINE:

- Fundamental aspects of silicate glass corrosion: mechanisms and kinetics (theoretical background)
- Nuclear glasses
- Experimental and analytical techniques to investigate glass corrosion
- Multi-scale modeling

REGISTER TODAY FOR THIS ONE-DAY SHORT COURSE, HELD IN CONJUNCTION WITH PACRIM12.

WEDNESDAY, MAY 24

All day concurrent technical sessions

THURSDAY, MAY 25

Morning and afternoon concurrent technical sessions
Conference dinner

FRIDAY, MAY 26

Morning concurrent technical sessions

GOMD AWARD SPEAKERS

Stookey Lecture of Discovery  |  May 23  |  8:30 a.m.
Peter C. Schultz, senior advisor and board member, OFS Fitel, director, secretary, advisor, viNGN, president, BioSensor Inc.
In pursuit of perfect glass: Fifty years and still at it

George W. Morey Lecture  |  May 24  |  8:30 a.m.
Kathleen Richardson, professor of optics and materials science and engineering, Center for Research and Education in Optics and Lasers, College of Optics and Photonics, University of Central Florida
The evolution of chalcogenide glasses in infrared photonics—beyond invisible

Norbert J. Kreidl Lecture  |  May 24  |  Noon
Yingtian Yu
Stretched exponential relaxation of glasses: Origin of the mixed alkali effect

Darshana and Arun Varshneya Frontiers of Glass Technology Lecture  |  May 26  |  8:30 a.m.
Leonid Glebov, research professor of optics, Center for Research and Education in Optics and Lasers, College of Optics and Photonics, University of Central Florida; OptiGrate Corporation
Volume holographic elements in photo-thermo-refractive glass: Features and applications

Darshana and Arun Varshneya Frontiers of Glass Science Lecture  |  May 25  |  8:30 a.m.
Himanshu Jain, professor, materials science and engineering, Lehigh University
Pathways of glass-crystal transformation

Visit ceramics.org/pacrim12 for program and hotel information, full schedule, and to register today!
The Cements Division of ACerS announces its 2017 annual meeting—Advances in Cement-based Materials—covering the latest advances in cement based research. Paulo Monteiro of University California, Berkeley, will give the Della Roy Lecture. Other events include a tutorial on novel carbon capturing technologies and a student event at the University Center.

**THE TECHNICAL SESSION WILL INCLUDE ORAL AND POSTER PRESENTATIONS:**

- Cement chemistry and nano/microstructure
- Material characterization techniques
- Alternative cementitious materials and material modification
- Durability and lifecycle modeling
- Computational material science
- Smart materials and sensors
- Rheology and advances in SCC

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In research, there is often incentive for immediate but specialized results. But I have found, both in smaller tasks and in general project direction, that taking the time to develop a robust solution can save time and improve results in the end.

In my first undergraduate research experience, I had the luxury of exploring a previously demonstrated technique. Under the direction of Kenneth Sandhage at Georgia Institute of Technology’s School of Materials Science and Engineering (Atlanta Ga.), I worked to further demonstrate the displacive compensation of porosity process (DCP)—a sort of alchemy by which a porous ceramic preform can produce a dense composite with the same dimensions.

DCP uses a volume-increasing reaction to fill the empty space of a porous preform. Reactant enters as a liquid and reacts to produce a more voluminous, solid product that occupies pore spaces. This reaction can produce composites with densities very close to theoretical (99.6%) if the porosity of the preform is carefully controlled. DCP preserves the shape of the original preform to within 1% of original dimensions and produces a product with microstructure similar to the original ceramic preform.

I was applying DCP to composites of ZrC/W, a very hard, high-temperature refractory cermet that is otherwise very difficult to shape. My initial goal was simple—use the process to make a ZrC/W machining part to demonstrate viability of the material and the process. But there were challenges—up to that point, methods for preform production were slow, difficult to scale, and ultimately limited in the types of shapes that could be made due to green strength.

Trying to make a part of the size I had in mind turned out to be unworkable with the available die and press equipment. Instead, I redirected my efforts toward improving the process. In the end, I developed a more robust, low-pressure hot press technique that made large shapes easier and improved green strength to make forms such as thin plates possible. Near the end of the project, I even started exploring the possibility of using DCP in conjunction with selective laser sintering to expand possible shapes into the realm of additive manufacturing.

Ultimately, I was able to create the original part with better results because I took the time to develop a more robust and generalized process. DCP brought ZrC/W from a specialized realm to a general one—it could be converted with any shape at comparatively low temperatures. In addition, my work, using a hot press with PMMA binder material, helped generalize DCP forming itself. And with additional exploration, secondary selective laser sintering could further generalize the process. Progressing ZrC/W composites from nearly unshapable to 3-D printing is remarkable!

Everyone makes decisions on how much effort they put into solving a problem. My advice is to occasionally step back and look at the larger picture—how will the solution to the problem affect other aspects of the study? Will it be useful beyond the intended scope?

The title of this article also has a second meaning: I highly recommend undergraduates do something different each year. Whether you are interested in industry or academia, a multidisciplinary field like materials science has such an abundance of directions that every project will be a unique experience. Each one will help you make decisions on your future direction. And even after several years in different positions, you will still only experience a fraction of the directions you could steer your career.

My own experience—from refractory composites to aqueous battery electrodes—has yet to repeat itself.

D. Keith Coffman is an undergraduate researcher with dual majors in materials science and engineering and physics at the Georgia Institute of Technology. He is vice president of Campus Freethinkers, member of ACerS PCSA and Material Advantage, and singer in the Georgia Tech Chorale. He is grateful to Dr. Naresh Thadhani for introducing him to materials science and engineering and research and to mentors and colleagues in the Georgia Tech Materials Science and Engineering Department.
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