Science & Technology at the Ames Laboratory

inquiry

2016
Issue 1

Materials Synthesis

Creating new materials through ...

- Powder Metallurgy
- Single Crystals
- Rapid Solidification
- Solid-state Processing
- Deposition
- Inorganic Chemistry
- Biosynthesis

AMES LABORATORY
Creating Materials & Energy Solutions
U.S. DEPARTMENT OF ENERGY

inquiry

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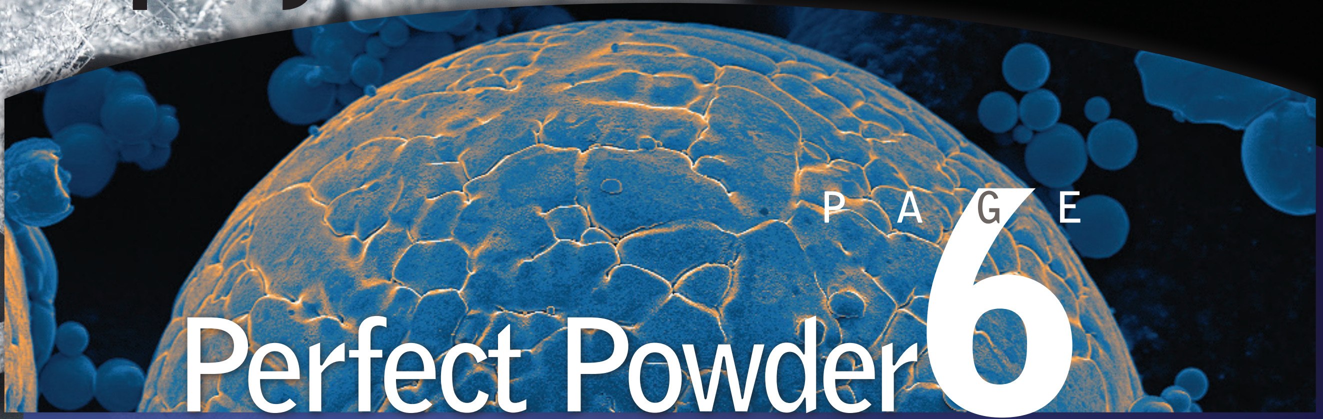

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Ames Laboratory is a U.S. Department of Energy national laboratory seeking solutions to energy-related problems through the exploration of chemical, engineering, materials and mathematical sciences, and physics. Established in the 1940s with the successful development of the most efficient process to produce high-purity uranium metal for atomic energy, Ames Laboratory now pursues much broader priorities than the materials research that has given the Lab international credibility. Responding to issues of national concern, Ames Laboratory scientists are actively involved in innovative research, science education programs, the development of applied technologies and the quick transfer of such technologies to industry. Uniquely integrated within a university environment, the Lab stimulates creative thought and encourages scientific discovery, providing solutions to complex problems and educating and training tomorrow's scientific talent.

Cover photo by Trevor Riedemann, Ames Lab Materials Preparation Center

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U.S. DEPARTMENT OF ENERGY | Office of Science

From the Director

From its inception, Ames Laboratory has been dedicated to materials synthesis. We developed a method for purifying uranium as part of the Manhattan Project and later used a similar technique to refine rare-earth metals. It's even part of our corporate tagline—"Creating materials and energy solutions."

We're home to the Critical Materials Institute, a U.S. Department of Energy (DOE) energy innovation hub that focuses on technologies that make better use of materials and eliminate the need for materials that are subject to supply disruptions. We recently were named the lead for CaloriCool™, a new research consortium for the discovery and development of more environmentally friendly and energy-efficient refrigeration technologies, sponsored by DOE's Office of Energy Efficiency and Renewable Energy.

While we are proud of these research efforts and plan to showcase their achievements in future issues of Inquiry, we want to focus this time on the variety of methods we employ to actually develop new materials. It's basic science at its best, combining experimental, characterization and theoretical work to synthesize materials, measure their various properties and then work to develop models that explain a particular material's structure and how that relates to the properties observed. That type of collaboration has also been a hallmark of Ames Laboratory.

