NAVAL SCIENCE AND TECHNOLOGY

FUTURE FORCE™

FALL 2015

BUILDING THE AIRFRAMES OF TOMORROW

POWERING FUTURE TECH

PLASMONIC POSSIBILITIES

ADVANCED MATERIALS

VOLUME 2
#04
FALL 2015

FUTURE FORCE

NAVAL SCIENCE AND TECHNOLOGY MAGAZINE

ARTICLES

COLUMNS

To submit an article or subscribe to *Future Force*, please visit our website or contact the managing editor.

Future Force Magazine
Office of Naval Research
875 N. Randolph Street, Suite 1425
Arlington, VA 22203-1995

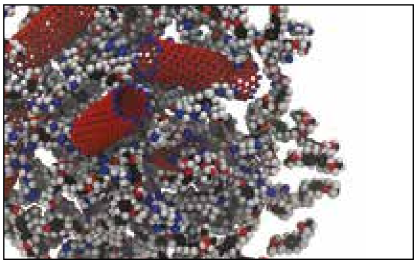
Email: futureforce@navy.mil
Phone: (703) 696-5031
Web: http://futureforce.navylive.dodlive.mil
Facebook: http://www.facebook.com/navalfutureforce

BEYOND FUTURE FORCE ▼

Interactive features are enabled with the digital copy of Future Force:

futureforce.navylive.dodlive.mil

Mobile Download



Future Force is a professional magazine of the naval science and technology community. Published quarterly by the Office of Naval Research, its purpose is to inform readers about basic and applied research and advanced technology development efforts funded by the Department of the Navy. The mission of this publication is to enhance awareness of the decisive naval capabilities that are being discovered, developed, and demonstrated by scientists and engineers for the Navy, Marine Corps, and nation.

This magazine is an authorized publication for members of the Department of Defense and the public. The use of a name of any specific manufacturer, commercial product, commodity, or service in this publication does not imply endorsement by the Department of the Navy. Any opinions herein are those of the authors and do not necessarily represent the views of the U.S. government, the Department of the Navy, or the Department of Defense.

Future Force is an unclassified publication. All submissions must be precleared through your command's public release process before being sent to our staff. To subscribe to *Future Force*, contact the managing editor at futureforce@navy.mil, (703) 696-5031, or *Future Force* Magazine, Office of Naval Research, 875 N. Randolph Street, Ste. 1425, Arlington, VA 22203. Please note whether you would like to join our email distribution list or, if you are a member of a command or organization, receive a print copy of the magazine.

All photos are credited to the U.S. Navy unless otherwise noted.

Front Cover: *ADV. MATS,* Illustration by Alvin Quiambao

SPEAKING OF S&T

▶▶ By Dr. Bhakta B. Rath

Dr. Bhakta Rath (right) receives an award from the Minerals, Metals and Materials Society in 2013. Photo courtesy of the Minerals, Metals and Materials Society.

This issue of *Future Force* showcases some of the latest developments in advanced materials and additive manufacturing technologies currently under development within the Navy's science and technology community. The timing of this issue is highly fitting given the growing interest in the opportunities offered by additive manufacturing, while considering the need for new materials tailored to take advantage of these new manufacturing processes.

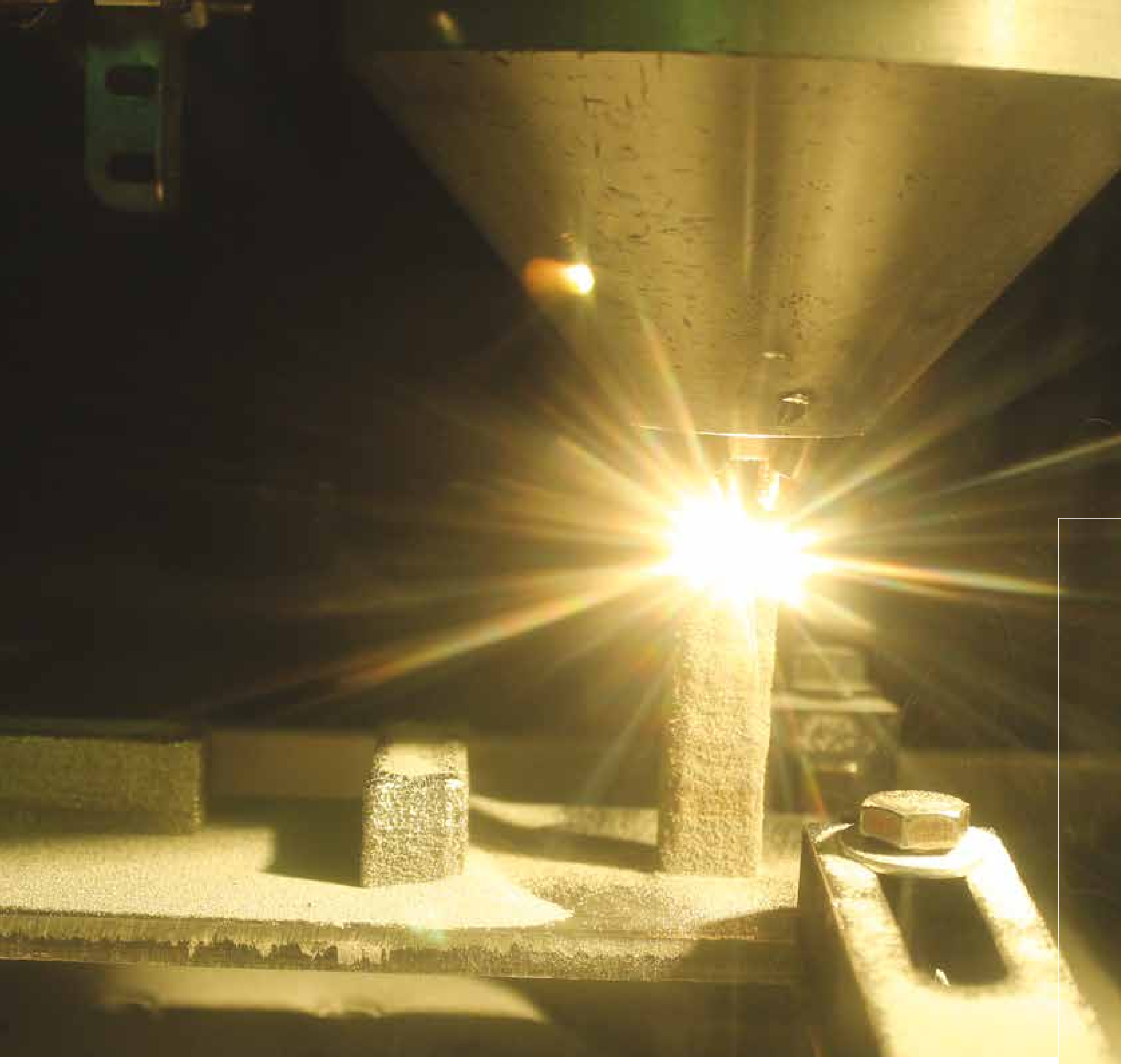
The Navy's research and development establishment is taking an active role in shaping the advancement of new materials and the implementation of agile manufacturing technologies for current and future applications, while reducing the barriers to their implementation within the fleet. Similar goals are being pursued by the commercial sector, but the Navy's unique needs and missions call for materials and structures able to perform in extreme maritime environments under a wide range of conditions.

This issue presents a snapshot representative of the wide range of research in new materials and devices being pursued by the Naval Research Enterprise. It includes a series of articles discussing advanced materials which can adapt to produce reconfigurable radio-frequency circuits for wide-band tunability, or sense the presence of hazardous agents at exquisitely low levels, or release huge amounts of energy while being extremely safe during storage and handling. A special section discusses the use of novel and agile composite materials in airframes followed by the development of next generation transduction materials for sonar development.

The Office of Naval Research (ONR), through the Naval Research Laboratory (NRL) and the naval warfare centers, is showing how to achieve the promise that advanced materials and novel manufacturing processes can offer to the fleet by identifying the appropriate material systems and the optimum additive manufacturing techniques. For example, at NRL teams of scientists and engineers are working together to develop predictive models, additive manufacturing processes and materials characterization techniques that will allow them to chose the material, optimize the design, and select the additive process best suited to make a part or component with the desired performance and required certifications.

Serious challenges remain in both materials choices and reliability of parts produced by current additive manufacturing or 3D printing processes. The current selection of materials compatible with additive manufacturing pales with the range of metals, alloys, ceramics, and composites found in any given Navy platform. Similarly, the goal of printing a replacement part with drop-in capabilities still remains elusive. But the work being pursued at NRL, the naval warfare centers, universities, and defense industry laboratories steadily advances the state-of-the-art and enables new capabilities, while new structures and designs manufacturable only by additive processes and uniquely suited for defense applications are being realized in growing numbers. As the articles in this issue illustrate, the combination of new materials with advanced manufacturing will play a key role in shaping the Navy after next.

Dr. Rath is an associate director of research at the US Naval Research Laboratory.



ADVANCED MATERIALS

The science and systems that harness chemistry and physics to discover new materials or innovative ways of using existing materials for naval applications.

The Optonec Laser Powder system above supports metal additive manufacturing. Fabrication of new metallic components and other materials are used by the Naval Sea Systems Command's Warfare Center additive manufacturing working group to advance 3D printing in the fleet. Photo courtesy of Combat Direction Systems Activity Dam Neck.

Extremely "COOL" electronics

By Elisha Gamboa

Throughout history, innovation has fueled advances in military capability. For example, in the early post-World War II era, scientists discovered that metals frozen to low temperatures could withstand more wear, which sparked the study of cryogenics. Today, cryogenics plays a huge role in the military, especially in the area of radio frequency (RF) devices and electronics. To keep up with military needs, Space and Naval Warfare Systems Center (SSC) Pacific has built a state-of-the-art Cryogenic Exploitation of Radio Frequency (CERF) laboratory that focuses on designing innovative technologies and transitioning them to real-world applications.

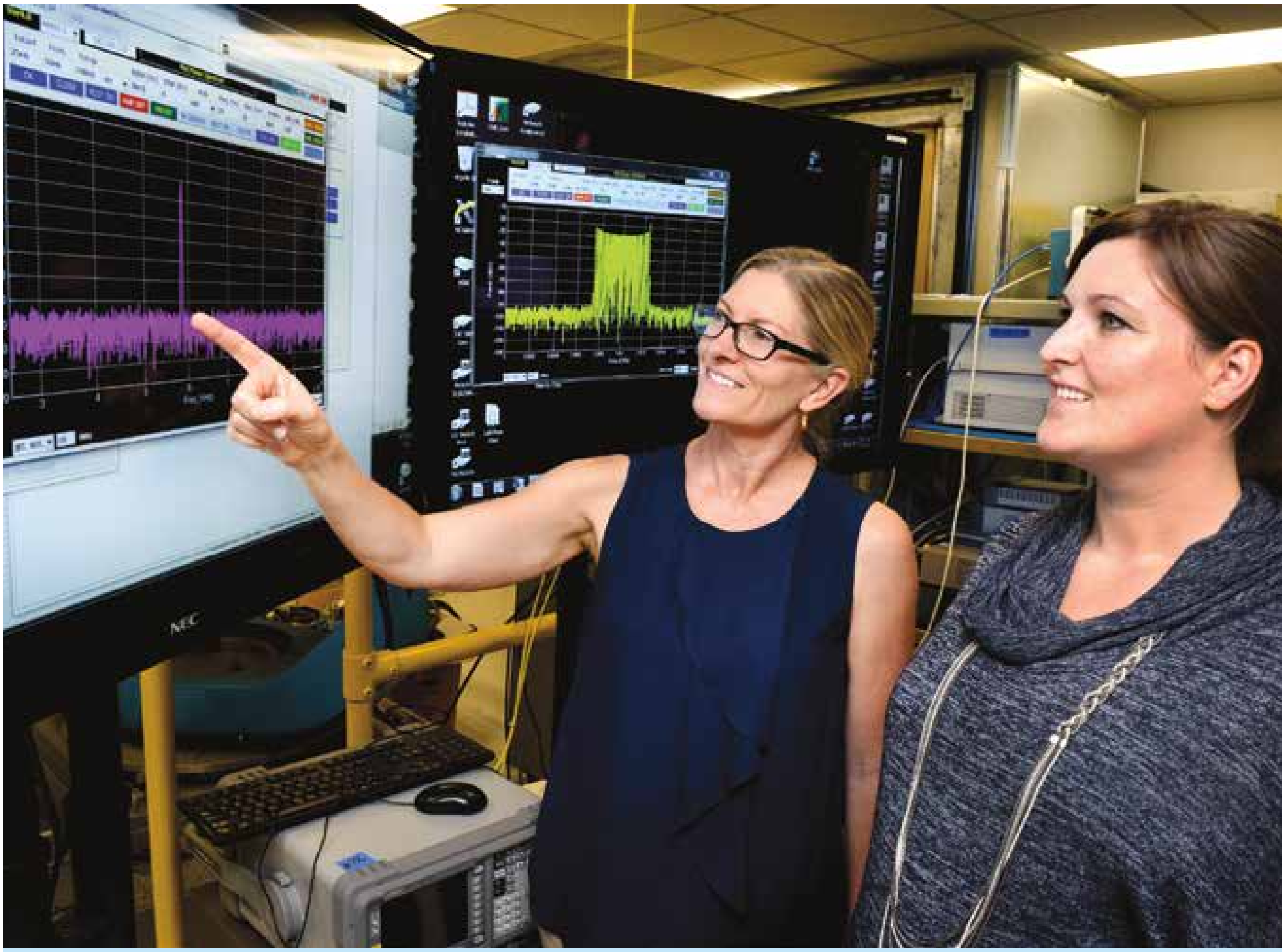
The CERF laboratory is a full-spectrum electronics and experimental device test facility that performs rigorous characterization, evaluation, and transition of both in-house and externally developed RF devices and electronics. The lab is located within the advanced concepts and applied research branch and is sponsored by the National Security Agency's tactical signals intelligence technology program. The CERF lab researches and develops advanced RF sensors, devices, and electronics that exploit the properties of superconductors and other novel materials. The lab's portfolio of technology interests includes not only the cryogenic properties, but also novel properties of materials and devices at room temperature.

The lab is an integrated product team of scientists and engineers that has designed, built, tested, and fielded superconducting electronics technologies that improve signals intelligence receiver sensitivity, enhance detection ranges, and reduce size, weight, power, and mean time between failures. The innovative technical efforts of the lab have led to the first use of superconducting electronics technologies in the real world that resulted in a military utility assessment of "Demonstrated significantly enhanced war fighting capability." This success stems from a technology roadmap that addresses real-world problems and military needs from beginning to end. This roadmap approach has led to the successful transition of several groundbreaking technologies for operational use, such as cryogenically cooled amplifiers and tunable filters. SSC Pacific's fielded cryogenic technology has significantly improved the United States' ability to prosecute military engagements across the globe.

This first introduction of superconducting electronics technology is paving the way for new applications in the form of more capable analog preprocessing units (also known as RF distribution units), automatically tunable filters, multiplexers, and higher speed analog-to-digital converters. Application of superconducting technology to these components promises to reduce size, weight, power, and mean time between failures while delivering superior RF performance.

Cryogenic temperatures are typically those below 123 degrees Kelvin (-238 degrees Fahrenheit or -150 degrees Celsius). Superconductivity is one of the most dramatic phenomena that can be observed at these temperatures, where electrical resistance disappears below a certain threshold called the critical temperature. Superconducting material exhibits the "Meissner effect," which occurs when a superconductor is exposed to a magnetic field. In such a situation, the superconductor, unlike with a regular metal, produces a repulsive force that has a net effect of excluding the magnetic field from the superconducting material. These two remarkable properties can be used to produce unique electronic devices that could not be possible in any other way.

Life cycle costs also will be reduced by providing common components across all ship classes. Today's conventional RF distribution systems are heavily tailored to each ship class because each has different topside interferers and different antennas. This plethora of different but similarly functioning conventional components drives up per-unit and logistics costs. Superconducting electronics broadband capability and small radar cross section, size, weight, and power requirements allow for a common configuration across ship classes, thereby establishing economies of scale in both procurement and sustainment costs.



Photos courtesy of SSC Pacific

Anna Leese de Escobar (left), founder of the Cryogenic Exploitation Of Radio Frequency (CERF) Laboratory, and Dr. Susan Berggren analyze data output from the lab's radio frequency distribution unit for improved signals intelligence.

Enhancing Communications

Dr. Marcio de Andrade, SSC Pacific physicist, prepares a device for testing at the cryogenic platform.

For military planners, the most critical element of information dominance is information control. Making information dominance a reality involves driving efforts to develop advanced technology that will enhance existing signal intelligence capabilities and give operational forces a strategic communications advantage on the battlefield.

Over the years, the number of topside antennas aboard U.S. Navy ships has grown significantly, even though the space available has not. This shipboard clutter interferes with the reception of critical data, creating problems such as antenna blockage, electromagnetic interference, and increased enemy awareness of Navy combat ships.

SSC Pacific is developing a sensor that will aid in reducing ships' topside antenna profiles, enhancing existing battlefield information capabilities, and extending the signals intelligence domain. The compact, highly sensitive broadband RF sensor offers frequency-selective capabilities for Navy ships and other key platforms.

The SSC Pacific CERF lab has collaborated with the University of California, San Diego, in research that is fundamental to developing a superconducting quantum interference device (SQUID)-based RF sensor. The sensor consists of arrays of interconnected SQUIDs that perform together as an interference device, often called a SQIF (superconducting quantum interference filter) RF sensor.

SQUIDs are devices where the superconductivity is exploited producing an extremely sensitive magnetic field sensor. Each SQUID consists of a loop of superconducting material that has regions that create a weak electrical link where superconducting electrons transit through normally impenetrable regions through a quantum mechanical process called tunneling. These regions form two (or more) parallel tunnel junctions or Josephson junctions that typically consist of thin insulating layers.

These sensors are low-power receivers that are highly compact and lightweight. They are sensitive and have a noise floor far below conventional state-of-the-art electronics. They also can detect almost the entire RF spectrum. The sensor's true broadband nature and high sensitivity deliver a more complete picture of events and increase warfighter awareness, significantly enhancing command-and-control capabilities and signals intelligence performance.

Supported by SSC Pacific's Naval Innovative Science and Engineering basic and applied research program, the project is now at the proof-of-concept stage. The goal is to field the SQIF RF sensor to provide the Navy with an improved and highly advanced intelligence, surveillance, and reconnaissance capability in the maritime domain.

The broadband nature of the sensors brings benefits to warfighters across a wide range of scenarios. If the sensors increase coverage, the number of signals detected, and the probability of signal detection, as well as reduce the time to search and target a source, the extension of vital battlefield awareness and control extended for warfighters will become a reality.

The compact size of the complete SQUID array sensor packages makes them suitable for use as signals intelligence, communications, targeting, and navigation systems on platforms, including submarines, surface ships, aircraft, unmanned aerial vehicles, and high-altitude craft. As an example, an operator/platform could extend the standoff distance for interception of signals from a region of interest, making counterdetection of a Navy asset less likely.

The Limitless Possibilities of Graphene

Challenged with the need to keep up with the pace of today's rapidly evolving technology, the Navy is interested in developing high-power, extremely wideband RF/electronic devices. SSC Pacific's CERF laboratory is experimenting with new electronic materials with unique properties to provide more effective information dominance solutions—and one of its top candidates is graphene.

The manufacture of high-performance devices requires high-performance materials. Graphene, a single-atom-thick plane of carbon, not only has outstanding transport properties—but also demonstrates many unique properties not found in any other high-performance electronic material. It is flexible, transparent, ultimately scalable, and the charge carriers can be continuously tuned between electrons and holes—an effect known as ambipolar conduction.

Today, typical antennas operate on the concept of resonance. Resonance occurs when an antenna stores and transfers energy between two or more different storage modes. Energy loss occurs, however, from cycle to cycle. This loss restricts antennas substantially, causing low sensitivity, limited frequency range, and unclear channels.

Resonance also refers to how antenna size directly relates to the wavelength of the electromagnetic waves it detects, which means antenna size limits wavelength detection.

To address these limitations, SSC Pacific is leading the way in the research and development of graphene-based devices. Current devices under development in the CERF lab include a photonic detector, RF antenna, and RF sensor.

The graphene-based photonic detector shows promise as a compact, fast, sensitive, low-noise device that could operate across the entire spectrum—from extremely low to extremely high frequencies—providing enhanced information, surveillance, and reconnaissance capabilities.

Graphene—which is made from carbon, one of the most abundant elements on Earth—also could reduce military costs. The material is a possible replacement for many rare and expensive electronic materials, and could prove a route to much cheaper devices.

Other potential applications for graphene include wearable electronics, digital communications, satellite and space technology, lighting panels, touch screen and computer technology, and solar cells. In addition to graphene, SSC Pacific also is looking into other two-dimensional materials it could possibly exploit and apply to the advancement of military technology.


Son Dinh, CERF Lab engineer, works out the details of the automation control, data acquisition, and analysis for the CERF equipment.

Graphene continues to draw attention for its extraordinary electronic, mechanical, and thermal properties—and the possibilities of developing novel products for enhanced warfighter capabilities are practically limitless. As further research continues on the material, SSC Pacific researchers expect emerging innovations for information dominance applications.

About the author:

Elisha Gamboa is a public affairs specialist with the Space and Naval Warfare Systems Center Pacific.

PHASE CHANGE MATERIALS
POWERING FUTURE TECH

FROM CDS TO SATELLITES, PHASE-CHANGE MATERIALS —WHICH CAN TRANSITION BETWEEN MULTIPLE SOLID PHASES —ARE REVOLUTIONIZING THE ELECTRONIC SYSTEMS OF THE FUTURE.

By Laura B. Ruppalt and James G. Champlain

Our naval forces have long benefited from the ability to dominate the electromagnetic (EM) spectrum. From the SK early warning radar, mounted on ships during World War II, to the electronic countermeasures suite installed aboard the EA-6B Prowler aircraft, effective use and management of EM resources have been key to maintaining an advantage on the battlefield. With the rapid proliferation of wireless technologies and transmissions, as well as the global commercial availability of radio frequency (RF) and microwave components, the EM environment faced by the fleet has become increasingly contested. To maintain our spectrum dominance and ensure our forces unfettered access to, and control of, their communications, sensing, and electronic warfare capabilities, naval electronics will require new RF systems that possess a level of adaptability and reconfigurability unnecessary in previous generations.

This increased functionality demands the introduction of a host of new hardware components, including wideband antennas to enable transmission and reception across multiple operating bands, tunable filters to enable on-the-fly selection of operating frequencies, and ultra-wideband, low-loss switches to enable seamless transitions between RF functional blocks. With most current devices designed to operate over a fixed, narrow parameter range, realization of these broadband and adaptive components requires the investigation of new materials, such as 2D semiconductors, as well as a reconsideration of

old materials for new uses. One class of old materials currently being reexamined for use in reconfigurable technologies is chalcogenide-based phase-change materials.

Phase-Change Materials

We generally think of a material as existing in one of three states of matter depending on its temperature: solid, liquid, or gas. In some materials, however, the solid state itself can take on multiple phases, with each phase characterized by a different arrangement of the constituent atoms. Particularly interesting for adaptive applications are materials that can controllably, and reversibly, transition between multiple solid phases—so-called "phase-change materials" (PCMs). One class of PCMs is the chalcogenide glasses, materials that contain a large fraction of sulfur, selenium, or tellurium (i.e., chalcogens).

These materials can be reversibly transitioned between two distinct solid states: a crystalline phase in which the atoms are highly ordered and an amorphous (or "glass") phase, in which the atomic arrangement is very disordered. The solid can be switched between the two phases by applying heat to the material in different ways. For an amorphous material, a moderate-temperature heat pulse can raise the material's temperature above its crystallization point, giving the atoms just enough energy to shift into their preferred, ordered arrangement. Once crystalline, a shorter, higher-temperature heat pulse can push the material above its melting point, imparting so much energy to the atoms that they move away from their desired locations. By removing the heat very quickly (a process known as quenching), the atoms can be "frozen" in their disordered positions, resulting in the amorphous phase. Both phases persist at room temperature without having to be externally powered (i.e., they are nonvolatile), and the process can be repeated to cycle the material between crystalline and amorphous states. What makes these PCMs interesting is that their crystalline and amorphous phases exhibit dramatically different properties: optically, the crystalline phase is reflective, while the amorphous phase is absorptive; electrically, the crystalline phase is conductive, while the amorphous phase is insulating.

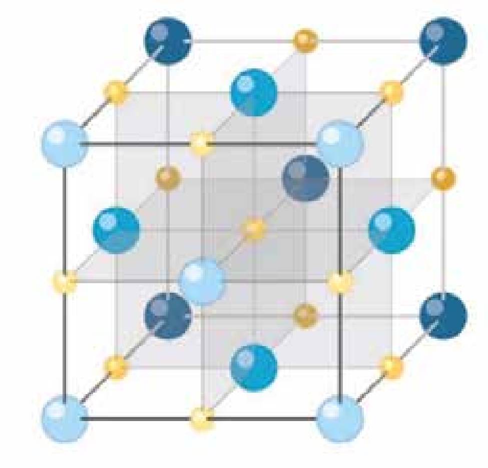
While there are published scientific reports on chalcogenide PCMs dating to the 1960s, their breakout commercial success came in the 1990s when they were first used as the recording media for rewritable optical digital data storage (i.e., CDs and DVDs). In a rewritable CD, a thin layer of PCM, often a silver-indium-antimony-tellurium (AgInSbTe) compound, is used to encode bits (zeroes or ones) by locally heating small regions of the PCM with a laser pulse, switching it into an amorphous or crystalline phase. The bits can then be read using the same laser at lower power to probe the reflectivity of the PCM—amorphous regions will absorb light, while crystalline regions will reflect light. More recently, the electrical properties of PCMs have been exploited to create nonvolatile electronic digital memory devices. As in CDs, the zeroes and ones are stored as regions of amorphous or crystalline material, but in electronic PCM memory, the material (which is often a derivative of germanium-antimony-tellurium, GST) is programmed and read using electrical, rather than laser, pulses.

PCM memory possesses several significant advantages over traditional memory technologies: it does not require power to hold its state, and it can be scaled to very small length scales, enabling high bit densities. While it is unclear at this point whether PCM memory will gain enough market traction to compete seriously with well-developed Flash systems, PCM-based digital memory devices remain an area of active research and investment.

PCM-Based RF Devices

Despite their demonstrated utility in both optical and electronic digital devices, until recently, chalcogenide PCMs generally have not been considered for analog applications. The ability to reversibly and nonvolatilely transition the material between a good conductor (in the crystalline phase) and a good insulator (in the amorphous phase), however, makes these PCMs a very appealing option for low-power-consumption, reconfigurable RF devices. Recent programs sponsored by the Defense Advanced Research Projects Agency and others have focused on evaluating the potential of PCMs for use in RF applications. In particular, the binary chalcogenide germanium-tellurium (GeTe), which possesses a very low resistance in the crystalline phase, leading to low RF loss, and a four-orders-of-magnitude increase in resistance in the amorphous phase, which provides high RF isolation, has emerged as a leading candidate for high-performance, broadband RF switches.

The most common concepts for reconfigurable RF systems rely heavily on switching between components and subsystems to achieve adaptability, frequency agility, and multimission support. The critical interconnect in these systems is the RF switch, which must be broadband to support operation across a wide frequency range, possess low insertion loss to limit signal loss along receive and transmit chains, and demonstrate high linearity to support applications in which signal strength can vary significantly. In addition, for systems with a high level of reconfigurability (and



CRYSTALINE PHASE

thus many switches), low power consumption and ease of integration are critical device features. Current semiconductor-based switches, including field effect transistors and P-I-N diodes, generally induce too much signal loss or are too power hungry to make complex reconfigurable systems feasible. Microelectromechanical-systems-based switches, which demonstrate the necessary bandwidth, insertion loss, and linearity, are a possible candidate but have not gained widespread adoption based on their slow switching times, difficulty in integration, and perceived lack of reliability. PCM-based switches that incorporate GeTe active layers, which can be fabricated with a small footprint using integrated-circuit-compatible processing, offer an appealing alternative.

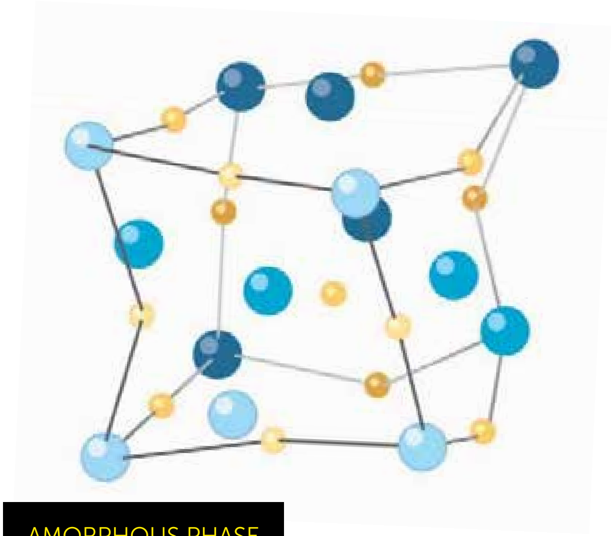
The best GeTe-based switches demonstrated so far make use of a compact, four-terminal architecture, with two connections for the RF signal and two control connections that contact a buried metallic heater, providing the heat necessary for switching. The switch consumes no power when remaining in the on or off state and can be toggled with heater powers on the order of one Watt or less for short durations (hundreds of nanoseconds to microseconds).

In addition, preliminary measurements indicate that these switches possess highly linear operation. The low RF loss, low power consumption, promising linearity behavior, and integrated-circuit integrability of GeTe switches make them excellent candidates for insertion in a wide range of conceived broadband reconfigurable RF systems. Furthermore, measurements have shown that these switches can be operated at cryogenic temperatures—down to -400 degrees Fahrenheit, nearly absolute zero—with no degradation in RF performance and only a modest increase in required switching power, suggesting their utility in extreme environments such as space, where semiconductor-based options generally do not operate effectively.

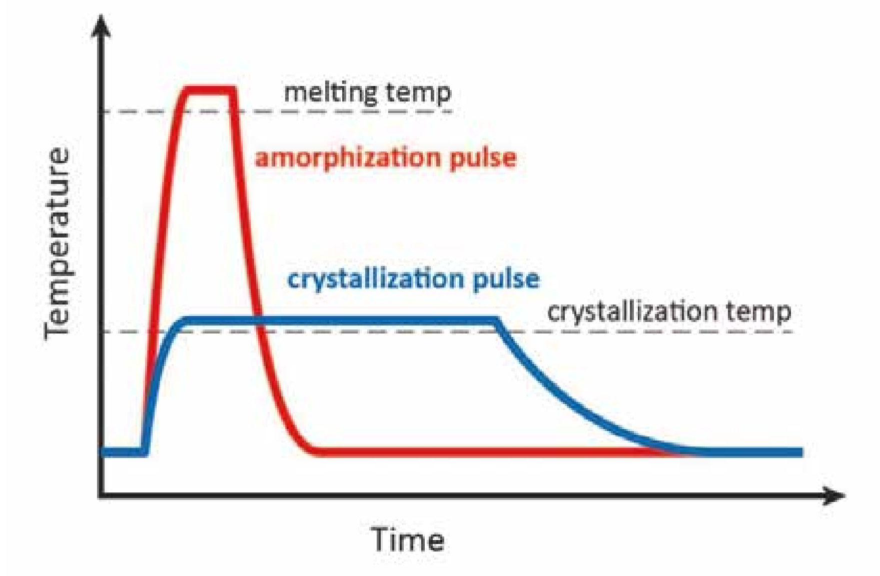
Challenges

Despite this promising initial performance, several outstanding challenges must be overcome before PCM-based RF switches reach the maturity and performance level necessary for widespread integration into fielded systems. In particular, the endurance, power handling, and switching speed capabilities of PCM devices must be proved and extended, as these represent critical parameters for many emerging reconfigurable RF system concepts.

The number of required switching cycles varies considerably by application, but it is expected that PCM-based RF switches for radar, electronic warfare, and communications will need to survive at least 1 million cycles to be operationally useful, with more stressing applications requiring up to 1,000 times more. At the opposite end of the spectrum, applications that need only occasional switching (component redundancy, for instance) may require the device to be exceptionally stable, retaining its on- or off-state characteristic unchanged for extended periods of time (days, months, or even years). With current devices still in the developmental phase, extensive endurance and retention testing has not yet been completed, but initial indications from the PCM memory field are encouraging: accelerated life-cycle testing has shown that PCM-based memory devices can undergo more than one billion cycles before failure and retain their state for greater than a year. PCM-based RF components, with their integrated heater, are in many ways more complicated in structure than memory



AMORPHOUS PHASE



In the crystalline phase (opposite, above), atoms sit in regular, ordered positions in a solid, whereas in the amorphous phase (opposite, below), the atomic positions rest in highly disordered locations. Chalcogenide PCMs (above) can be reversibly switched between crystalline and amorphous phases by applying heat in different ways: a long, lower temperature pulse crystallizes the material, while a short, high temperature pulse quenches the material into the amorphous phase.

devices and are subject to RF stresses not present in memory operation. As a result, their endurance and retention must be proven under representative conditions before they can be deployed operationally.

The ultimate power-handling capability of PCM devices also will need to be investigated, and potentially improved, before they can be used in naval RF systems. GeTe-based switches have demonstrated RF power-handling up to about 0.5 Watts (continuous-wave) before failure, sufficient for many, but not all, envisioned applications. One of the primary failure modes is field-induced crystallization of the insulating amorphous state: even with no power applied to the heater, increasing the RF signal intensity (which increases the electric field across the device) can lead the atoms to rearrange and form a narrow conducting filament, creating a low-resistance path between the terminals. The current through this filament can lead to significant heat generation within the PCM, eventually raising the temperature enough to crystallize the GeTe layer, or even destroy the device. The microscopic origins of field-induced crystallization are currently under investigation, but it is likely that material or device architecture modifications will be necessary to increase the power-handling capabilities of PCM RF switches to support more demanding applications.

The speed at which a PCM-based switch can be toggled is currently limited by the time required to crystallize the amorphous material. In demonstrated devices, crystallization requires heat pulses on the order of 1 microsecond in length, limiting the maximum switching rate to several hundred kilohertz. While this is sufficient for many systems, there are applications in radar, electronic warfare, and communications where being able to switch at significantly faster rates (greater than 1 megahertz) would be desirable. Decreasing the time necessary for switching generally requires improving heat delivery efficiency to the active PCM layer. Methods for achieving this may include altering the device geometry to reduce the thermal resistance between the heater and the PCM; introducing new, higher thermal conductivity materials into the device stack to more quickly transfer heat to the PCM layer; or developing new modalities for heating (perhaps by laser pulse). Additional efforts are necessary to determine whether these, or other approaches, can decrease the switching time of PCM-based devices to the level necessary to support the most advanced reconfigurable RF applications.

Outlook

Despite these unknowns, chalcogenide-based PCMs appear to be a promising option for reconfigurable and adaptive RF technologies. The impressive broadband and low-loss performance demonstrated by preliminary GeTe switches already is sufficient for many existing low-power, reconfigurable subsystems, and if the endurance, power handling, and switching time can be proven and improved, they may find use in a host of other systems ranging from satellites to demanding radar and electronic warfare applications. Just as exciting, though, may be the opportunities that chalcogenide PCMs bring to the broader field of reconfigurable components, opening the door to the development of a variety of adaptive electronic and optoelectronic devices—such as tunable surfaces, adaptive waveguides, reconfigurable optical reflectors—whose behavior can be dramatically varied by the inclusion of a PCM.

About the authors:

Laura Ruppalt and **James Champlain** are engineers with the Naval Research Laboratory's electronics science and technology division. Their research was developed with funding from the Defense Advanced Research Projects Agency.

Using Crystalline Metals for Solid-State Electronics

By Drs. D. Scott Katzer, David J. Meyer, and Brian P. Downey

The key to the Navy and Marine Corps' dominance of the electromagnetic spectrum is the ongoing development of next-generation, solid-state electronic devices and circuit architectures. By improving the performance of solid-state electronics technology used in radio-frequency (RF) amplifiers and power switches, new system-level capabilities and functionality can be attained in various applications—including sensing, communications, radar, electronic warfare, efficient power transmission and power management, and new high-performance weapon systems—to ensure a technological advantage for warfighters against emerging threats. The Naval Research Laboratory (NRL) has a long history as a driving force in the basic research of solid-state electronics technology and continues to discover and develop novel electronic materials and devices.

One of the key drivers for advancing this technology's performance is the development of the underlying materials used to fabricate core electronic devices. Since device performance is fundamentally limited by the properties of the materials used to produce them, researchers are constantly looking for new materials with exotic properties that may open the door to achieving new levels of power, gain, bandwidth, and efficiency performance. To date, nearly all high-performance, solid-state electronic devices are constructed from carefully designed multilayer composites of thin film crystalline semiconductor materials such as silicon (Si), gallium arsenide (GaAs), indium phosphide (InP), silicon carbide (SiC), aluminum nitride (AlN), and gallium nitride (GaN).

While these single crystal or "epitaxial" semiconductor thin films have traditionally been used for the active region of solid-state devices, theoretical predictions made in the 1960s have shown that extremely high-frequency performance can be achieved in materials structures that contain integrated epitaxial *metals*. Up until now there has been very little progress made toward incorporating epitaxial metals into multilayer device structures because of practical limitations in materials growth and thermodynamic incompatibility with existing semiconductors. A recent basic research breakthrough made at NRL, however, has led to the successful synthesis and integration of a novel epitaxial metal material, niobium nitride (Nb_2N), with SiC, AlN, and GaN.