A key method is single crystal growth, detailed on pages 8-10. By creating materials with a uniform crystalline structure, researchers can probe their properties without having to account for the effects of grain boundaries between crystals. It helps provide a clearer picture of what's taking place within the material.

Conversely, we also create materials by cooling them very quickly so that their normal crystal patterns aren't allowed to form. Rapid-solidification (pages 11-13), which also includes gas atomization (pages 6-7), allows for creation of materials not typically possible by other methods. The resulting properties are also out of the ordinary in many cases.

We're also looking at creating materials in solid state (pages 14-15) without the use of solvents or high temperatures to drive the reaction to form new compounds. High-energy ball milling and friction are just two of the methods being employed to form unique materials not possible by other methods.

Our inorganic chemists are busy developing nanomaterials for possible use in solar cells and catalysis (pages 19-21). And others are studying fascinating nanoscale, two-dimensional materials (pages 16-18).

In yet another technique, we are looking at the ways Mother Nature creates beautifully complex structures on multiple scales from atomic to macro. Biosynthesis (pages 22-23) is harnessing those natural processes to allow creation of man-made materials by following nature's template.

For any of these techniques to work, it's vital to start with pure ingredients. Otherwise, you can't know if the resulting properties are intrinsic to the new material or caused by impurities. Fortunately, our Materials Preparation Center (detailed on pages 4-5) provides us, and researchers throughout the world, with the perfect ingredients we need for materials synthesis.

Materials are everywhere and in everything, and Ames Laboratory is working hard to find new materials and new ways to create them.

On a somber note, we marked the passing of senior metallurgist and Iowa State University distinguished professor Karl A. Gschneidner, Jr. in April. Karl was an inspiration here and around the world as the foremost authority on rare earths. He was a dedicated scientist, colleague and friend and we miss him greatly.

Adam Schwartz, Director

Jacob Fischer, undergraduate research assistant, prepares the injection casting system for operation. The injection casting system is used to study the solidification behavior of alloys by rapidly solidifying ingots with diameters on the order of 1-2mm.

BY STEVE KARSJEN

Materials Preparation Center

After 34 years of producing research and developmental quantities of metals for internal Ames Laboratory, university, industry, and government facilities, the Materials Preparation Center (MPC) has developed an international reputation as the go-to center for scientists' materials needs.

The MPC offers unique capabilities in purification, preparation and characterization of high-purity rare-earth metals and alloys, intermetallic compounds, and single crystals that are not commercially available.

Since inception in 1982, MPC scientists have been involved in over 5,000 projects. The largest percentage of those projects has been with U.S. industry, followed by U.S. universities, foreign institutes and universities, and federal laboratories.

"Many of our customers over the years have been repeat customers," said Matt Besser, manager of the MPC.

On any typical day, MPC staff produces materials for materials scientists, chemists and physicists conducting laboratory-scale research experiments. But occasionally a scientist will request material for a project that's a bit out of the ordinary.

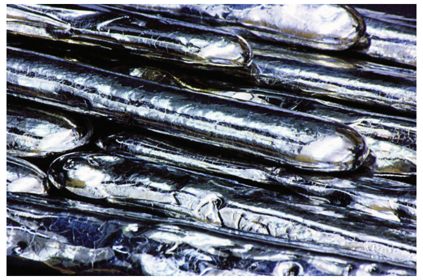
Two of the MPC's more memorable requests came from NASA. One was for the production of materials for use on the Space Shuttle Endeavor's Brilliant Eyes Ten-Kelvin Sorption Cryocooler Experiment (BETSCE). That successful project led to more work with NASA's Jet Propulsion Laboratory for the preparation of materials for the instrument cooling system on board the European Space Agency's PLANCK space satellite.

Another key ingredient in the MPC's success is its materials supply chain, which Besser said assures customers a quick turnaround on the metal they're requesting.

"I have a collection of elements in place, and if I don't have the one a customer is looking for on hand, I know where to go to find it," Besser said.