To grow Nb_2N crystals that are integrated with SiC, AlN, and GaN in a controlled environment, NRL has built a customized molecular beam epitaxy system with an electron-beam evaporator source capable of evaporating transition metals with melting points greater than 2,000 degrees Celsius. Sophisticated characterization equipment is used during the growth of Nb_2N to monitor film growth in real time. Since the crystal structure of the Nb_2N film is very similar to that of SiC, the surface of the Nb_2N film essentially mimics the SiC wafer surface, allowing it to serve as a high-quality crystalline "template" for AlN, GaN, or SiC electronic material growth. While Nb_2N is just emerging from its experimental inception, initial testing indicates that its use will play an important role in advancing Navy and Defense Department

Nb_2N

+

SiC

+

GaN

NEXT, NEXT-GEN
SOLID STATE
TECHNOLOGY

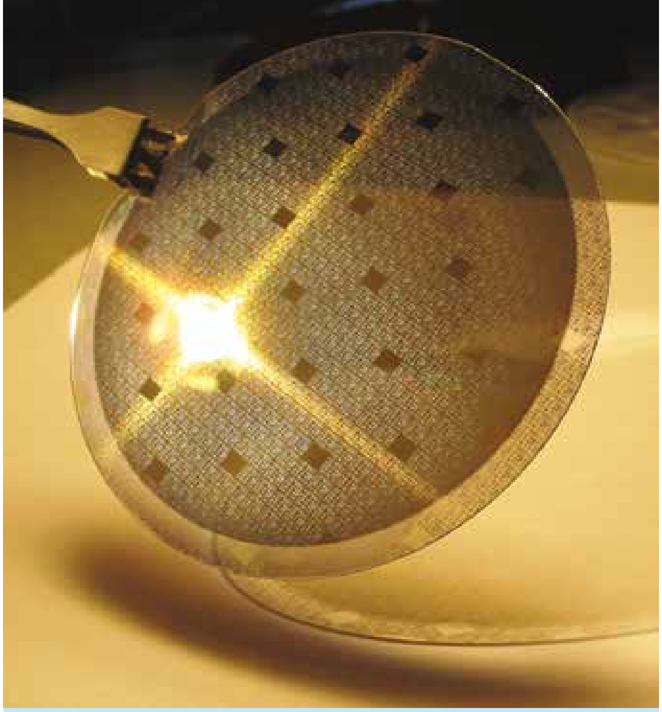
system performance and reliability by enhancing current-generation electronics and enabling next-generation, solid-state electronics technology.

Current Electronics

A recent example of another material that enables improved system performance is GaN, whose properties allow RF transistors to operate at 10 times the power density of previous generations on GaAs- and InP-based transistors. Consequently, the Navy and the Defense Department have invested heavily in developing this technology over the past two decades. Programs of record such as the Air and Missile Defense Radar and Next-Generation Jammer have adopted active electronically steered array systems (AESAs) based on radiating elements powered by GaN-based monolithic microwave integrated circuit (MMIC) amplifiers.

One of the primary challenges encountered in Navy AESA systems is thermal management of the MMICs. As is the case for consumer electronics such as personal computers, controlling the temperatures of components is essential to ensure highly reliable operation. Under normal RF operation, GaN MMICs experience self-heating that can cause the transistor temperatures to rise to more than 175 degrees Celsius. If the peak temperature in the transistor exceeds 225 degrees Celsius, a known failure mechanism will accelerate rapidly, causing amplifier performance and lifetime to drop off dramatically. For this reason, successfully removing the excess heat from the MMIC is extremely important and requires advanced device, circuit, and packaging design, as well as the incorporation of new materials and processing techniques. One thermal management solution could involve removing the GaN circuit from the SiC substrate (which is only used as a template for the crystal growth of GaN) and transferring it to higher thermal conductivity substrates such as water-cooled copper heat sinks or diamond. SiC's strong chemical resistance, however, currently precludes a straightforward way to remove or etch away the substrate to leave only the GaN device layers for transferring.

The results of NRL experiments determined that Nb_2N possesses a potentially useful property in that it can be selectively dissolved away in a bath of hydrofluoric and nitric acid or reactive xenon difluoride (a gas used in commercial integrated circuit processing), leaving GaN and SiC materials unaltered. By inserting an Nb_2N layer between the GaN device layers and SiC substrate, full transistor processing can occur prior to release and transfer to an alternative substrate. NRL is in the midst of developing this process and has had initial success with growth and fabrication of high electrical quality GaN transistors on Nb_2N/SiC. In the near future, NRL will be working to demonstrate successful release and transfer of GaN devices to other substrates to investigate potential advantages in thermal management.



This shows a prototype GaN device wafer that incorporates an Nb_2N layer.

Next-Generation Electronics

While epitaxial Nb_2N could have a significant effect on current-generation electronics, the longer-term and potentially greater impact for this material capability may involve fundamentally higher performing next-generation, solid-state transistors. Realizing theoretical epitaxial semiconductor/metal/semiconductor devices has so far remained elusive, but the combination of metallic Nb_2N and GaN-related semiconductors may provide a long-sought-after solution.

In addition to growing GaN transistors on Nb_2N, NRL has been able to grow very thin, high-quality alternating layers of epitaxial Nb_2N and GaN materials on SiC substrates. The Nb_2N layers have been grown to thicknesses of less than five nanometers (or about 1,400 times smaller than a red blood cell) and remain electrically conductive. This thickness regime is of interest for many revolutionary RF transistor device designs. Work is under way to optimize the growth of these materials to reduce defects and begin fabricating transistors using some of these theoretical device designs. In addition to future solid-state electronics, this new material technology also can affect optical, optoelectronic, and microelectromechanical systems and plasmonic device topologies.

About the authors:

Drs. Katzer, Meyer, and **Downey** are with the Electronics and Science Technology Division at the Naval Research Laboratory. The authors would like to acknowledge support from the Office of Naval Research and the Defense Advanced Research Projects Agency.

GALFENOL:

A Disruptive Technology

By Marilyn Wun-Fogle and Dr. James B. Restorff

In late 1999, researchers at the Naval Surface Warfare Center Carderock Division invented an exciting new smart material: Galfenol, an iron-gallium (Fe-Ga) alloy system. Smart materials are designed materials that have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, temperature, moisture, pH, or electric or magnetic fields. Galfenol is a “magnetostrictive” material with a combination of properties unmatched by any existing smart material. Magnetostriction is a process whereby some materials alter their physical dimensions when a magnetic field is applied to them. It is important because it offers an avenue to convert electrical energy into mechanical energy, similar to the more familiar electric motor. These materials also can be used in the inverse manner and act as sensors.

Magnetostriction is not new. It was discovered in 1847 when James Prescott Joule measured the change in length of an iron rod when it was placed in a magnetic field. In some applications such as magnetic recording or transformers, magnetostriction is considered to be highly undesirable because it leads to audible noise and energy loss. One person’s problem, however, is another person’s opportunity; materials with significant magnetostrictions have proven to be technologically valuable. In World War II, the United States and its allies used nickel in sonar transducers. Magnetostrictive materials were so crucial to the war effort that the Japanese, for whom nickel was unavailable, developed a new iron-aluminum (Fe-Al) magnetostrictive alloy to perform the same function.

Funded by the In-House Laboratory Independent Research program and the Office of Naval Research (ONR), the magnetic materials group at Carderock began a search for materials with room-temperature magnetostrictions larger than that provided by nickel and Fe-Al in the early 1970s. This culminated in 1979 with the discovery of the technologically useful giant magnetostrictive alloy Terfenol-D ($Tb_{0.3}Dy_{0.7}Fe_{1.98}$), which has a useful strain of about 1,800 parts per million.

Magnetostrictive materials can produce very high forces, but the range of motion is small. A 2.5-inch-diameter rod of Terfenol-D that is 10 inches long, for example, can lift an 80,000-pound object (such as a fully loaded tractor trailer truck) 0.018 inches with the application of a modest magnetic field. These materials use low voltages and are generally rugged, impervious to adverse environmental conditions, and highly reliable. Terfenol-D is now commercially available for transducer applications. `

In 1998, Carderock began a search for another magnetostrictive material that was less expensive, had a high strain, and could support substantial amounts of both compressive and tensile force. The search was prompted by the brittleness of Terfenol-D and its ceramic counterparts. These materials cannot be exposed to tensile stresses during either operation or handling. This search ended successfully with the discovery of Galfenol in collaboration with Ames Laboratory. Galfenol is the second room-temperature magnetostrictive material with large magnetostriction discovered by the Carderock group. A U.S. patent for Galfenol was issued in November 2012.

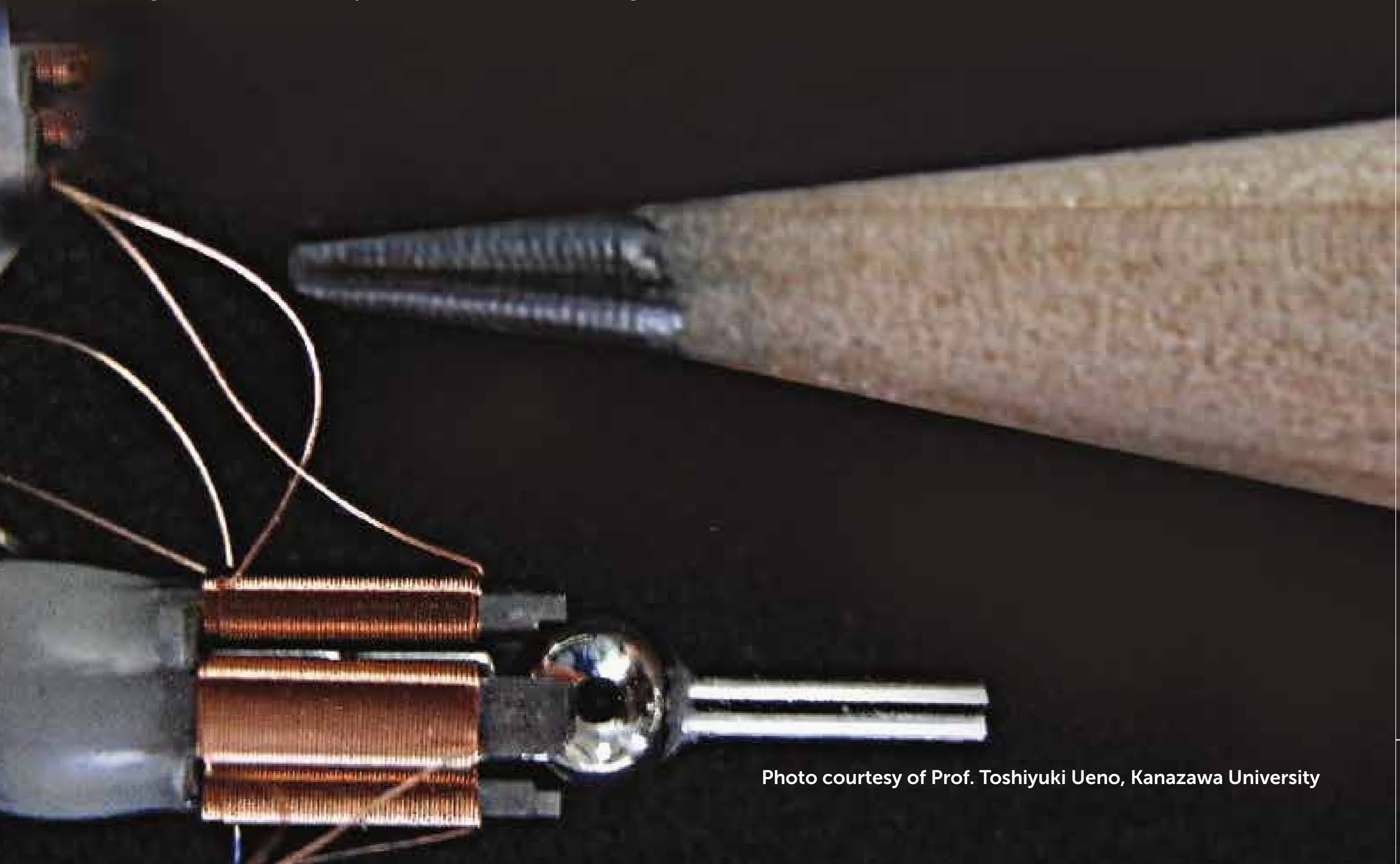
The Galfenol alloys fill a void in the spectrum of smart materials. They are mechanically tough and have saturation magnetostrictions as high as 400 parts per million in single crystal form and 300 parts per million in the more easily produced, highly textured polycrystalline form. In addition, these alloys can sustain approximately 350 megapascals of tensile stress and are stable over a wide temperature range of minus 450 degrees Fahrenheit to above 300 degrees Fahrenheit. Galfenol alloys can be machined and welded with conventional metalworking technology. The full magnetostriction can be accomplished with an easily obtainable magnetic field. Galfenol alloys also can be stress-annealed by heating with a compressive force. This eliminates the need to apply an external compressive stress when the material is used in a device and it simplifies device design. Stress-annealed Galfenol is also magnetostrictively active under a tensile load that is not attainable with either Terfenol-D or piezoelectric ceramic materials.

"The magnetic materials group at Carderock has once again come up with an amazing new material," said Jan Lindberg, an ONR science officer. "Galfenol is a new active transduction material that both answers many current needs and challenges transducer designers to discover new mechanisms that, before the advent of the material, could not even be imagined. It is truly a disruptive technology because it is simple yet complex."

Galfenol is scientifically as well as technologically interesting. Unlike previous active materials, the physical mechanism that generates the magnetostriction is not well understood. In 2006, a five-year, multi-university research initiative led by the University of Maryland was awarded by ONR to investigate the entire class of alloys related to Galfenol, to advance strategies for processing of structural magnetostrictive alloys, and to demonstrate heretofore unachievable actuation and sensing capabilities for these alloys in critical Navy applications. The research goals focused on understanding the fundamental mechanisms of magnetostriction in alloys such as Galfenol, learning how to optimize alloy fabrication and processing at the nano- and macroscale, and developing proof-of-concept devices and systems that demonstrate novel sensing and actuation capabilities. The systems investigated were compact, highly sensitive, and shock-tolerant sonar sensors, load-bearing active elements for shock and vibration mitigation, energy harvesting devices, and nanowire-based artificial cilia sensors for underwater acoustic sensors and communication systems.

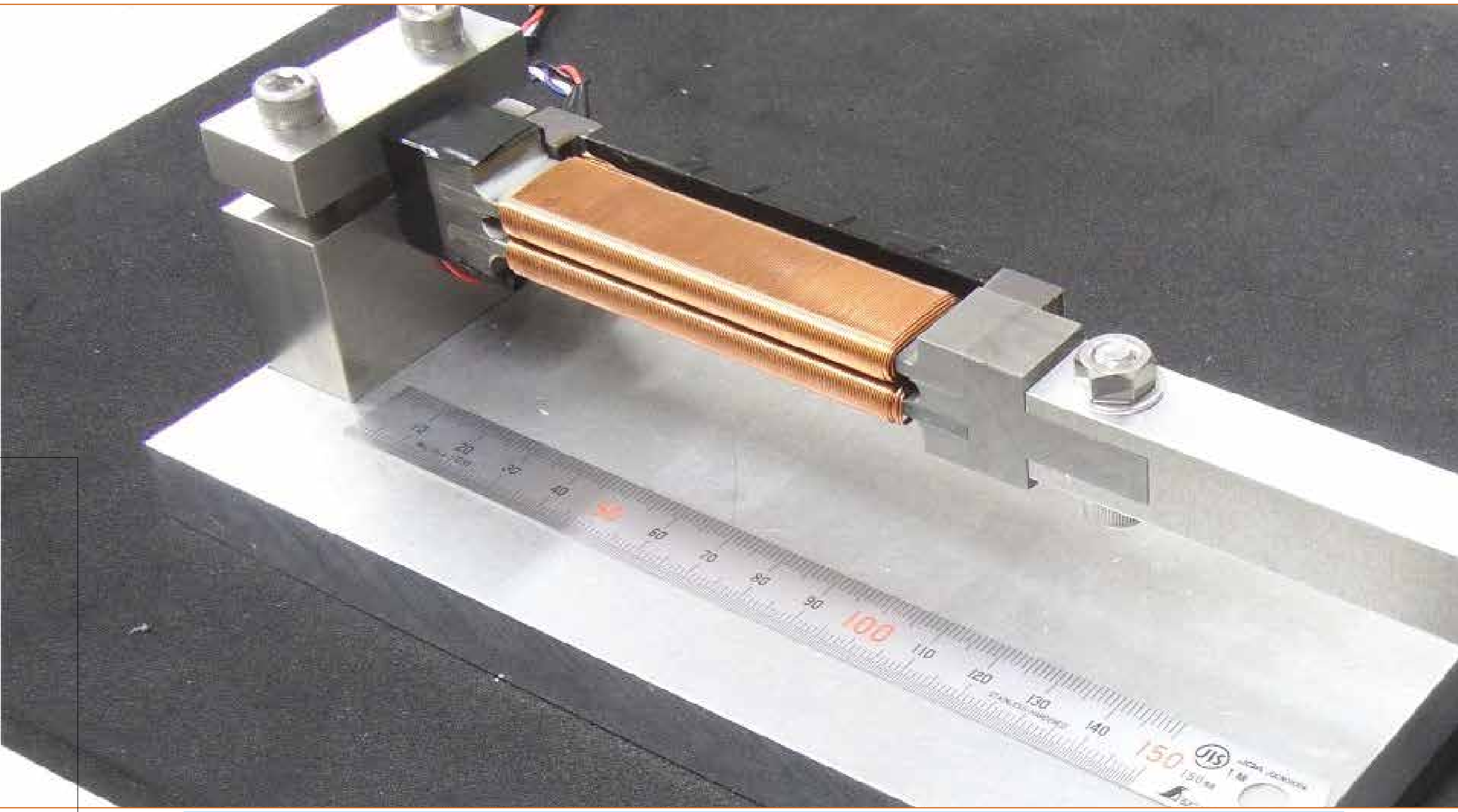
The initiative's objective was to accelerate the development of the next generation of structural iron-based magnetostrictive alloys through fundamental science and engineering studies that focused on three key research areas:

- The modeling needed to understand where the magnetostriction in Fe-Ga alloys comes from, how mechanical and/or magnetostrictive performance might be improved through the addition of ternary elements to these alloys, and to use this understanding to identify alloys of different compositions that exhibit similar or even more desirable attributes



The Galfenol rods of this tiny spherical motor are only three millimeters long.

Photo courtesy of Prof. Toshiyuki Ueno, Kanazawa University



This Galfenol power generator was developed by Prof. Toshiyuki Ueno, an associate professor of electrical and computer engineering at Kanazawa University in Japan.

- Investigations into the processes for making alloys with desired magnetomechanical performance at the nanoscale, microscale, and macroscale

- The development and use of models for design, building, and testing of prototype hardware to demonstrate and take advantage of the novel capabilities of these unique alloys in sensor, actuator, and energy harvesting systems.