Once the MPC makes a sought-after alloy, it employs its experience with a wide variety of Ames Laboratory equipment and techniques to fashion the metal into whatever form the customer wants, from wires to ribbons and more.

The MPC offers what Besser calls "an incredible knowledge base" built up over time from the work done by the MPC's staff.



Arc-cast ingots of high-purity Erbium metal, one of the rare-earth metals, are prepared for MPC customers.

"For example, we had a customer who wanted an alloy of tungsten and boron, two metals that are hard to combine, but one of our technicians had the expertise to meet the customer's needs," said Besser. "That comes from his years of experience working in this environment."

Besser said "enabling science" is the MPC's mantra. "Once a satisfied customer said to me 'No one else in the country can do this work for me,' and he was right."

RARE-EARTH MATERIALS PRODUCTION

If you think of the MPC as a pie, one of the largest slices would be the production of rare-earth metals.

Rare earths have been part of the Ames Laboratory since Frank Spedding, the Laboratory's first director, got involved in metallurgical work for the Manhattan Project. The ion-exchange separation process Spedding developed at Ames Laboratory to purify rare-earth oxides gave rise to the knowledge base the MPC utilizes today for producing highly pure rare-earth metals for clients in academia and industry.

The largest portion of MPC's rare-earth-using clients is generally from research institutes with condensed matter physics, materials chemistry, and materials science programs involved in fundamental research.

According to Trevor Riedemann, MPC assistant scientist, the MPC also provides rare earths to industrial clients from large multinationals to start-up companies that are looking for better materials to optimize properties of existing products or products under development.

"What all of our clients have in common is a strong research component," said Riedemann. "And the rare earths help them fine-tune whatever materials properties they're studying."

Riedemann explained when clients call, they're usually looking for high-purity rare-earth metals because purity is critical to the success of today's materials research.

"And no one can match the purity of our rare-earths," Riedemann said.

Riedemann added all MPC metals are provided on a cost-recovery (non-profit) basis. And because rare-earth metals can cost as much or more than gold per ounce, the MPC works to meet customer needs in the most efficient manner.

"Our high-purity-metals are expensive because input costs are high and rare-earth production is a labor-intensive process," said Riedemann. "But because the rare earths provide scientists a fabulous 'tool set' for fine-tuning a material's properties or systematically unraveling the mysteries of materials science, they are willing to pay the high price. Scientists understand it's hard to do high-quality materials science with low-quality materials."

PRECISION-ALLOY PREPARATION

Precision-alloy preparation plays an integral role in the MPC success story, according to Besser, who also heads the MPC precision-alloy section.

"If a scientist wants an alloy that contains specific amounts of iron and carbon, we begin by purchasing the highest purity, or clean, metal we can find," said Besser. "And then we mix it to the precise composition asked for, melt it, and serve it up in exactly the form the client wants."

The MPC also focuses on material size and fabrication. Besser said while many commercial providers can only provide large quantities of materials, the MPC can accommodate much smaller requests.

"Researchers want only what they need, and we can provide anywhere down to a gram, half gram or even smaller amounts of metal," Besser said.