The initiative investigated a broad range of fundamental issues focused on the development of the next-generation, structural, iron-based magnetostrictive alloys. Eight partner institutions (University of Maryland, University of Minnesota, Ohio State University, Pennsylvania State University, Iowa State University, Virginia Polytechnic Institute and State University, University of California at Irvine, and Rutgers University) participated. More than 125 journal publications, 16 doctoral degrees, and eight master of science degrees resulted from this project.

Carderock also has been engaged in a cooperative research and development agreement with industry partner Etrema Products for further development and widespread use of Galfenol. For more than a decade, Carderock, Ames Laboratory, and Etrema Products have collaborated to design the alloy, develop production processes, and perfect methods of producing the material in large solid form, rolled sheets, and wires in an effort to shorten the usual 20-year time frame between the discovery and commercial/military use of a new material. The diversity of forms allows Galfenol-based parts to be used in a variety of new applications, both commercial and military.

GALFENOL IS A NEW ACTIVE TRANSDUCTION MATERIAL THAT BOTH ANSWERS MANY CURRENT NEEDS AND CHALLENGES TRANSDUCER DESIGNERS TO DISCOVER NEW MECHANISMS THAT, BEFORE THE ADVENT OF THE MATERIAL, COULD NOT EVEN BE IMAGINED. IT IS TRULY A DISRUPTIVE TECHNOLOGY BECAUSE IT IS SIMPLE YET COMPLEX.

ONR supported the magnetic materials group's efforts in two initiatives: the Naval International Cooperative Opportunities Program (NICOP) and the Technical Cooperation Program (TTCP). Under NICOP, the Carderock group worked with Mechano Transformer Corporation in Japan and the University of Tokyo on Galfenol uses as a microactuator in a microspeaker, microinjector, and other components. NICOP involvement was extended to the University of Kanazawa in Japan, where they are researching the use of Galfenol for energy harvesting applications. Under the TTCP, Carderock collaborated on an operating assignment with the defense laboratories in Canada, Australia, and the United Kingdom, with an eye toward using these materials in defense applications. The success of this assignment resulted in a TTCP achievement award for significant advances in the development and exploitation of novel magnetostrictive and magnetic shape memory alloy technologies for defense applications—laying the groundwork for developing international acceptance standards and contributing to future substantial enhancement of military capabilities of the TTCP member nations.

Since the discovery of Galfenol in 1999, it has advanced from being a curiosity in a laboratory to a material being investigated worldwide by a variety of university and government laboratories. In the United States, efforts to commercialize the material are well under way and showing substantial progress. Continued development of magnetostrictive materials will result in their optimization for as-yet-untapped potential in structural applications: vibration sensors, vibration control actuators, and energy-harvesting devices and systems. We believe this material has a bright future and will give designers a material with previously unavailable performance.

About the authors:

Marilyn Wun-Fogle and **Dr. Restorff** are scientists in the metallurgy and fasteners branch at the Naval Surface Warfare Center Carderock Division.

SEARCHING FOR PLASMONIC POSSIBLITIES AT THE NANOSCALE

By Alison F. Smith and Dr. Sara E. Skrabalak

What class of materials opens the door to advanced technologies ranging from energy storage to chemical detection? Plasmonic nanomaterials—which is a transformative class of materials with applications in structural health and food safety monitoring, enhanced chemical detection, fingerprints for tagging, tamper detection, interconnection technologies, and light-capture enhancement for solar energy conversion devices.

Nanoscale materials have properties that are vastly different from their bulk counterparts. One such property is that free electrons in a metal can be excited by and couple with visible light, and these waves of electrons are confined to the nanoparticle (NP) surface. This property—the perturbation of mobile electrons from their equilibrium positions induced by light interactions—defines metallic plasmonic nanomaterials. Enhanced electromagnetic (EM) fields on and near the surface of these particles make enhanced chemical sensing a reality in surface-enhanced Raman spectroscopy devices; this capability is particularly true for stellated or star-like particles with lots of sharp features where the EM fields are most intensified. These metallic NPs also scatter light primarily in the visible region, making them excellent sensor candidates for characterization with standard light microscopy methods. Plasmonic nanomaterials also are of interest as waveguides and in electronic devices as the interface between optical and electronic circuits (interconnection technologies).

The past 15 years have witnessed an explosion in nanomaterials synthesis, moving well beyond simple single-metal spheres (such as gold spherical NPs) to complex shapes and compositions that include a multitude of dielectrics and, more recently, bimetallic NPs. Synthetic strategies are currently mature enough for large-scale nanoprocessing; this leap in synthetic control over composition and structure has expanded the number of potential applications so much that nanomaterials can be and are being used toward many naval-relevant applications such as food safety indicators and enhanced chemical sensing.

Bimetallic Benefits

The properties of plasmonics depend on several factors, including the composition and shape of the NPs. For example, a cubic gold NP has a different plasmonic response than a spherical gold NP. Decoupling the compositional and structural (shape) contributions to the plasmonic response of a NP can be difficult, especially when there is a complex composition beyond a simple monometallic structure. Efforts to tease out these contributions for bimetallics are worthwhile because the integration of two metals into one nanomaterial offers multifunctional sensing platforms in which one metal serves as the primary optical sensor and the second metal serves some other desired function. For example, hydrogen sensors have been developed by coupling optically active gold with hydrogen absorbing palladium.

Researchers at the Naval Surface Warfare Center Crane Division and Indiana University at Bloomington are working to establish engineering guidelines for complex-shaped, bimetallic NPs for refractive-index-based sensors, catalysis, hydrogen sensing, tagging, and tamper detection. Now that synthetic strategies can provide a variety of plasmonic structures, advanced plasmonic technologies are becoming a reality. To fully expand this set of technologies, engineering standards that encompass the structure-function correlation of these materials need to be established. Once established, these standards will serve as a toolbox for researchers to design plasmonic platforms on demand to meet the needs of specific applications.

Creating and Using the Toolbox

One example of creating and using these engineering standards is the creation of refractive-index-based hydrogen sensing platforms. Hydrogen sensing is needed for critical electronics, where hydrogen can be detrimental to the system. In addition, hydrogen storage and sensing is of interest for energy applications. Using an eight-branched gold-palladium plasmonic NP as a model system, the Indiana University group is answering questions such as, how does the structure and composition affect the signal intensity and how does the composition effect RI sensitivity? The answers to these questions establish plasmonic design criteria that will enable the optimal design of sensing platforms.

> **THE PAST 15 YEARS HAVE WITNESSED AN EXPLOSION IN NANOMATERIALS SYNTHESIS, MOVING WELL BEYOND SIMPLE SINGLE-METAL SPHERES… TO COMPLEX SHAPES AND COMPOSITIONS.**

Plasmonic nanomaterials provide a multitude of possibilities for military and commercial applications, from enhanced sensing to medical therapeutics and diagnostics. It is truly a cross-cutting class of materials that will solve a wide array of naval and defense challenges. Strides toward developing engineering standards for plasmonic materials will catch up to the significant advances seen in plasmonic material synthesis, and the resulting plasmonics toolbox will enable researchers to rationally design plasmonic platforms.

About the authors:

Alison Smith is a Ph.D. fellow at Naval Surface Warfare Center Crane Division working in the area of bimetallic plasmonic materials for naval-relevant applications at Indiana University.

Dr. Skrabalak is the James H. Rudy associate professor of chemistry and a dean's fellow at Indiana University.

SPECIAL SECTION:

Building the Airframes of Tomorrow

By Bill Nickerson

Do you know what your aircraft is made of? It's a simple enough question, but it doesn't always involve a simple answer. The material with which an aircraft is constructed has a decisive influence on how big it is, what and how much it can carry, the stresses it can take, and how far it can fly—affecting, in other words, just about everything that an aircraft does. Airframe structure is the core capability for all naval aviation operations, whether fixed or rotary wing, manned or unmanned. Airframe materials are the underlying enabling technology for all naval air vehicle structures.

The current trend in airframe design has been hybrid material construction, where the majority of the skin, control surface, and outer mold line (OML) structures are polymer-matrix composites, and the majority of the internal substructure and critical components are metallic alloys. Future air platform system design will rely heavily on our ability to more appropriately select and optimize durable materials for a variety of operational environments and damage mechanisms. Future airframe sustainment will also make use of fully engineered redesign analysis and production repair procedures, transitioned through the relevant engineering and depot commands.

Sea-based aviation (SBA) demands structures and materials requirements that are often unique, or more demanding than the same land-based platform requirements. A strong program that focuses on aircraft science and technology activity is critical to the health of naval aviation. The Sea-based Aviation National Naval Responsibility, established in 2011, contains a core structures and materials focus area to address the science and technology challenges for naval aircraft. Very few of the extant materials and structures challenges are limited to existing platforms, or design specific; instead, they are fully represented in planned future platform designs.

The structures and materials focus area of the national naval responsibility is funding innovative research and technology in five subareas: structural mode characterization; high-loading, lightweight structural materials; advanced structural concepts; materials degradation and corrosion; and structural protection and maintenance. Research is targeted towards balancing strength, weight, and durability improvement goals. Along with the other SBA focus areas, the structures and materials focus area also will support the infrastructure necessary to maintain technology superiority while serving as a pipeline of future scientists and engineers.

The Office of Naval Research (ONR), through its SBA initiative's structures and materials program, has partnered with other government agencies, academia, and industry to develop enabling technologies for the airframes of tomorrow. What follows is a short summary of these basic and applied research efforts in novel and agile composites, advanced metallic structures, and advanced protective coatings.

About the author:

Bill Nickerson is the sea-based aviation structures and materials program officer with the Office of Naval Research.

Photo By Lockheed Martin

WHAT IS IT MADE OF? TODAY'S AIRCRAFT ARE BUILT WITH BOLD NEW MATERIALS, GIVING THEM ADVANCED NEW CAPABILITIES

NOVEL AND AGILE COMPOSITES

HYBRID NANOCOMPOSITES

By Anisur Rahman

Polymer (and ceramic) matrix composite structures offer many possible benefits in structural optimization, future durability, and weight vs. range/payload trade space. They are mechanically tailorable, environmentally resistant in many exposures, and can potentially be functionally tailored through graded/hybrid construction. Composites possess high specific stiffness and strength in most loading conditions compared to metallic alternatives. In addition, composite structures can be modified to create smart, multifunctional structures; combining mission- or environment-specific surface response with strong, durable mechanical properties.

All these benefits make composites ideal for naval air applications. Currently the use of composites in naval airframes is between 25 and 30 percent by weight. The potential exists, however, to increase tremendously the volume proportion of composites to produce lightweight but agile air vehicle structures to meet the needs of naval air vehicles. Structural composite materials are made of stiff fibers such as carbon or glass in a cured (hardened) polymer matrix. Composites usually are constructed as unidirectional plies of different orientations glued together by an adhesive. These composites (called laminated composites) possess excellent in-plane (two-dimensional) strength and stiffness. When subjected to out-of-plane loads such as bending, however, they are prone to matrix cracking and delamination. Matrix cracks are cracks across the interlaminar region within the plies and delamination is when cracks run between adjacent plies. These types of failures have been noted in currently used composite components such as rotorcraft hubs and tail rotor flex-beams.

Attempts have been made to inhibit delamination by using fiber weave through thickness or by using pins to tie the different plies together. These attempts, however, often have damaged the plies and degraded the in-plane properties. Professor Brian Wardle and his team at the Massachusetts Institute of Technology (MIT) are using a novel nanostitching approach to tie the various plies of graphite/epoxy composite. Aligned mats or forests of carbon nanotubes are placed between the plies. The tie is so strong these nanostitched composites when tested do not fail at interface but the rather by matrix cracking in the plies.

In another ONR-sponsored program, Professor Khalid Lafdi and his group at the University of Dayton are toughening the plies by using “fuzzy fibers.” Fuzzy fibers are made by carbon nanotubes growing radially out of parent fibers. These nanotentacles embed in the polymer matrix and acts as crack stoppers. One big challenge in growing the nanotubes in this fashion was that in earlier attempts the growth process damaged the parent fibers. Researchers now have solved the problem by changing the processing condition and the catalyst used so that the degradation does not happen or is negligible. Initial testing is showing promise in improving out-of-plane properties both in tension and bending. The improvement increases with the concentration of nanotubes grown. This growth is not proportional, however, and drops off after reaching a maximum. Current research at the University of Dayton is focused on understanding the strengthening mechanisms and to find the sweet spot of nanotube concentration that maximizes the improvement. While both nanostitching and nanofuzzy technologies are showing promise, the idea is to combine these two technologies in the same composite structure to produce a composite that provides superior properties.

The benefits of hybrid composites go beyond enhancing mechanical properties. Aligned carbon nanotubes such as that used for nanostitching can be used as heaters. In a Navy-sponsored project, Metis Design Corporation has worked with MIT to develop a de-icing system for unmanned aerial vehicles. The carbon-nanotube-based system is more compatible with conventional copper-based thermoelectric systems and also requires 50 percent less power.

About the authors:

Anisur Rahman is a structures engineer with the Naval Air Warfare Center Aircraft Division.

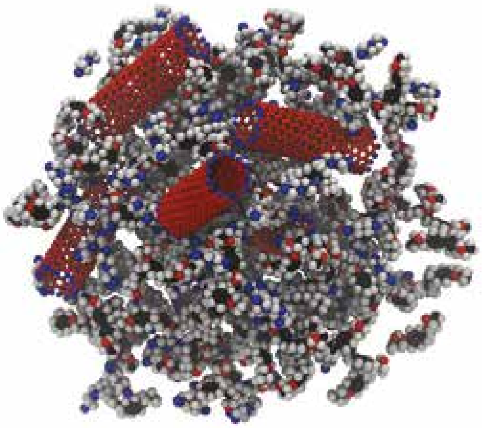
HYPERHYDROPHOBIC COMPOSITE RESINS

By Anisur Rahman and Joseph Tsang

The objective of this research effort is to increase the performance and durability of the Navy's composite structures under demanding operational environments, such as exhaust impingement in high humidity conditions. This ONR-sponsored effort is headed by Dr. Joseph Tsang at the Naval Air Warfare Center in China Lake, California. The Navy often operates in the most humid and chemically aggressive environments, causing water uptake, and the resulting loss of structural capability, to be a challenge for most typical commercial composite resins. Water retention in composite structures induces a considerably long list of negative attributes. For example, the thermos-mechanical properties of the resins (including their stiffness and ultimate usage temperature limits) are reduced substantially with increasing levels of absorbed water. Concurrently, there is an overall weight gain of the composite structures that is a considerable penalty for aircraft. Steam generation by rapid heating of absorbed water also can weaken the composite microstructures and reduce their long-term durability. In addition, an increase in galvanic corrosion processes for neighboring or connected metal parts can happen through additional electrolyte pathways.

Research performed at China Lake to date has tailored epoxy resins to address the challenges faced by the current materials set. In this novel approach to hydrophobic (water-hating) resins, multiple sources of water absorption have been mitigated. This was accomplished through the design, synthesis, and polymerization of novel hydrophobic monomers and the subsequent testing of their fully cured resins. All starting materials selected for this study are commercially available, cost-effective, and scalable to manufacturing quantities.

Researchers have gained an understanding of the correlation between hydrophobicity and material properties through the study of the structure-property relationships of these resins. The level of water absorption is inversely proportional to the degree of hydrophobicity. New epoxies prepared in our laboratories have much lower water uptake by weight while exhibiting comparable or even superior ultimate use temperatures to those of existing epoxies used in the fleet.



This represents a molecular dynamics simulation of a carbon nanotube polymer.

Another objective achieved by this research is the rapid fabrication of highly reproducible and defect-free test specimens. This methodology allows for substantially accelerated test cycles, and high confidence in test results. Rapid fabrication of defect-free specimens also provides additional insights to potential challenges in polymer processing and the relationship between material performance, processing, and cost. These are important considerations for eventual increased fabrication for fiber-reinforced composites, and the feasibility of transitioning these materials into future aircraft platforms. With this combined molecular design and test methodology in place, the next target composite resins are the bismaleimides, which are widely used in the latest generation of aircraft, namely the F-35 Lightning II and V-22 Osprey.

About the authors:

Joe Tsang is a polymer scientist with the Naval Air Warfare Center Weapons Division.

Anisur Rahman is a structures engineer with the Naval Air Warfare Center Aircraft Division.

MULTIFUNCTIONAL FLEXIBLE CERAMIC MEMBRANES

By Chengying Xu

Multifunctional materials demonstrate a combination of functionality, adaptability, and survivability for future engineered applications. With ONR sponsorship, Dr. Cheryl Xu and her team at Florida State University are developing one kind of novel multifunctional ceramic membrane that shows enhanced strength and toughness, great flexibility, and promising electrical and thermal conductivity. One application example is high-temperature, electronically functional components that are capable of adapting to the shape change of the aerostructure while maintaining key functionality such as sensing and actuating.

In laboratory testing, the synthesized ceramic membrane demonstrated excellent ductility and flexibility. It can be bent to 75 percent of the original length without breakage and the flexibility testing can be repeated numerous times without any cracking or performance degradation—the material strength showed no reduction even after a 1,000-cycle flexibility test. The tensile strength of the ceramic membrane was measured at 500 megapascals (MPa) and the modulus at 100 gigapascals. Ceramics often are thought of as having excellent thermal and wear properties, but they have poor flexibility and fracture under mechanical loading conditions.

Laboratory tests have confirmed that the membrane not only has superior strength and stiffness but greatly improved electrical and thermal conductivity compared with unmodified ceramics. The electrical conductivity has been shown to be of range of copper or zinc. Because of its lightweight, high mechanical strength, excellent high-temperature resistance, and low chemical reactivity, the ceramic membrane has the potential to play important roles in many defense-related applications, such as liquid-fueled rocket engine combustion devices (thrust chambers and nozzles), aircraft brakes, and thermal protection systems on hypersonic vehicles.

About the authors:

Cheryl Xu is a professor at Florida State University.

Photo by Lt. Cmdr. Darin Russell

MULTISCALE MODELING

By Anisur Rahman and Aditi Chattopadhyay

High-performance, lightweight, multifunctional composites provide unique opportunities to create structural materials with improved properties that can be tailored for a number of significant military applications. There are, however, scientific barriers pertaining to scalability, reliability, and durability of these complex composite systems that also are major impediments limiting their applications. Practical implementation of the technology requires the development of a methodology capable of quantifying the effectiveness of dispersed nanofeatures (carbon nanotubes, particles, etc.) in the polymer, their impact on other material constituents, and the overall structural response under service conditions. Current state-of-the-art research on nano-enhanced materials relies heavily on experimental methods and models that are not quite capable of addressing the necessary technical challenges associated with real applications.