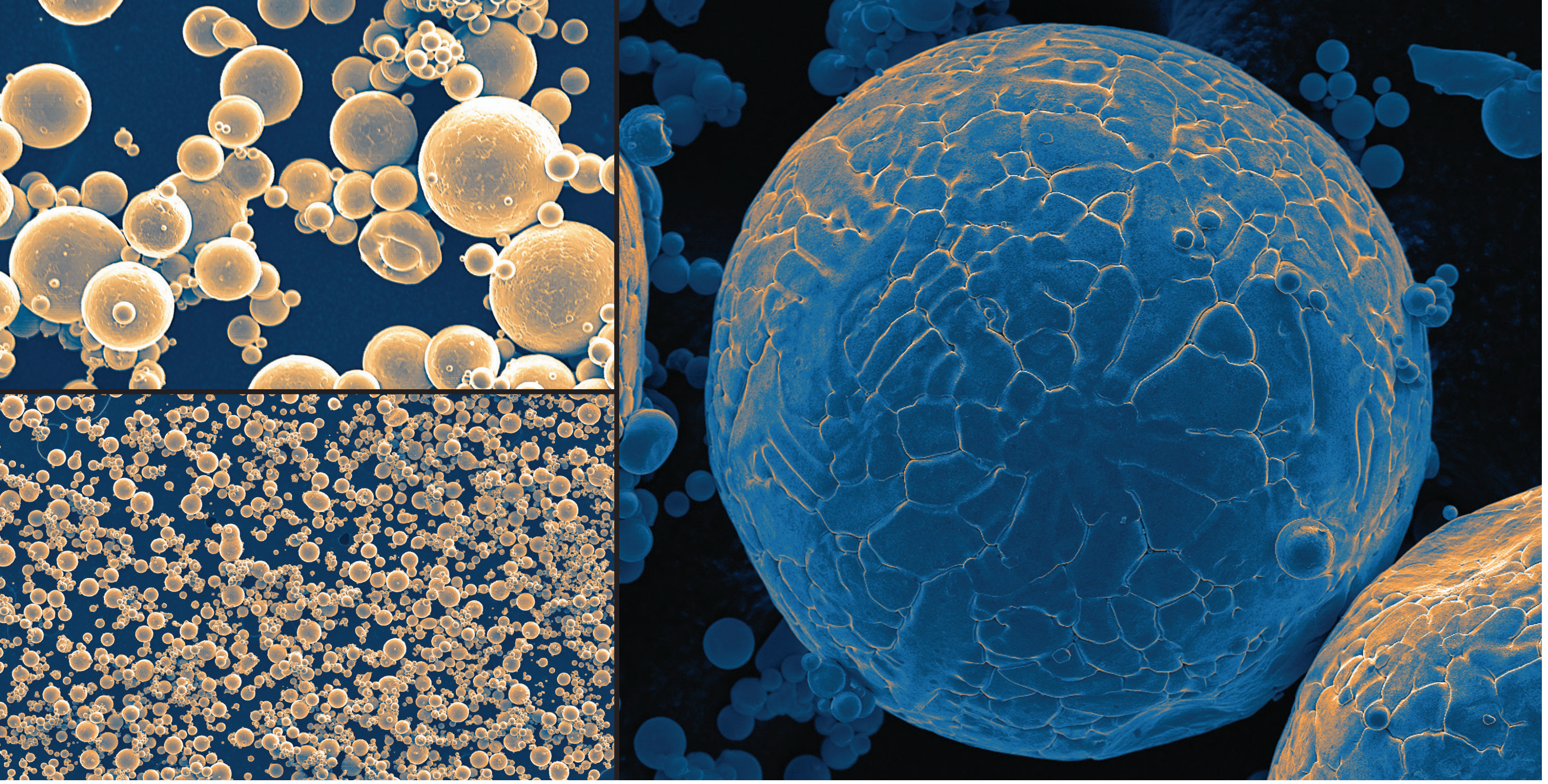
Once the customer has decided on the amount of material needed, the MPC can then fabricate it to their specifications.

"Sometimes customers want their material in a very specific form," said Besser. "For example, once we started with a cast ingot of Galfenol about an inch in diameter and as long as your forearm. When we were done working with it, we had hundreds of feet of wire; rolled, swaged and drawn until it was the dimension the customer needed. The wire was used in an energy-harvesting project."

Beads of scandium metal are shown on a cast on a copper hearth plate. Scandium is one of the high-purity rare earth metals prepared for MPC customers.

Customer satisfaction is the most essential element of the MPC's success, which Besser said requires extensive communication with clients.

"Sometimes customers want one thing, but that might be nearly impossible for us to produce. So we'll talk with them about options, plan A and plan B, and almost always we can guide the interaction to a realistic conclusion," said Besser. "Response to need is very important to us."



High-pressure gas atomized metal powders at various levels of magnification showing the perfection of the spherical end product.