In an Office of Naval Research-sponsored initiative, a team at Arizona State University is developing physics-based, multiscale, constitutive models for carbon-nanotube-enhanced composites to enable accurate estimation of material response, deformation, and failure. The multiscale modeling approach is initiated at the nanoscale using molecular dynamics simulations to study atomistic interactions in the CNT-polymer phase. A novel hybrid force field is incorporated to capture the fiber/matrix interphase behavior and the inelastic response of the material system caused by successive bond breakage in the polymer chains. Critical input parameters at this length scale are identified through a systematic sensitivity study, and robust models are implemented to transfer key information to continuum length scales. The continuum model simulates the fiber and the CNT-dispersed matrix and corresponding local variations in material architecture arising from stochastic effects. Damage initiation and evolution are investigated by integrating a set of scale-dependent appropriate damage criteria capable of evaluating multiple failure modes and model interactions, and predicting the damage and failure at the relevant length scales.

The multiscale model is integrated into a general finite element framework to study the structural response of nanocomposite T-joint stiffener and predict the first load drop during a pull-off test. The computational modeling technique is validated with results from tensile experiments performed on a nanocomposite T-joint stiffener. It is envisioned that the developed simulation framework will lead to computationally assisted design and certification of new and improved polymeric materials. The predictive modeling framework will also help enable the optimization of the nanocomposites with tailored properties for specific naval applications.

About the authors:

Anisur Rahman is a structures engineer with the Naval Air Warfare Center Aircraft Division.
Aditi Chattopadhyay is a professor at Arizona State University.

Photo by MC3 E. T. Miller

DURABLE AND MORE CAPABLE METALLIC STRUCTURES

INTEGRATED COMPUTATIONAL MATERIALS ENGINEERING

By David Snyder and Jason Sebastian

The Office of Naval Research (ONR), in conjunction with the laboratories at the systems commands, has been in the forefront of efforts involving the Integrated Computational Materials Engineering (ICME) process. ICME seeks to streamline the material and component development timeline and improve fleet readiness using computational tailoring of designer metallic alloys. Typical materials development and qualification times for flight-critical components can take up to 20 years—it is the goal of ICME to cut this cycle in half by replacing costly and time-consuming, trial-and-error approaches with computational modeling to validate by targeted experimentation.

One such performer is QuesTek Innovations, a global leader in the application of ICME. ONR, Naval Air Systems Command, and other science and technology commands have funded QuesTek to develop new classes of high-performance, computationally designed materials to address a number of fleet needs. Among the technologies developed is a new ultra-high-performance steel—Ferrium M54—for demanding aerospace applications and a new class of advanced aluminum alloys optimized for additive manufacturing.

In 2007, the U.S. Navy released a Small Business Innovation Research solicitation for proposals to "develop and demonstrate innovative low-cost, high-strength, high-fracture-tough, corrosion-resistant metal alloys." At interest was a lower-cost alternative to the steels available on the market, capable of withstanding the demanding conditions experienced during aircraft carrier takeoffs and landings—especially AerMet 100, a strong but expensive steel used in landing gear.

QuesTek was able to accelerate the material development of its Ferrium M54 steel from a clean sheet design to a fully qualified, commercially available alloy in just six years. The diagram below details the accelerated material development milestones for M54 steel, completed entirely under Navy sponsorship. The alloy was computationally designed in a single iteration, achieving properties at laboratory scale in 2008. By mid-2009, Latrobe Specialty Metals was licensed and producing the first commercial-scale heats. By coupling production with an ICME-based optimization of material processing, the alloy successfully met the target property goals, and achieved SAE Aerospace Material Specification by mid-2011.

With confidence in M54's ICME-based design, the Navy supported the production of three prototype hook shanks for the T-45 Goshawk aircraft for rig testing and qualification. In parallel, with 10 full-scale (10-ton) heats produced, approval by the Federal Aviation Administration to have the minimum design allowable properties included in the Metallic Materials Properties Development and Standardization was secured by late 2013.

The development of Ferrium M54 culminated in successful rig testing of the hook shank components in 2013. With prototype hook shanks surpassing twice the component life over the incumbent Hy-Tuf steel, Ferrium M54 was qualified for the arresting gear components for the T-45. In October 2014, a T-45 equipped with an M54 hook shank completed its first field service test flight. An order was placed by the Navy to procure 40 new shanks as flight assets, with an estimated cost savings of more than $3 million afforded by the increased component lifecycle with the material upgrade.

The next case study for Navy-led ICME is the development of a new class of advanced aluminum alloys specifically for additive manufacturing. Generally speaking, additive manufacturing (AM) is a process of creating components in a layer-by-layer fashion (hence the term "3D printing"), using computer drawings as input rather than physical molds or machining tools. By allowing for rapid net-shape fabrication of highly complex

geometries, AM could reduce material usage, energy consumption, component cost, and fabrication time. The technology has matured significantly in recent years, with particular interest in using it to manufacture aircraft parts.

There are many high-strength aluminum alloys currently in use on aircraft. Unfortunately, nearly all of these alloys are not suitable for AM because they have a strong tendency to crack under the intense residual stresses of the process (a phenomenon called "hot tearing"). Aluminum is particularly susceptible to this problem. In addition, AM processing results in many new types of material defects that are not typically an issue in conventional processes. To enable broader adoption of AM for applications for the fleet, new aluminum alloys are needed to circumvent these issues and ensure good parts are printed.

To address this deficiency, ONR initiated the development of new aluminum alloys for additive manufacturing with a 2014 solicitation for proposals. The target application was helicopter gearbox housings, where the beneficial corrosion resistance of aluminum is offset by its inability to be conventionally cast into complex geometries (a problem solved by AM).

QuesTek commenced the design of a new class of aluminum alloys to couple high performance (e.g., strength) with AM processability. New alloys were designed that spanned a range of concepts and target properties by integrating a range of computational modeling tools to simulate material behavior during processing. Key design metrics include hot tearing susceptibility during printing, evolution of material structure during processing, development of AM-specific defects such as inclusions or porosity, and final material properties needed for the application. The delicate interaction of all of these metrics, combined with the high relative cost of alloy powder, makes this application a perfect candidate for computational design.

Within the Phase I Small Business Innovation Research project, a first-generation alloy candidate was processed into alloyed powder by the direct metal laser sintering process. Initial results point to successful proof-of-concept, and highlight specific areas in which ICME design tools can be extended or developed to further refine new second-generation alloys.

This project demonstrated that ICME-based design of new materials can successfully solve platform needs at a pace far more quickly than traditional trial-and-error methods. QuesTek is continuing the development of new additive, manufacturable alloys, with the goal of transitioning the technology and scientific knowledge gained along the way to the fleet as was accomplished with Ferrium M54.

About the authors:

David Snyder and Jason Sebastian are researchers with Questek Innovations.

U.S. Air Force photo by Staff Sgt. Katerina Slivinske

ADDITIVE REPAIR FOR AIRCRAFT STRUCTURAL COMPONENTS

By Luke Brewer and Fred Lancaster

A rapid and portable means for repairing corrosion, wear, and erosion damage in aircraft components is of increasing importance with an aging fleet. Full replacement of structural components is costly both in terms of the repair and operational costs. Cold gas dynamic spray deposition (also known as "cold spray") of pure aluminum has been developed for repairing corrosion damage on non-load-bearing areas of magnesium components for naval rotor- and fixed-wing aircraft. In the cold spray technique, a special nozzle accelerates aluminum powder particles to supersonic velocities while in a gas jet. When these particles impact a substrate, they form permanent mechanical bonds without melting. By rastering the nozzle over the part, material can be added until all of the lost material is dimensionally restored. For non-load-bearing components, this additive approach to dimensional restoration is working well—but what do we do for loading-bearing components?

A team at the University of Alabama has recently started an Office of Naval Research (ONR)-sponsored project to develop additive repair methods using cold spray deposition of high-strength aluminum alloys such as AA7075 and AA2024. These alloys have much higher levels of strength than pure aluminum and are the materials that comprise structural members of naval aircraft. In collaboration with Naval Air Systems Command and the Naval Surface Warfare Center Carderock Division, this team is developing cold spray processes to allow for additive repairs of complex two-dimensional and three-dimensional components. Using the new VRC Metal Systems Generation III deposition system, they will develop the relationships between processing, microstructure, and mechanical behavior that are required for strong, reliable repairs for the fleet readiness centers of the future.

About the authors:

Luke Brewer is a professor at the University of Alabama.
Fred Lancaster is a materials engineer at the Naval Air Warfare Center Aircraft Division.

MATERIALS SELECTION FOR DURABILITY

By Keith Legg and Craig Matzdorf

Traditionally, airframe structures are designed for immediate mechanical performance and loads-only structural response. The lifetime of aircraft structures is predicted on these analyses, and environmental degradation of properties over the life cycle and during operations is often an afterthought. Although the maintenance of aircraft structures is primarily determined by material degradation, galvanic management of airframe designs and corrosion resistant material selection never has been done systematically. From end of life tear-down inspections, we know that a significant portion of metallic structural failures are initiated from corrosion features, especially those accelerated by dissimilar material coupling. In its most simplistic form, this environmental exposure ("loading") creates corrosion features, such as pitting, that produce cracks and then grow under the combined influence of mechanical stress and corrosion, eventually leading to structural failure. There is a strong correlation between corrosion and structural damage, which we think of as corrosion fatigue and stress corrosion cracking.

Office of Naval Research's (ONR) Sea-Based Aviation program is developing computational approaches to corrosion activity prediction, crack initiation, and crack growth, with the ultimate aim of predicting service life in terms of the combination of mechanical and chemical stresses. This approach is intended to be the basis for design of durable aircraft structures using design principles that will take into account both stress and corrosion in the design phase, rather than designing for stress and then maintaining for corrosion.

A materials selection and galvanic analysis tool was developed by Boeing Research and Technology under funding from ONR. The initial transition to platform structural engineering teams was begun in 2014 at Fleet Readiness Center Southwest in Jacksonville, Florida. This material selection tool, which predicts the expected galvanic interactions in a simplified one-dimensional analysis based on the polarization behaviors, allows for a quick comparison of predicted relative durability between different possible combinations of materials. This will allow for engineers to make material change recommendations during rework based on quantified electrochemical analysis of aviation-specific substrates and finishes. The analysis is based on a quick potentiodynamic curve-crossing method that compares the relative magnitude of expected current density at the intersection of two (or more) dissimilar materials.

Modern naval aircraft are designed with sophisticated computer-aided-design software to model stress, fatigue, and heat flow, but not corrosion. Under the ONR Sea-based Aviation program, Corrdesa LLC has developed a new approach to analyzing actual component designs. Corrdesa is qualifying a computational corrosion analysis software kit that overlays a galvanic corrosion map directly onto the three-dimensional design of the aircraft, much as we predict stress. The output maps where corrosion will occur, projects severity, and anticipates how quickly it will damage the aircraft's protective finishes.

The approach replaces outdated galvanic tables with a scientifically accurate method for predicting galvanic currents. It gives depot engineers a simple method for estimating interfacial galvanic coupling, together with rigorous finite element analysis to predict the location and severity of corrosion in complex mixed-material structures. This technology is already affecting original equipment manufacturer design and depot sustainment, providing a tool to predict and prevent corrosion at the design stage, and to stop it being reintroduced in sustainment. This new approach has an immediate effect on legacy systems, and will greatly impact the material and geometry optimization for future platforms. This capability will allow galvanic durability to be included in the design process with production affordability, operational performance, and mechanical functionality.

About the authors:

Keith Legg is a mechanical engineer with Corrdesa, LLC.
Craig Matzdorf is a materials engineer at the Naval Air Warfare Center Aircraft Division.

ADVANCED PROTECTIVE COATINGS

ADVANCED ALUMINUM-RICH PRIMER

By Brenna Skelley

The materials engineering laboratory at Naval Air Warfare Center Aircraft Division, Patuxent River, Maryland, has patented a novel nonchromated primer using an activated aluminum alloy pigment; this novel pigment provides both barrier and cathodic inhibition protection to metallic substrates. This primer has exhibited corrosion performance superior to that of the current high-performance nonchromate and legacy chromate primers the fleet is using. It has shown superior results on steel and aluminum substrates, meaning it could be used as a future higher-performance alternative to chromated and zinc-rich primers within the Department of Defense.

In addition to the pigment composition, the lab also has developed a process for passivating (i.e., making it less susceptible to the effects of air and water) the aluminum alloy pigment (and other metallic pigments, such as nickel-loaded conductive greases and sealants) to provide an optimized balance between pigment stability and substrate protection. The pigment surface modification process gives the coating greater resistance to self-corrosion and extends coating life to protect the substrate.

Over the past year, under funding from the Office of Naval Research, researchers focused on continuing to optimize the formulation for use on steel and aluminum substrates, studying the primer's ability to inhibit stress corrosion cracking on sensitized 5083 aluminum alloy steel for ship life extensions, formulating a touch-up kit for wet installation of bushings, fasteners and other inserts on aircraft joints, and interacting with existing and potential licensees. To optimize the formulations for steel and aluminum substrates, variables such as resin system chemistry, solvent packages, volume concentration, and metal pigment geometry were investigated.

The main performance parameter is corrosion protection, especially of galvanic interfaces. The goal is to make a primer that could match or exceed the corrosion performance of chromated primers. Through the various research-and-development efforts, aluminum-rich formulations have been developed that protect aluminum substrates, steel substrates, and mixed metal structures. The project team has optimized the composition for air, ground, and ship alloy protection.

The core principle of the aluminum-rich primer involves using a passivated, electrochemically active aluminum alloy pigment in an epoxy based primer. The technology can be applied to various organic or inorganic coating and sealant resins, and the surface modification process is viable for a variety of other metallic pigments as well. The passivation of the aluminum alloy pigment allows for additional corrosion prevention through improved adhesion of the pigment to the resin and lower self-corrosion of the pigment, extending the functional protective lifetime of the coating. The aluminum pigment is lighter than leading metal powders such as zinc, so weight savings are a benefit when considering the aluminum-rich primer as a zinc-rich primer alternative.

Recent results of the aluminum-rich primer on galvanic panels after 500 hours in cyclic testing show the primer performing better than the chromate and 53022 controls. The aluminum-rich primer was applied to the galvanic panels at 1.0-1.5 mils thickness. The corrosion is significantly worse on the control primers (chromated [-23377] and nonchromated [-53022]) than on the aluminum-rich primer.

A set of scribed test panels with the same metal-rich primers used on the P-3 Orion demonstration were placed on the racks at NASA's Kennedy Space Center beach front facility. After 28 months both formula variants are performing very well with three different topcoats. The second aluminum-rich variant formulation is yielding superior protection when compared to the commercial nonchromate controls. Taken together, this long-term beach exposure and aircraft data show the excellent performance of the aluminum-rich primer formulations and their potential use as chromated primer alternatives.

The Naval Air Warfare Center is in process of transitioning the aluminum-rich primer to initial industry partners through its business office. These companies can then supply the Navy-developed, advanced-performance primer back to the original manufacturers and other commercial users for future force platforms.

The aluminum-rich primer has shown potential in multiple laboratory and beach front tests as well as in an initial limited field demonstration to be used as an alternative to chromated primer. In many instances this primer performs equally to or better than the chromated primer. Over the next few years, multiple demonstrations are planned to validate the primer's in-service performance and potentially transition the technology into the fleet.

About the author:

Brenna Skelley is a coatings engineer with the Naval Air Warfare Center Aircraft Division.

ADVANCED NON-ISOCYANATE TOPCOATS

By Erick Iezzi

Navy and Marine Corps platforms such as aircraft, amphibious vehicles, and support equipment currently use high-performance polyurethane/polyurea topcoats to provide visual camouflage, flexibility, and hydrocarbon, heat, and erosion resistance for the underlying substrates. Unfortunately, these polyurethanes/polyureas are formed from toxic isocyanate-based catalyst materials, such as hexamethylene diisocyanate and homopolymers, which are harmful to the environment and can cause serious health issues for coating applicators and those in proximity to airborne mists and off-gassing vapors during curing. Exposure to isocyanates, especially during spray applications on aircraft and vehicles, can result in severe irritation to the eyes, nose, and skin as well as symptoms of asthma, sensitization, and, in extreme reactions, even death. Because of their toxicity, polyurethane topcoats restrict the amount of painting that can occur at depots, and thus maintenance activities cannot be conducted by workers in nearby areas when these topcoats are applied.

The topcoats used on Marine Corps vehicles were originally designed by the Army with the intent to provide chemical warfare agent resistance for vehicles. These topcoats, however, provide limited first-line corrosion resistance for platforms that operate in and around seawater, such as amphibious vehicles. They also tend to absorb chemical warfare agents and trap them in the coating rather than resisting their uptake. The Defense Threat Reduction Agency recently stated that "when it comes to chemical and biological threats, they [polyurethanes] sometimes soak up chemical warfare agents like a sponge, potentially exposing warfighters to deadly hazards."

An isocyanate-free and nontoxic topcoat technology that meets or exceeds the performance of polyurethanes does not currently exist. To address this issue, the Naval Research Laboratory (NRL) recently developed novel single- and two-component polysiloxane-based polymers that are isocyanate free and provide similar, if not greater, performance characteristics than polyurethanes/polyureas. Under funding from the Office of Naval Research (ONR), these novel polymers have been formulated into sprayable camouflage topcoats. The NRL lead, Erick Iezzi, has collaborated with Craig Matzdorf, Brenna Skelley, and Frank Pepe at the Naval Air Warfare Center Aircraft Division, Patuxent River, Maryland, to apply and test these coatings to current aircraft requirements. Testing of several laboratory formulations has proven promising, and ONR has provided an additional year of funding to demonstrate a single-component polysiloxane topcoat as a touch-up/repair solution for aircraft in an effort to advance the technology. ONR also is providing research funds to evaluate the hydrophobicity and chemical warfare agent simulant resistance of NRL's novel polymers for potential use in ground vehicle topcoats, and the Environmental Security Technology Certification program is providing funds for early validation studies of the topcoats.

Isocyanate-free advanced topcoats will allow the Navy and Marine Corps to reduce health issues and improve proper maintenance procedures at depots and in the field by allowing workers to remain in nearby areas when topcoats are applied. Advanced topcoats also will provide for greater color (visual camouflage) stability and corrosion and chemical warfare agent resistance, thereby providing longer service lives, enhanced protection for warfighters, and reduced total ownership costs.

About the author:

Eric Iezzi is a coatings researcher with the Naval Research Laboratory.

A NOVEL PATH TO ADVANCED ENERGETIC MATERIALS

By Dr. Victor J. Bellitto

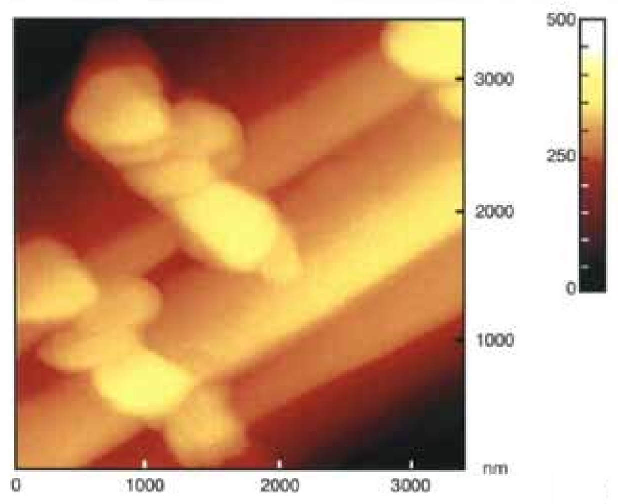
The next generation of planned weapon systems—whether weaponized unmanned underwater vehicles, unmanned aerial vehicles, or high-velocity penetrating weapons—are being designed to be increasingly lethal, smaller, lighter, capable of longer ranges, and survivable. In past years, weapon developers could simply turn to off-the-shelf energetics to accomplish the mission. However, the well of energetics research that engineers could turn to for their designs is reaching its limit, and advanced energetics research is very much a necessity. A 2009 National Academies of Sciences report put it more bluntly by stating that "using yesterday's energetic materials in today's battlefield systems would be as effective as trying to run a Ferrari on kerosene."