Perfect Powder:

AMES LABORATORY'S PROCESSES PERFECT METAL POWDERS FOR MANUFACTURING

BY LAURA MILLSAPS

LIKE SAND THROUGH AN HOURGLASS

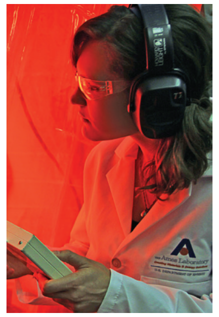
Iver Anderson and Emma White, metallurgists at Ames Laboratory, like to show off samples of metal powders encapsulated in custom-made hourglasses to visitors. Dull gray, the powders are barely remarkable in and of themselves, let alone in comparison to each other.

Until the hourglasses are flipped and observers can compare how the powders flow through the narrow necks of glass. The powder created by traditional manufacturing methods doesn't flow, exactly. It starts and trickles and stops. It needs shaking and manipulating to get through. The other powder, produced at the Laboratory's high-pressure gas atomization facility, pulses smoothly through the hourglass of its own accord.

Iver Anderson

It's all because of the smooth spherical particles produced by Ames Laboratory's gas atomization method, an improvement over traditionally manufactured powders.

"You can see they're chunky, randomly sized, with rough edges," said White of the traditionally-made powder particles, comparing scanning electron microscope images of the two. "They don't flow past each other, and that's going to require a pulsing mechanism or an agitator in the manufacturing process. That's going to cost the manufacturer more in energy to run their production line."



Emma White

It's only one of the many benefits of powders created by the gas atomization process, which has garnered the Laboratory at least 16 patents over the last two decades. It also helped create spin-off company Iowa Powder Atomization Technologies, which was recently acquired by Praxair, and exclusively licenses Ames Laboratory's titanium atomization patents to introduce titanium powder to an eager marketplace.

SPLITTING LIQUID INTO DROPLETS

Gas atomization is a powder production method that uses high-pressure gas flow to distintegrate molten metal into particles. In the Metals Development building at Ames Laboratory, Anderson, a senior metallurgist, and White, a post-doctoral researcher, are able to produce experimental quantities of powder with the Laboratory's experimental apparatus, about half of a liter volume per production run. Another, larger gas-atomizer at Iowa State University's Applied Sciences Complex can produce around three liters.

The basic operation is the same in both. Metal is melted by an induction furnace and held in a crucible with a stoppered opening in the bottom. When the stopper is lifted, the metal flows through a specially designed pour tube into an atomization nozzle (also unique to Ames Laboratory) that focuses a number of round-hole gas jets on the molten metal in a tight pattern. The individual jets of gas—argon, nitrogen, or helium depending on the run—knit together to form a supersonic "curtain" that flows directly across the liquid metal flow and forces the melt to couple directly with the high kinetic energy of the supersonic gas, creating a controlled droplet spray.

"This energetic coupling happens because the gas curtain creates a suction that pulls the melt into the atomization zone and simultaneously forces an upward directed gas counter-flow to form that splits the liquid as though there was an umbrella stuck underneath it and makes it flow sideways, across to the outer edge of that round nozzle," said Anderson, who is also an Iowa State University adjunct professor of materials science and engineering. "So it gets presented to the gas as a thin film that is forced by the gas to turn in the gas flow direction so it can shear past the surface of that film, and strip off waves of liquid that break at their crest to form droplets.

"It's the same phenomenon you can see on the surface of a pond hit with a gust of wind. You see small ripples and a spray of water come off that gust."

Once the droplets form, they solidify rapidly as they fall through the spray chamber and are cooled by additional gas halos. The resulting powder particles are separated from the combined gas flow and settle into two powder collector cans that are connected to the end of the spray chamber. The cleaned inert process gas exits through two types of final filter devices and is exhausted from the lab.

ADVANTAGES

Ames Laboratory's gas atomization method produces powders that are customizable, consistently sized and smoothly spherical. The advantages of a perfectly formed powder are multiple. Besides the advantage of smooth powder flow already mentioned, the individual round particles have little internal porosity and pack together optimally in bulk. Both qualities reduce dead air space and improve the quality of parts produced using these powders.