Besides its mission in the arena of explosive ordnance disposal (EOD), Naval Surface Warfare Center Indian Head EOD Technology Division also is focused on the research, development, testing, evaluation, and manufacturing of energetic materials. The path to novel energetic materials is not solely accomplished through the design of molecules but also through materials research. One such approach is the metal encapsulation of explosive/oxidizer particles.

Composite explosives and propellants are heterogeneous admixtures of crystalline explosive, oxidizer, and metal powders in a rubbery binder. The binder basically holds the mixture together. Materials such as aluminum are added to enhance specific performance characteristics. Aluminum can well exceed 30 weight-percentage in high-performance propellant and explosive compositions. The aluminum, although improving performance, may not be efficiently or completely consumed for various—reasons largely having to do with the size of the aluminum particles.

Proximity of the aluminum to the oxidizers and explosives within the composite would provide performance enhancements, as the material would have more complete combustion and faster energy release rates as problems with heat transfer and diffusion rates are overcome. As the combustion of the explosive was to occur, so would the combustion of the aluminum, overcoming the thermal disparities of the two materials.

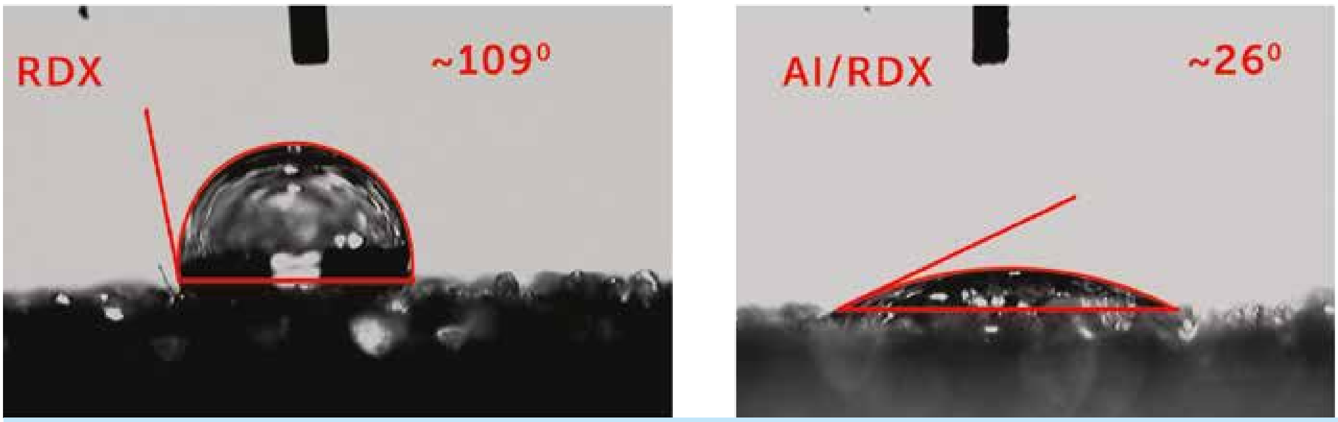
In 2003, researchers sought to gain a fundamental understanding of the metal-explosive interaction with the goal of depositing layers of aluminum metal on the surface of explosive crystals. The initial investigations focused on studying the interaction of aluminum with cyclotrimethylenetrinitramine (RDX), one of the most stable high-energy compounds and widely used in military applications. In its pure state RDX is a white, crystalline solid; as an explosive it is usually used in mixtures with metals or other explosives and binders.



This is an atomic force microscopy image of an impacted single crystal of RDX, a common explosive. This shows the formation of shear bands and melted RDX extrusion created during plastic flow.

The project was initially funded through the In-House Laboratory Independent Research (ILIR) program. ILIR is a fundamental research and development program funded by the Office of Naval Research, and administered by each warfare center around $100,000 or about 1/3 of a work-year per selected basic research proposal. The purpose of the ILIR program is the development of the next generation of Navy scientists and engineers, to ensure that the Department of the Navy maintains a leading edge in warfighting technologies for national defense, and "to foster creativity, stimulate cutting-edge research and support high-value, high-risk technologies."

During the experiments, novel interfaces were produced that are not obtainable under ambient conditions. The research revealed possible avenues for the development of new energetic materials with improved performance. It was found that the initial layer of aluminum would oxidize and serve as a sacrificial segment, forming a base for the deposition of additional layers of metal.



H2O contact angle analysis of particles of bare RDX and RDX-coated with about 900 nm of aluminum.

In depositing thicker layers, it was necessary to find another method of deposition since the initial evaporative method was limited in its rate. Development of a plasma vapor deposition process followed as an alternative method of metal deposition. The sputtering of aluminum onto explosive particles was a better alternative to evaporative deposition, since less heat is radiated from the source. It also was determined that less heat is transferred by the aluminum atoms onto the energetic particles and provides better control of aluminum film thickness and uniformity.

Once prepared, samples were analyzed to examine compatibility, thermal properties, and exothermic reactivity using differential scanning calorimetry (DSC). DSC measures the difference in the amount of heat required to increase the temperature of a sample and a reference as a function of temperature. More or less heat flow to the sample depends on if the process is exothermic (releases heat) or endothermic (absorbs heat). The DSC data showed that an aluminum coating on the RDX particles modifies their thermal properties without inducing any incompatibilities of the two materials (i.e., large temperature disparities). The DSC thermal curves showed that the RDX of varied aluminum-coating thicknesses exhibited increased exothermic response as compared with bare RDX (210-250 degrees Celsius). These data indicate an increase in energy density, and if it can be translated into improved performance at larger scales it would be of some benefit in maintaining performance while reducing weight.

The aluminum coating also modifies the surface properties of the explosive particles. One technique that provides a very good visual demonstration of the major modifications to the surface properties of the RDX imparted by the aluminum coating is contact angle analysis. Here, images were obtained of bare RDX and RDX coated with an approximately 900-nanometer coating of aluminum. The images revealed shifts in contact angle from about 109 degrees for the bare RDX powder to about 26 degrees for the aluminum/RDX, indicative of a major change in the surface energy and thus suggesting better wettability and adhesiveness of the surface. This improved adherence provides better mechanical coupling of binder to energetic particles. R45-M resin, a common polymer used in explosive and propellant compositions, was observed to exhibit similar affinities for the aluminum-coated RDX particles over the uncoated RDX particles. An improved mechanical coupling of binder and energetic particle may lead to improvements in shock/impact insensitivity through mitigation of shear. The improved wettability may also preclude the requirement for compositional additives such as wetting and/or bonding agents.

This novel method of processing with the placement of metal in direct contact with the explosive also is expected to provide improvements in thermal and shock/impact insensitivity through its modified surface properties. The basis of this is the understanding of the processes through which initiation occurs in crystalline explosives subjected to shear-induced plastic flow from a shock or impact proposed by Drs. Charles Stevens Coffey and Jagadish Sharma. The theory, based on atomic force microscopy (AFM) experiments, demonstrated that: the plastic flow in crystals is caused by the creation and motion of dislocations; these dislocations then distort the explosive molecules; and this distortion and dislocation motion introduce microshear bands. These microshear bands are sites of heating, melting, sudden crystal failure, and chemical reaction initiation. In the AFM experiments of impacted RDX crystals, shear bands along with melted globules of RDX were discernible in the crystal locations experiencing high shear.

In a composite explosive, a metal coating of aluminum on the crystalline explosive (RDX) may minimize shear through improved mechanical properties. This is due to the better adherence of the binder to the metal than to the bare explosive particles. The coating also may provide for heat dissipation and therefore minimize the initiation reaction caused by hot spots. In addition, it may play an important role in minimizing self-heating effects that lead to catastrophic events.

The research is being furthered through preparation of compositions using high explosives such as RDX that have been metal-encapsulated. The effort aims to reduce the shock and thermal sensitivity while maintaining or improving required explosive power of munitions. The aluminum-coated RDX is intended to be a "drop-in" material for formulations that currently use RDX. The novel compositions are being formulated, tested, evaluated, and compared with baseline RDX-containing compositions.

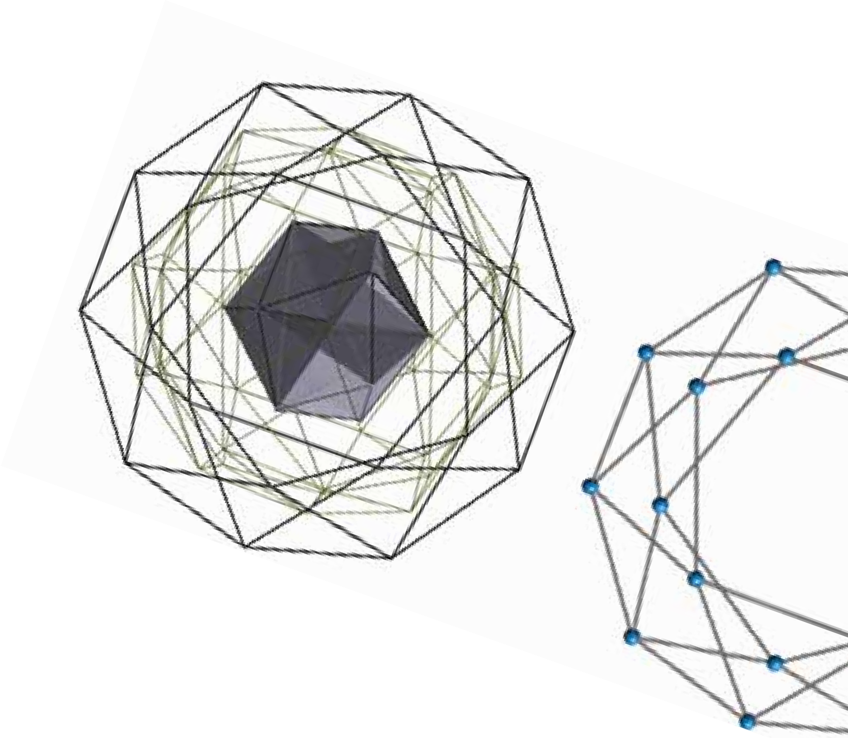
Extensive investigation of the potential for performance-enhancements by aluminum-coated RDX is required because the possibility for delivering a portion of the energy from the metallic coating at or nearer the reaction time frame of the explosive detonation may exist. If so, it may offer additional metal-accelerating performance or, alternatively, the possibility for decreasing the volume-fraction of explosive filler while maintaining the performance of the control composition. This diluted but equally performing composition may display improvements in sensitivity and stability. This material has the potential to increase performance of existing and future munitions while rendering them safer to handle, store, and transport—and serves as a prime example of a material with improved properties and fleet relevance that is directly attributable to investment in basic research.

> **THE EFFORT AIMS TO REDUCE THE SHOCK AND THERMAL SENSITIVITY WHILE MAINTAINING OR IMPROVING REQUIRED EXPLOSIVE POWER OF MUNITIONS.**

About the author:

Dr. Bellitto is a research scientist in the High Energy Materials Branch, Research & Technology Division at the Naval Surface Warfare Center Indian Head Explosive Ordnance Disposal Technology Division.

Aluminum Cluster Materials Are the Future of Energetics



By Dr. Dennis Mayo

Former Marine Corps Commandant Michael Hagee described energetics as critical to "battlespace dominance." Over the past century, researchers have sought to increase the energy outputs of explosive and propellant materials in weapons. Traditional monopropellants (e.g., TNT, RDX, and HMX) are organic molecules—compounds composed of carbon, hydrogen, nitrogen, and oxygen. The principles of organic chemistry tell us that there are many ways of arranging these elements within a molecule. The big challenge scientists and engineers have faced is that although there are many possible permutations of molecular structure in organic compounds, their energy outputs are limited by their densities and heats of formation. Therefore, other novel materials such as fast-reacting metals are needed to realize greater range, quicker delivery, and increased energy imparted to targets. Higher energetic output could result in smaller and lighter munitions and increased range and lethality in current weapons.

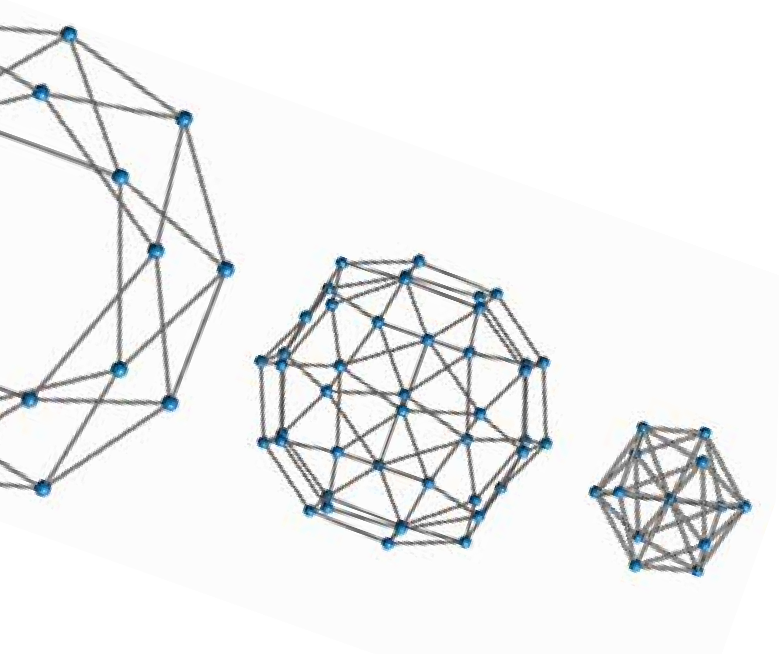
The discovery of metal clusters (subnanometer-scale compounds containing a core of metal atoms surrounded by an organic outer shell) and the applications arising from their unique physical and chemical characteristics is an active field of academic research. What is largely unexplored is the strong potential use of metal clusters as critical ingredients for weapon systems. To that end, our research team at Naval Surface Warfare Center Indian Head Explosive Ordnance Disposal Technology Division collaborates with our colleagues at Johns Hopkins University, the University of Maryland, Naval Postgraduate School, Naval Air Warfare Center China Lake, and Naval Research Laboratory to study that potential.

Our basic research program is relatively young (less than six years old) and already has made significant advances. We have fabricated specialized instrumentation required to study these materials. We also have made and characterized small quantities of the largest aluminum cluster compound (a molecule with 77 aluminum atoms arranged in a series of shells) using a different methodology than the original report. And we have investigated the basic properties of these materials, finding that they can be chemically compatible with chemical environments such as those in explosive fills and demonstrating these materials' potential as formulation additives.

We need energetic materials that have high energy density and a rapid kinetic release of that energy on combustion that packs the biggest punch we can muster. Metal clusters have a great potential for that use.

Higher Potential: Away from CHNO

The underlying idea in our research is to move away from combinations of only carbon, hydrogen, nitrogen, and oxygen (CHNO) to increase combustive output. The majority of elements in the periodic table are metals, and when most metals sit out in the open, they form oxides. This transformation—metal and oxygen combining to form metal oxide—is thermodynamically favored and often exothermic. That exothermicity, or the release of heat upon oxidation, is useful from an energetics standpoint. For most metals, the heat of combustion is high, and for some elements—namely boron, silicon, and aluminum—it results in extremely high energy density. These elements are great candidates for energetic fill



These are structural representations of the anionic 77-atom aluminum cluster obtained at the University of Maryland. From left: inner shell of 13 aluminum atoms, middle shell of 44 atoms, outer shell of 20 atoms, and wireframe representation of the full structure.

materials, and some have been put to use in current energetic formulations.

Ideally, one would get as much energy as possible out of these materials on a timescale that is useful for detonation or combustion. There are scientific challenges, however, to the energy output available from bulk metals. For example, decades of research were put into developing boranes (boron hydride materials) for energetics use, only to discover that boron compounds do not fully combust in air because of a kinetically stable partial combustion product—i.e., they do not burn all the way down to boron oxide, and they do not release all of their potential energy as heat. The challenge for aluminum energetics is different. Aluminum combusts well under the right conditions, but it has a native oxide layer that makes the kinetics of aluminum combustion slow. That oxide layer can be advantageous (its presence is why the aluminum foil in your kitchen and your laptop at work do not spontaneously combust or decompose), but it also is a significant challenge from an energetics standpoint. If you watch thermite reactions on YouTube, you will see that the heat release of aluminum oxidation is quite impressive, yet rather slow.

The kinetic barrier to aluminum combustion has been a challenge for a long time, and there have been many attempts to get around this obstacle. One such method is making smaller and smaller aluminum particles with the hope that they may burn more quickly. This method is not without its own challenges: when aluminum particles are a few nanometers in diameter, the oxide layer represents the majority of the aluminum in the particle. The nonoxide (or fuel) portion of the particle becomes increasingly smaller in terms of mass percentage of the particle. We need to come up with clever ways to circumvent this challenge.

One possible way around it involves what we refer to as aluminum cluster materials, or molecular species that are smaller than nanoparticles, with roughly the same molecular size as traditional CHNO fuels. The aluminum cluster materials reported in the literature bear a structural resemblance to bulk aluminum metal: the coordination around the aluminum atoms is often only slightly distorted from that of the bulk metal. That structural resemblance gives us hope that the materials may behave similarly to the bulk metal.

Synthesis through Aluminum

Aluminum cluster materials are highly challenging to synthesize and characterize, and one specific synthetic method has been crucial to their discovery in gram quantities. German researchers at the Karlsruhe Institute of Technology, led by Professor Hangeorg Schnöckel, have reported on the synthesis of a few incredibly interesting cluster materials containing shells of aluminum atoms: little balls of fuel waiting to have their energy released. These cluster compounds, which have as many as 77 aluminum atoms and up to four shell layers, are prepared using an aluminum monohalide starting material. These materials have been calculated to have high volumetric heats of combustion and specific impulse values, and should release their potential aluminum oxidation energy quickly. Aluminum monohalide starting materials are quite unusual—aluminum prefers to be in either the 0 (metallic) or +3 (aluminum oxide) oxidation state; intermediate oxidation states of aluminum are exceedingly rare. Monohalides serve as a source of aluminum in the +1 oxidation state and are the only reliable synthetic pathway to these multi shell cluster compounds in the condensed phase.