Using gas atomization, Ames Laboratory has produced powders of iron, aluminum, nickel, copper, tin, magnesium and various other metals and alloys, in addition to titanium, one of its key research accomplishments.

"The titanium industry is extremely interested in powder metallurgy and final-shape consolidation methods," said White. "Titanium is expensive and the large amount of titanium waste produced during machining cast parts into final shapes significantly increases their costs. They see advances in powder metallurgy as an effective cost control strategy by making parts into near-final shapes and minimizing waste titanium."

The powders produced by this method have also been used in the production of stronger alnico (aluminum, nickel, cobalt, and iron) permanent magnets, and in the production of an experimental power transmission cable fabricated out of an aluminum and calcium composite.

And the possibilities of these metal powders don't just look to the future, but may also redeem materials from the past that had been abandoned by researchers and industry as impossible to work with.

> "You can create an alloy with fantastic properties, but if you can't make something useful out of it, it will never get off the lab bench. This method enables us to revisit materials that have been around a long time, give them a second chance, and find new potential applications for them."

"You can create an alloy with fantastic properties, but if you can't make something useful out of it, it will never get off the lab bench. This method enables us to revisit materials that have been around a long time, give them a second chance, and find new potential applications for them," said Anderson.

IMPOSSIBLE SHAPES OUT OF INCREDIBLE ALLOYS

Ames Laboratory is seeking to expand its powder production capabilities beyond research capacity, with the goal of being able to produce up to 200 pounds of powder in one production run.

At that scale, new opportunities for research are possible, explained Anderson and White. Large batches provide sufficient samples amounts for shared research projects among multiple national laboratories and industry partners.

With new 3D printing and additive manufacturing capabilities expanding rapidly, Ames Laboratory will be able to position itself as a provider of custom metal powders for these research areas, continuing to fine-tune the abilities of the gas atomization process.

All of this is a natural progression of the research goals Anderson has worked toward for decades.

"The ability to make impossible shapes out of incredible alloys is my mission in life. I want to work on ways to get this done," Anderson said.

The Power of One

Single crystals provide clarity

BY KERRY GIBSON

Ames Laboratory scientist Paul Canfield removes a sample from a flux-growth furnace.

When it comes to creating new materials, single crystals play an important role in presenting a clearer picture of a material's intrinsic properties. A typical material will be comprised of lots of smaller crystals and the grain boundaries between these crystals can act as impediments, affecting properties such as electrical or thermal resistance.

"Those boundaries can have profound effects, both good and bad," said Ames Laboratory materials scientist and deputy director Tom Lograsso. "Generally, a material that has smaller and smaller crystals actually has improved mechanical properties."

An exception to this rule is that at high temperature, relative to the melting point, small crystals can have a tendency to slide past one another, a property called creep. It's for this reason that turbine blades in some jet engines or generators are actually formed from single crystals of nickel-based alloy.

A few other everyday applications using single crystals are semi-conductors, detectors, such as infrared or radiation sensors, and lasers.

"The active component in a laser is a single crystal," said Lograsso, who is also an Iowa State University adjunct professor of materials science and engineering, "because the crystal grain boundaries would scatter the light."

From a research viewpoint, especially when creating a new material, scientists want to remove as many variables as possible to best understand a material's properties. A primary way to do this is to begin with raw materials that are as pure as possible and to produce the material as a single crystal.

"You don't want defects in the crystal structure and you don't want impurities, which can be a source of extra nucleation," Lograsso said. "New materials can have new physics, and we can determine what those are if we make measurements on a clean, pristine sample (i.e. single crystal). And if we do that consistently, we can make comparisons to other materials and see how it fits into our understanding of particular behaviors."

Ames Laboratory scientists employ a number of techniques to grow single crystals, with each suited to producing crystals from different types of materials. However, the basic premise is the same—oversaturate a solution, then precipitate out the crystal.

"As kids, we're familiar with adding rock salt or sugar to hot water until you supersaturate the liquid," Lograsso said. "Then, as the water cools and eventually starts to evaporate, crystals of salt or sugar start to form and then grow."