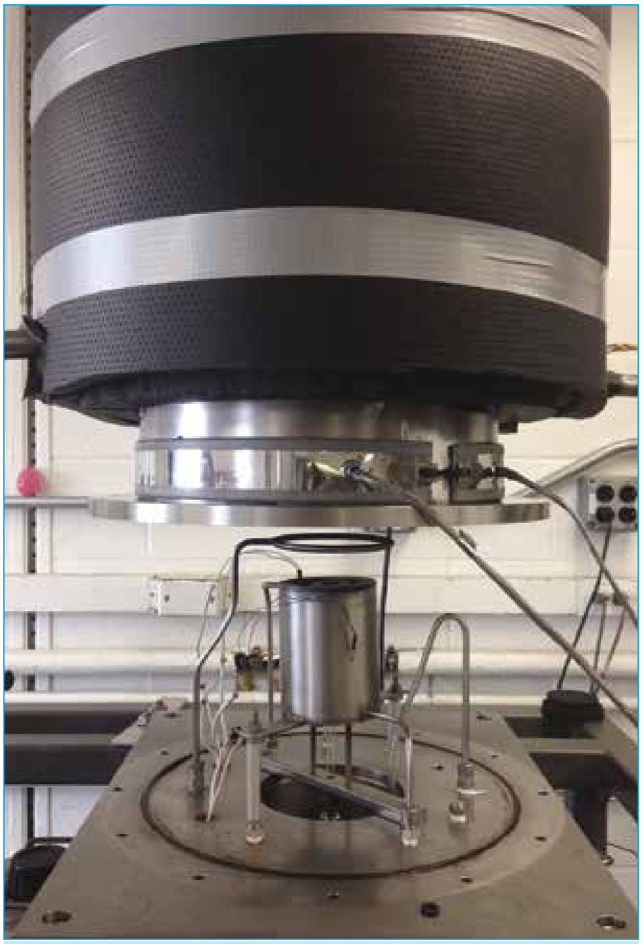


Photo courtesy of author.

Metal halide co-condensation reactor built and operated by Johns Hopkins University, University of Maryland, and Indian Head. Inside the furnace (lower center), molten aluminum is reacted with hydrogen halide gas to produce metastable aluminum monohalide vapors that are condensed on the stainless steel bell jar.

The aluminum monohalides involved in this work are not accessible under standard atmospheric conditions; successful formation involves a high-vacuum/high-temperature reaction chamber. In this chamber, aluminum metal is placed inside a furnace, the atmosphere evacuated, and the furnace heated to around 1,800 degrees Fahrenheit. Once the furnace is hot, hydrogen chloride gas is passed over the surface of the metal and gas-phase aluminum monochloride is formed along with hydrogen gas. The generated aluminum is then deposited along with solvent on the liquid nitrogen-cooled walls of the chamber. After a few hours the reaction is complete, the oven is turned off, and a cold solution of aluminum monohalide is drained into a cold bottle and stored at -112 degrees Fahrenheit for later use.

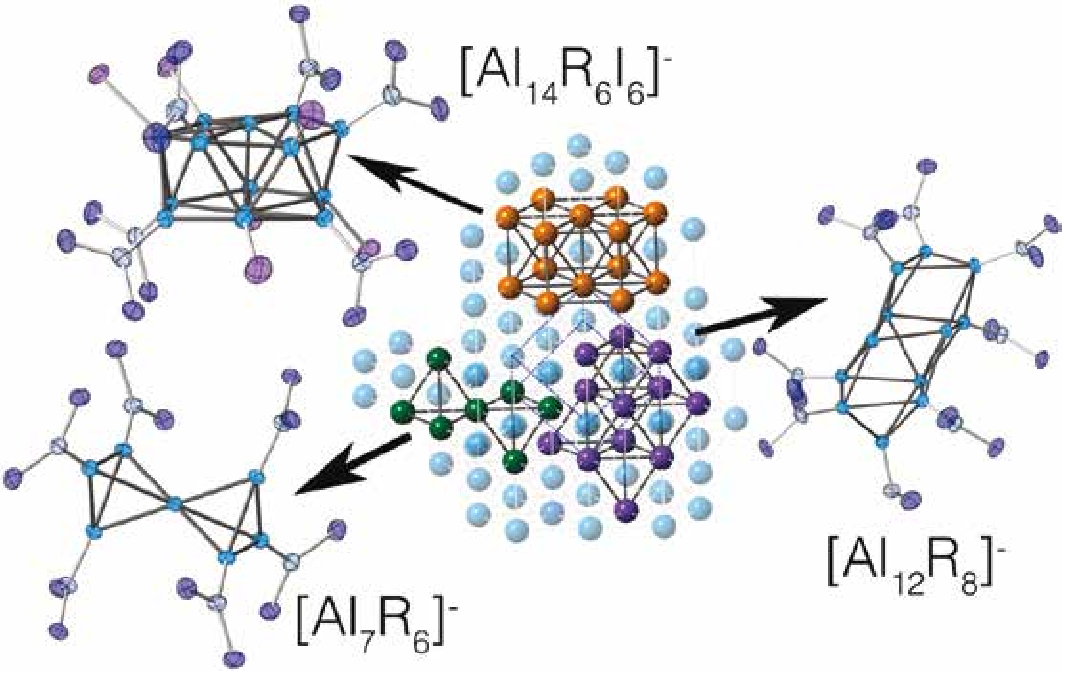
Screening, Planning, Projecting

The aluminum cluster materials discovered by the Germans are limited in terms of the reactants (ligands) that were mixed with the aluminum monohalides. Most contained one specific bis(trimethylsilyl)amide ligand that carries a negative charge on a nitrogen atom that binds directly to the aluminum clusters. This ligand has proven to work very well in stabilizing aluminum cluster compounds. In fact, it stabilizes the largest aluminum cluster compound reported to date—a four-layer molecule with 77 aluminum atoms. And depending on the ratio of aluminum to ligand used and the heat applied, different products form with this same ligand. In collaboration with the University of Maryland and Johns Hopkins University, we reproduced the largest of these cluster materials. The reproduction of the anionic Al77 cluster represents a huge (and unexpected) step: the precursor materials used by the Germans and used in our lab are different, meaning the 77-atom aluminum architecture may have some special stability relative to other possible molecular configurations, and may be synthetically accessible through other, more accessible methods.

In addition to reproducing materials from the literature, we thought it would be advantageous to expand the scope of ligands employed in these systems, both in terms of the kind of ligands used (e.g., what element is bonded to aluminum) and the ligands' size (affecting how close the ligands can be to one another). By doing that, we hoped to find new cluster compounds. With that in mind, we have looked into a variety of systems to try and understand the influence of ligands on cluster size and shape.

Our initial use of phosphorous-based ligands supported what the German researchers found: that phosphorous-carbon bonds will break down in the presence of aluminum cluster compounds, resulting in oxidized aluminum and ligand fragmentation (i.e., no multilayer clusters are formed). Since that discovery, we have been working with theoretical physicists at the Naval Postgraduate School to understand better the electronic effects of the ligands used in our systems. This will help us eliminate what appear to be less promising systems before we mix any reagents together, saving time and effort.

The materials we are studying are quite novel, making their fundamental properties difficult to assess. Related compounds in the literature are limited, meaning there is not a lot out there about chemical compatibilities between



This represents the structure of bulk aluminum metal (center) and three aluminum cluster compounds, all containing the same nitrogen-based ligand. Segments of bulk aluminum resembling the aluminum core of each cluster structure are highlighted.

these aluminum clusters and organic functional groups that are used frequently in energetics. To test these compatibilities, we made a series of ligands with a variety of organic functional groups and mixed them with aluminum monohalide solutions. We synthetically modified the functional groups in the ligand and left everything else in the system identical to minimize the variables involved with the studies. What we found is that a whole lot of functional groups, including nitro groups, are compatible with reduced aluminum materials under certain conditions. This is a really exciting result—it demonstrates a baseline of compatibility between very reactive aluminum compounds with some of the functional groups that are common in energetic fills. The results of these studies have given insight into what elements reduced aluminum prefers to bond to, and led us to investigate an entirely different class of ligand compounds. This information will be highly useful as we develop cluster materials for later use.

Next Steps

Over the course of the past five years of research, a tremendous amount of work has gone into understanding the conditions under which we can make aluminum cluster materials. We have discovered new compounds, reproduced others from the literature, and are investigating other methods by which we can synthesize and characterize cluster materials. Going forward, we aim to prepare novel materials and scale them up to investigate their fundamental properties (e.g., combustion behavior and sensitivities). Ultimately, synthesis of cluster materials will be achieved through scalable means.

Our collaborators at Johns Hopkins and the University of Maryland have recently been awarded a Multidisciplinary University Research Initiative grant through the Office of Naval Research, providing a sustained source of funding to an expert group of researchers to study methods to generate ordered assemblies of related metal cluster materials. We plan to work closely with them, building on our years of collaboration.

This work on metal-rich cluster chemistry is out at the frontiers of what is synthetically possible; it is, in a sense, exploration on a molecular scale. Every new compound that we have discovered gives us another reference point. From there, we work to find similarities and trends between materials and find a way to put these materials to use, ultimately getting to a stage where we are fielding novel materials for energetics usage in the field. The field of cluster science is fascinating, exciting, and incredibly challenging. These new metal-based materials should have higher energy content than traditional explosives, resulting in greater firepower for warfighters, whether that is manifested as greater ordnance range, lighter weapons, or a bigger "boom" in existing platforms.

About the author:

Dr. Mayo is an American Society for Engineering Education Science, Mathematics, and Research for Transformation fellowship recipient and scientist at Naval Surface Warfare Center Indian Head Explosive Ordnance Disposal Technology Division.

BUBBLING UP: Pioneering New Buoyancy Materials

By Troy Clarke

Engineers dream of a material as strong as steel and light as a feather, but the nature of materials has a way of dashing those dreams. Some of the strongest bulk materials become comparatively weak when engineered to become lighter-weight cellular solids. While it is hard to imagine that fragile glass could meet or exceed the strength of aluminum, titanium, or steel, scientists at Naval Surface Warfare Center (NSWC), Corona Division have patented a method for making such a material: glass foam.

These scientists are transforming millions of microscopic glass bubbles—about the diameter of a human hair—into a new super strong, super light cellular solid material that may one day be used for weapons or equipment. And it can shed more mechanical energy for a given volume than any current cellular material.

The Corona team has discovered that their shock-absorbing foam has additional applications as a strong, buoyant foam. The progress made in designing lightweight, strong cellular solid materials has sparked interest within the special warfare community.

“The new method for fabricating cellular solids from glassy hollow spheres is very versatile,” said Corona physicist and glass foam inventor, Dr. Aaron Wiest. “You can customize the properties of a cellular solid material by using hollow spheres with the necessary initial properties” to create materials that are lightweight, buoyant, or super strong.

Wiest recalls the genesis of this idea came during casual conversations between coworkers. Discussions of physics, materials, engineering, and Navy requirements led to a theory that hollow spheres of glass could be bonded in ways crystalline materials have not been. Materials scientists know that glasses and other materials that lack a crystalline structure are amorphous and soften at a specific temperature to become a highly viscous liquid, thicker than molten tar. At these temperatures, Wiest theorized, hollow spheres should stick to each other and a cellular solid material should be formed upon cooling.

At the time, NSWC Corona didn’t have the testing facilities for this type of project, so Wiest tapped into connections at local universities for proof-of-concept testing. Professor Dale Conner at California State University, Northridge, one of the other inventors of the glass foam, directed graduate students to test the concept and was instrumental in developing the experimental architecture.

Corona has now acquired a material testing laboratory facilitating further development of the foam. This laboratory, which would have cost taxpayers more than $1 million, was pieced together from Defense Logistics Agency excess equipment and repurposed for less than $5,000—the cost of shipping—thanks to leadership from Item Unique Identification Branch Head Jamie Lizarraga and Product Engineering Department Head Doug Sugg.

“Innovation is one of the key ingredients for sustaining a successful organization,” said Corona’s Chief Technology Officer Arman Hovakemian. “In order for NSWC Corona to

remain relevant as a scientific organization, we must innovate. We can only accomplish this by fostering an environment where they have the freedom to innovate through experimentation and prototyping. An example of what can be accomplished with this approach is the new foam material being created by Corona scientists and engineers."

> **ONE CAN EASILY IMAGINE AN INCREDIBLE RANGE OF POSSIBLE APPLICATIONS FOR VIRTUALLY ANY DEVICE OR PLATFORM THAT REQUIRES CUSTOMIZED BUOYANCY, STRENGTH AND DENSITY CHARACTERISTICS**

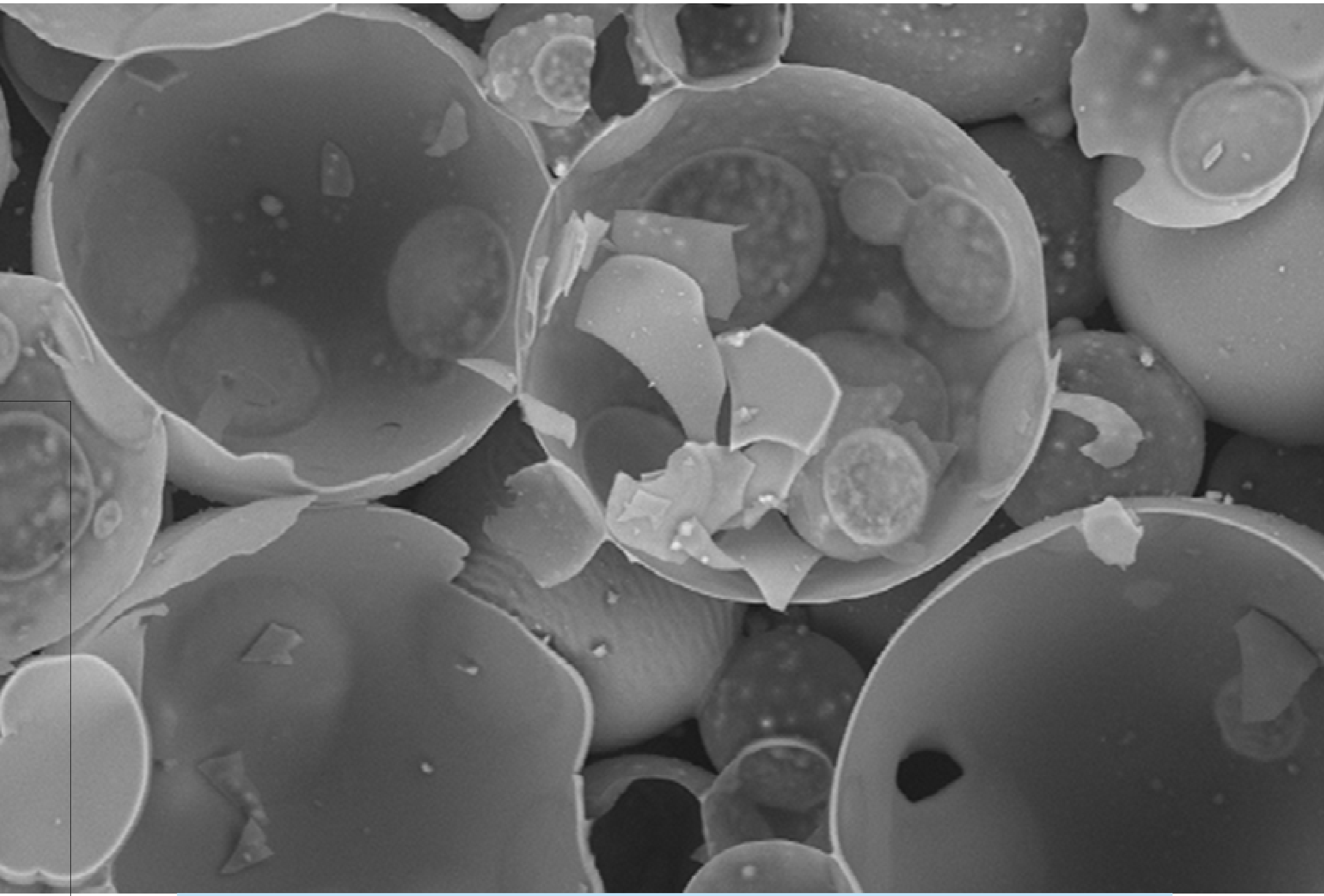
Hovakemian and other senior leaders have used the new cellular solid materials research not only to motivate other scientists at the warfare center, but to spark the interest of new recruits with doctorate degrees and vast experience in academic and industrial research. Corona leadership is looking at possible commercial applications and potential technology transfer agreements.

Capt. Stephen Murray, Corona's commanding officer, echoes Hovakemian's view. "We have an entrepreneurial workforce here. Whether you are a young petty officer or a veteran civilian with a doctorate in physics, we are encouraging everybody to push ideas and work toward a truly innovative Navy," Murray said. "A workforce that thrives on excelling is going to come up with the next innovation that changes the way the Navy operates."

Naval Surface Warfare Center Corona Division

Naval Surface Warfare Center, Corona Division's mission and innovative spirit originated with its work on torpedoes during World War II. Today, Corona enables warfighters to train, fight, and win through measurement, analysis, and independent assessment. Corona is responsible for gauging the warfighting capabilities of ships and aircraft, analyzing missile defense systems, engineering and operating the training ranges for the Navy and Marine Corps, and serving as the measurement science and calibration agent for the Navy and Marine Corps.

The warfare center uses its prime location in Southern California to tap into a larger brain trust to solve technical challenges. Close relationships and education partnership agreements with local universities—including University of California, Riverside, California Institute of Technology, California State University, Northridge, California State Polytechnic University, Pomona, California State University, Los Angeles, and California Baptist University—broaden access to scientific resources and intellectual horsepower. Graduates from these universities come to work at the warfare center and help solve problems facing the Navy. The Navy materials community of interest and efforts of the chief technology officers have allowed other warfare centers to collaborate more effectively, and Section 219 congressional authority for Naval Innovative Science and Engineering research has created a climate where major advances in science and materials can benefit warfighters and the nation.



Thes are glass bubbles processed at 1500 Fahrenheit for five minutes. Note the thin bubble walls and partial bonding visible through broken bubbles. This material and processing parameters yielded a low-strength, low-density foam.

The innovative glass foam caught the attention of Corona's executive officer, Capt. Corry Shedd, who quickly saw how a new cellular solid material could potentially save the Navy significant money in the design of undersea combat platforms and other craft. Shedd, whose career has included tours with the Navy's special warfare community, sees the new material as a potential game changer in the ever-present challenge of gaining maximum combat capacity and capability of a given platform without sacrificing other key performance and design criteria.

"One can easily imagine an incredible range of possible applications for virtually any devise or platform that requires customized buoyancy, strength and density characteristics, especially where the proper trade-offs of those competing factors can result in increased combat capability," Shedd said. "For instance, incorporating this technology into the design of tactical undersea vehicles, like those utilized by special warfare forces, may allow for a more optimal balance of the vehicle's internal buoyancy control and stability systems and overall material strength that could result in achieving critical increases in passenger/cargo capacity. In the world of asymmetric operations, delivering even one more Navy SEAL or a few more pounds of combat equipment to the fight is a huge advantage. This technology has the potential to serve as a true force multiplier."