"You can do the same with about any two materials, using one as the solvent and then using heat or high temperatures to supersaturate the solvent," he continued. "The tricky part is to get a single crystal to first form and then grow."

This "practitioner's art" requires patience and skill, though the various techniques described here provide some assistance as well. Generally, a high temperature gradient also helps promote a stable growth transition from liquid to solid.

BRIDGMAN TECHNIQUE

One of the better known methods, the Bridgman technique—named for Harvard physicist Percy Williams Bridgman—uses a crucible with a pointed, conical end. This fine point promotes the growth of a single crystal as the crucible exits the heated portion of the furnace. Heat is provided through a heating element similar to the one in a home oven (resistance) or via a magnetic field (induction).

"Crucibles age over time and become better at producing single crystals," Lograsso said. "Unfortunately, you sometimes break the crucible removing the crystal. Because they grow inside a crucible, crystals formed in this manner may also develop stresses such as cracks or voids."

Ames Laboratory also has a special Bridgman furnace that allows crystal growth at higher pressures—up to 15 Bar. This allows growth of crystals from alloys that contain volatile components. The high pressure prevents these components, which have a lower boiling point than alloy's other components, from flashing off as a vapor before the crystal can form.

This furnace utilizes induction heating, which provides a steeper temperature gradient, allowing faster crystal growth rates to further minimize evaporation and reaction with the crucible.

Ames Laboratory scientist Deborah Schlagel holds a graphite crucible (left) and a Bridgman-grown copper crystal (right).

CZOCHRALSKI TECHNIQUE

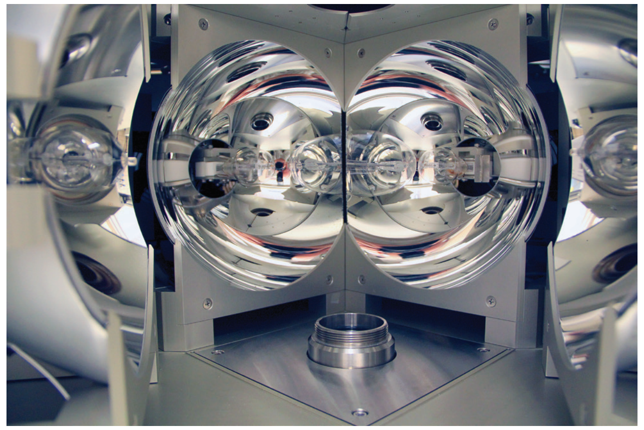
This method also heats the material in a crucible, but here, the crystal is actually drawn from the molten solution. Lograsso likens it to dipping a candle "except you only dip once."

A seed crystal of the material is attached to the end of a rod. The rod is lowered until the seed crystal just touches the surface of the molten material in the crucible. The rod is then rotated and withdrawn very slowly, pulling the newly formed crystal from the liquid.

"Because the crystal is freestanding, it doesn't have the stresses that you sometimes get with the Bridgman method," Lograsso said. "Depending on the material, crystals can also be 60 cm in diameter, or larger, and several feet in length. This is a very common method for producing large silicon crystals which are sliced into wafers for use in semiconductors."

FLOAT-ZONE TECHNIQUE

Optical float-zone technique uses focused, high-intensity light to create single crystals, particularly those containing metal oxides. According to associate scientist Yong Liu, the technique offers a couple of advantages for growing many types of crystals.



Four semi-spherical reflectors focus light energy from high-powered halogen bulbs onto the material, which is suspended over the port in the center.

"It's container-free—you don't need or use a crucible to grow the crystal so it eliminates any potential reaction between the sample and the container," Liu said. "Because the melt zone is very focused and narrow, we're able to achieve a very large temperature gradient between the solid and liquid phases, which results in high-quality crystal growth."

A typical optical float zone furnace consists of four high-powered halogen bulbs arranged in a ring around the sample. Semi-spherical reflectors around each bulb focus the intense light energy in a narrow band around the sample at temperatures up to 2,100 degrees Celsius.