For his Naval Innovative Science and Engineering project, Wiest explains that glass breaks because it has defects in the bulk material. Fiberglass has much higher strength than window glass partly because the small fiber size minimizes the number of defects that weaken the material. Fiberglass is used today in high-strength composites by weaving cloths of the microscopically thin fibers and bonding them in a resin.

Glass foam uses similar physics for minimizing defects by bonding hollow glass spheres with wall thicknesses similar to fiberglass dimensions – resulting in a cellular solid with ultra-high strength. This novel approach created a significant scientific breakthrough.

Wiest, Conner, and the team showed that processing the glass bubbles at 1,550 degrees Fahrenheit for 30 minutes under vacuum in Pyrex tubes yielded the highest strength materials. This processing bonded them into a super strong material that could dissipate large amounts of mechanical energy. Corona conducted low-speed (low strain-rate) crush tests, while Susan Bartyczak and Dr. Kenneth Jordan at Naval Surface Warfare Center Dahlgren Division and Dr. Vasant Joshi at Naval Surface Warfare Center Indian Head Explosive Ordnance Disposal Technology Division performed high-speed (high strain-rate) testing. The material performed well and dissipated large quantities of mechanical energy at crush rates from 0.0001 m/(m*s) to 4000 m/(m*s). Test results show that Corona's invented cellular material dissipated more mechanical energy for a given volume than any other cellular material on the planet (14.8 megajoules per cubic meter).

THIS NEW MATERIAL CAN HAVE A SIGNIFICANT IMPACT ON NAVY SYSTEMS AND MAY VERY WELL REVOLUTIONIZE THE MATERIALS INDUSTRY

For Wiest, the science is challenging and highly rewarding, but it becomes more so because it supports an even greater mission.

"The key to customizing and optimizing the cellular material for lightweight submersible applications will be finding the perfect hollow sphere material and dimensions to bond into a cellular solid so it can withstand the pressures of making a deep dive while being light enough to meet the vehicle requirements," Wiest said. "We have much work to do and are fortunate to have a great team and strong support from our senior leadership while taking on this exciting project."

About the author:

Troy Clarke is a public affairs officer with Naval Surface Warfare Center, Corona Division. The command recieved the Navy's 2014 Thompson-Ravitz Best in Show award for excellencein public affairs for its program, "Better Together: Harnessing a Navy Federal Laboratory for Innovation and Growth."

Engineering Tomorrow's Sonar Transduction Materials

By John B. Blottman and Adam A. Heitmann

A thermodynamic-based modeling technique developed for the design and performance prediction of optimal relaxor ferroelectric single crystals has become an important part of the process of creating next-generation transducer materials. We are maturating the model to encompass the unique features of textured polycrystals that are currently under investigation for sonar transducer applications. Textured polycrystalline materials promise to compete with the high performance of single-crystal ferroelectric material, but at a cost comparable to traditional lead zirconate titanate (PZT) ceramic. We are collaborating with the Pennsylvania State University Materials Research Laboratory and the Virginia Polytechnic Institute and State University Center for Energy Harvesting Materials and Systems, each developing high-performance textured material, by measuring its performance against stringent Navy standards. Our modeling technique will provide a tool to engineer the material composition for optimal properties without the traditional time and labor intensive empirical "make and measure" approach that is guided by past experiences. The ability to engineer and optimize piezoelectric materials would, without doubt, provide great benefit to the U.S. Navy's effort to bring high-power, low-cost, high-performance transduction materials to fleet sonars.

What Is Sonar Transduction?

An electroacoustic transducer can transform electrical energy into acoustical energy that propagates an acoustic wave, or take a received acoustical signal and transform it into an electrical signal. Most underwater projectors today use piezoelectric ceramic as the active transduction element. Piezoelectric materials change shape (strain) in response to an electric field. The type

Photo by MC2 Sunday Williams

of piezoelectric material used and its performance characteristics are key to designing sonar transducers.

The Navy sonar community operates in the full spectrum of underwater acoustics extending from subaudible and audible frequencies (where acoustic wave propagation can occur over large distances) up to ultrasonic frequencies (where echo distances are reduced but increased accuracy of distance measurements is desirable). Operation across the full spectrum demands high-power, broad-bandwidth compact transducers capable of meeting stringent requirements for acoustic communications, target detection, and classification. Capitalizing on novel piezoelectric materials is essential to ensure the Navy's continued dominance in the undersea domain. To support this mission, the Naval Undersea Warfare Center has embarked on the search for materials and devices meeting these technical needs, while reducing the total cost of ownership of the next generation of sonar systems.

Transduction Materials

In the early years of the last century, single-crystal resonators of quartz and Rochelle salts were discovered to contain domains of oriented electric dipoles large enough to exhibit piezoelectricity. Application of an electrical or mechanical stimulus caused the spontaneous electric dipoles to rotate, converting pressure waves into electrical energy and vice-versa. Motivation for development of undersea acoustic devices first arose shortly after RMS Titanic's encounter with an iceberg and intensified with the threat of submarines during World War I.

Following World War II, PZT ceramics were introduced and quickly became the piezoelectric material of choice. PZT is fabricated from a powder mix of constituent elements, combined with a binder, and heated to sintering temperature. During cooling, a dense polycrystalline structure is created and adjoining crystals form domains that have a net dipole moment. These domains are randomly oriented in the bulk material, but application of a high direct-current electric field polarizes a large fraction of the individual domains causing them to align with the applied field. A remanant polarization is retained upon removal of the polarizing field. These piezoelectric ceramics replaced earlier single-crystal quartz materials because of the greater piezoelectric activity or coupling factor, which defines the effectiveness of the conversion between mechanical and electrical energy. To this day, PZT ceramics are still the workhorse in a wide range of transduction devices and systems.

Over the past half century, extensive research focused on PZT solid solution to optimize its performance. The randomly oriented grains of a polycrystalline material, however, reduce the total polarization and domain rotation that is possible with a single crystal form. Over the past two decades, ceramicists have demonstrated the ability to grow large single crystals composed of only a single grain, which means they are not susceptible to the limitations imposed by the grain structure as found in a polycrystalline ceramic. This is accomplished using a ceramic formulation grown from a highly oriented seed crystal using the Bridgman method, where a large temperature gradient is applied to partially melt the seed in a platinum crucible and then slowly grow the single crystal from the seed. The resulting single-crystal material then is polarized along the preferred crystallographic direction. While the single crystal removes the inherent grain misalignment issues of polycrystalline ceramic, the loss of the intergranular boundaries is found to degrade the mechanical strength of the material. The piezoelectric performance of the single crystal form is typically an order of magnitude greater than that of the conventional PZT ceramics, but the high cost and slow fabrication process associated with single-crystal materials makes their widespread adoption in the Navy impractical. Development of innovative single-crystal growth processes such as solid-state-crystal growth or continuous-feed Bridgman growth strive to eliminate these fabrication drawbacks.

Textured piezoelectric ceramics promise to bridge the gap between polycrystalline and single-crystal materials. A textured ceramic is a polycrystalline material whose grain structure is engineered to lie along a single crystallographic direction, unlike conventional ceramics whose grain structure is randomly oriented. Orientation of the grain structure allows textured ceramics to have the substantially higher performance characteristics associated with single crystal materials while retaining the robust toughness that is afforded by the multigrain structure of conventional polycrystalline PZT ceramics.

Similar to single-crystal materials, textured ceramics can be composed of a host of binary and ternary relaxor ferroelectric systems such as lead magnesium niobate-lead titanate (PMN-PT) and lead magnesium niobate-lead zirconate titanate (PMN-PZT). Fabrication of a textured ceramic material is achieved by coupling the templated grain-growth process together with conventional tape casting techniques. The result is a polycrystalline material whose crystal grain structure is highly oriented along a particular crystallographic direction. The grain structure is oriented using seed crystals (templates) that provide a blueprint for the nucleation and growth of the crystal grains. These high-aspect-ratio template particles are added to a fine matrix powder slurry. The slurry is then shear-formed by extruding through a small gap to align the anisotropic (directionally dependent) particles in the direction of least resistance to flow. The uniform sheet of material is drawn onto a sacrificial backing as it moves along a conveyor belt. During sintering and annealing of the green ceramic sheet, the textured ceramic grows epitaxially on the template grains.

This method mechanically aligns the crystalline structure similar to the single crystal Bridgman method. The resulting anisotropy of the polycrystalline material is enhanced by this texturing process, yielding performance gains in specific crystallographic directions. The textured material exhibits piezoelectric properties close to that of single crystals, but because it is a polycrystalline ceramic the textured material does not suffer from fracture toughness issues. The tape-casting process enables flexibility and scalability of processing, permitting spatial control of the texture axis for application in nonplanar electroded geometries not possible with single-crystal segmented elements. Fabrication of monolithic geometries such as flat plates, cylindrical elements poled radially or tangentially, and other shapes have been demonstrated. The green ceramic must still then be sintered and poled, but now all the grains are aligned.

A Phenomenological Model

The development and characterization of new relaxor systems has proven to be both time- and labor-intensive. Almost exclusively, new relaxor piezoelectric systems and compositions are selected by empirical make-and-measure approaches guided by past experiences. These empirical processes are highly iterative in nature and, as a result, there exists only limited predictive capability for finding new piezocrystal compositions even in known piezocrystal systems.

An engineering solution to piezocrystal design motivated the development of a comprehensive phenomenological theory and a unified parameterization scheme applicable to relaxor piezocrystal systems. This modeling framework provides a unified theory capable of modeling all past- and current-generation relaxor piezocrystal systems. Prior to its development, in-depth experimental measurements on several compositions within a given material system were required to characterize an unknown material system. The new unified framework requires only specific characteristic information of the individual material constituents—not the final composition. Coupled with the phenomenological model, only limited experimental measurements are required to predict and identify suitable new relaxor piezocrystal systems and compositions. The Naval Undersea Warfare Center's current endeavor seeks to broaden the utility of the framework to encompass not only new relaxor piezocrystals but also new textured polycrystalline ceramics.

The phenomenological model is based on the change in free energy of a system with changes in temperature. As the temperature changes, crystalline material goes through successive phase transitions that are defined

OPERATION ACROSS THE FULL SPECTRUM DEMANDS HIGH-POWER, BROAD-BANDWIDTH COMPACT TRANSDUCERS CAPABLE OF MEETING STRINGENT REQUIREMENTS FOR ACOUSTIC COMMUNICATIONS, TARGET DETECTION, AND CLASSIFICATION.

as a change or loss in crystal symmetry. Physicist Lev Landau described phase transitions through an order parameter that identifies the deviation from a high-symmetry (cubic) phase to a lower-symmetry phase. The particular form of the free energy potential is dependent on the symmetry of the current phase and the transformation properties of the ferroelectric order parameter. The change in free energy from the initial, nonpolar cubic phase is a function of temperature, pressure, and composition. The total free energy describes the coupling between thermal, mechanical, and dielectric responses of the material system. The physical properties of interest are then computed by taking first and second partial derivatives of the total free energy with respect to temperature, polarization, and stress.

The expansion coefficients quantifying the free energy contributions are constructed by simple linear interpolation between end member constituents comprising the material system composition. Input data includes the Curie-Weiss constant, Curie temperature, saturation polarization at room temperature and the room temperature unit cell volume. This reliance on individual constituents as opposed to the binary or ternary solid solutions between them allows for the model to be used in a more exploratory fashion.

The framework for the phenomenological model of ferroelectric materials extends from a single grain boundary microstructure of single-crystal to a multidomain textured polycrystal by expansion of the free-energy functions. Template growth is driven by the difference in surface free energy between the matrix grains and the larger template crystal during heat treatment. To characterize the surface free energy at the grain boundaries is the focus of current research at the Naval Undersea Warfare Center. Textured piezoceramic is more readily amenable to the phenomenological theory than traditional PZT piezoceramic because of the alignment of grains along the preferred crystallographic direction.

The development of this framework has opened up new avenues to identify and characterize current and future piezoelectric material systems specifically tailored to meet the harsh and stringent requirements needed for use in the undersea domain. This work provides a solid foundation upon which a comprehensive and robust modeling tool capable of not only guiding but also optimizing the single-crystal and textured ceramic manufacturing process can be built.

About the authors:

John Blottman and **Adam Heitmann** are engineers at the Naval Undersea Warfare Center Newport Division in the Sensor and Sonar Systems Department.

A LOOK AHEAD

ASSURE ACCESS TO MARITIME BATTLESPACE

By Dr. Frank Herr

The next issue of *Future Force* will focus on the varied and diverse range of technologies that contribute to assured access to the maritime battlespace. Assuring access involves naval forces striving to attain global maritime, littoral, riverine, and inland access to denied areas. It means maintaining the ability to penetrate and operate in hazardous areas, where others cannot, to hold antiaccess targets and deny sanctuary to adversaries.

US naval superiority in undersea missions will be tested over the next decade by the increasing use of fixed and mobile off-board autonomous sensors and, likely, weapons aboard autonomous vehicles. Autonomous underwater vehicles, embedded signal processing, and detailed physical environmental modeling are all maturating rapidly. International concern for climate and the United States' strategic swing to the Pacific are putting a spotlight on the oceans. This focus is driving technology development for ocean observations worldwide. Sensing methods that had been largely the purview of naval forces are being deployed for civil societal concerns. The endurance of these sensors is increasing and satellite communications provide the means to acquire real-time information from remote locations at sea. Underpinning these technical advances, the cost of ocean capable systems is decreasing as new materials and embedded computing allow greater capability in smaller packages. Lower costs, in turn, allow greater numbers of sensors and platforms.

These technological trends support many uses for offensive undersea warfare. The same technologies, however, have defensive applications. Access to the maritime battlespace in far forward areas almost certainly will be denied and contested. The geopolitics of the next decade suggest that prudent naval strategic planning be undertaken to assure access to western Pacific marginal seas, the European subarctic, the high Arctic, and straits in the margins of the Indian Ocean. All of these factors point to undersea warfare entering a new era characterized by autonomous vehicles and off-board sensor suites working closely with submarines, mine countermeasures embracing autonomous vehicles for sensing and clearance, and smart sea mines becoming an even greater threat.


Photo by MC2 Daniel Rolston

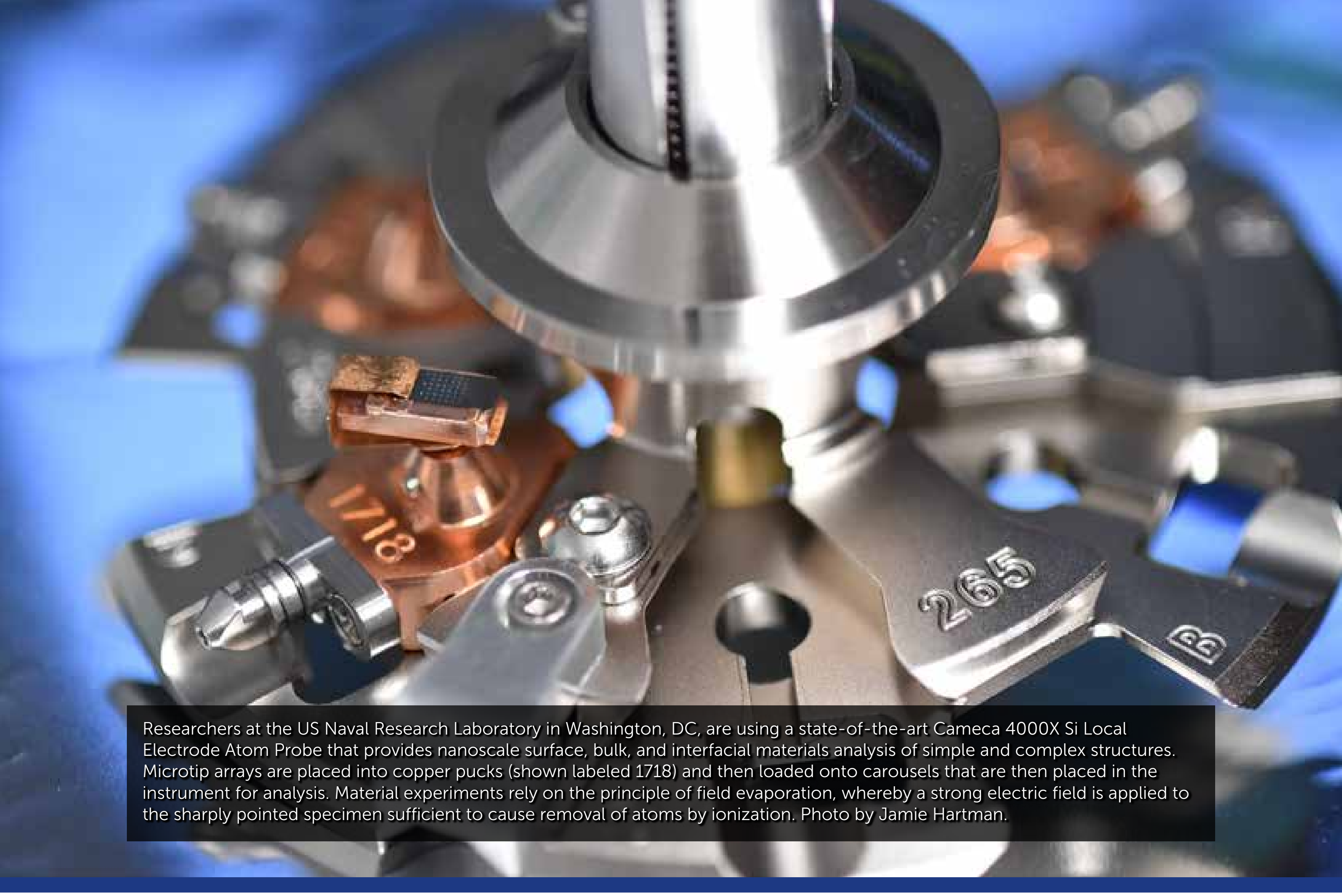

Photo by MC3 Jonah Stepanik


Photo by John F. Williams

Dr. Herr is the director of the Ocean Battlespace Sensing science and technology department at the Office of Naval Research.

Photo by MC Daniel Rolston

Photo by MC2 Daniel Rolston



Researchers at the US Naval Research Laboratory in Washington, DC, are using a state-of-the-art Cameca 4000X Si Local Electrode Atom Probe that provides nanoscale surface, bulk, and interfacial materials analysis of simple and complex structures. Microtip arrays are placed into copper pucks (shown labeled 1718) and then loaded onto carousels that are then placed in the instrument for analysis. Material experiments rely on the principle of field evaporation, whereby a strong electric field is applied to the sharply pointed specimen sufficient to cause removal of atoms by ionization. Photo by Jamie Hartman.

FUTURE FORCE is a professional magazine of the naval science and technology community published quarterly by the Office of Naval Research.

Future Force
Office of Naval Research
875 N. Randolph Street, Suite 1425
Arlington, VA 22203-1995

Email: futureforce@navy.mil
Phone: (703) 696-5031
Web: http://futureforce.navylive.dodlive.mil
Facebook: http://www.facebook.com/navalfutureforce