The sample ingot itself starts in two pieces. The shorter "seed" side is on the bottom and held in a base. The longer "feed" side is suspended closely above the seed side. As the two sides begin to melt, a small pool of liquid collects on each surface and as they are brought closer together, the surface tension of the pools connect to form an hour-glass-shaped band of molten material between the seed and feed sides.

By twisting the two sides in opposite directions, the liquid sample is effectively "stirred" to ensure a uniform distribution of material in the melt zone. The sample is then slowly lowered through the focused circle of light, allowing the narrow melt zone to progressively melt, mix and solidify its way up the feed side of the sample.

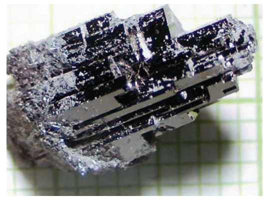
"For materials with low vapor pressure, we can grow crystals at a rate of one millimeter per hour," Liu said. "We can use the technique on a variety of materials, but we always start with the phase diagram (kind of a growth map) to determine if it's possible. We can't grow crystals with high vapor pressure or that may be toxic using this method."

SOLUTION/FLUX GROWTH

While the other three methods work well for materials where the crystalline outcome is known, researchers also look to discover and grow single crystals of new binary, ternary, quaternary or higher compounds. In many cases, the materials in these compounds don't melt congruently meaning they do not melt at a single temperature.

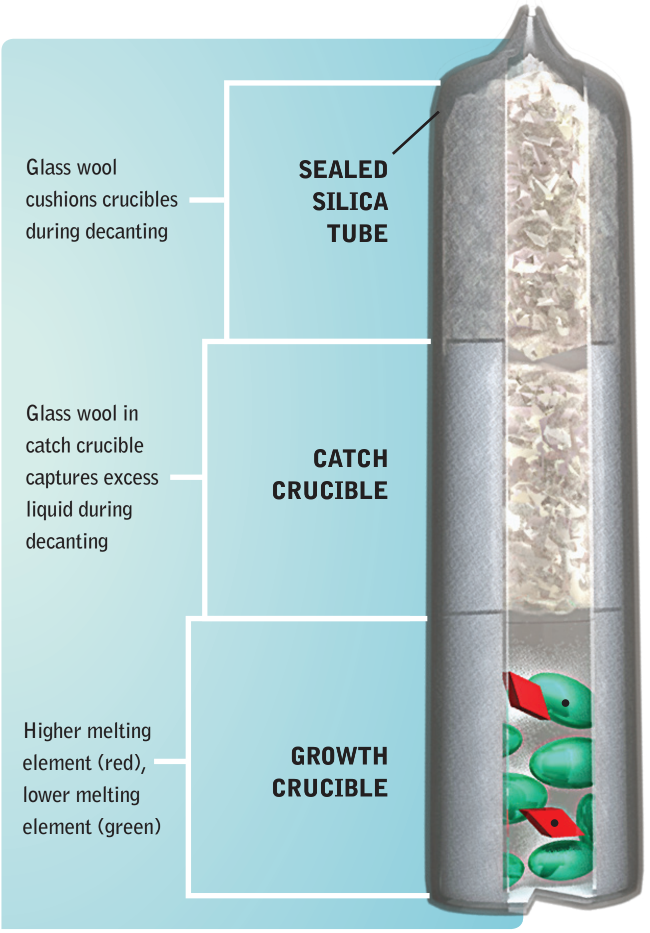
"Solution growth is extremely versatile, and you can often optimize and cycle through it rapidly," said Ames Laboratory physicist and Iowa State University Distinguished Professor Paul Canfield. "In general, it does not give you as large a crystal, but for basic physical measurements, something between a millimeter and a centimeter is more than adequate."

In practice, the compounds for the target crystal are combined with a material that will serve as the solution in which the crystal compound will dissolve. For example, to grow a cerium-antimony crystal from a tin solution, or flux, you may start with four percent each of Ce and Sb with the other 92 percent Sn.



A flux-grown ytterbium-silver-germanium crystal.

The materials go into a "growth" crucible that's paired with a "catch" crucible. These are then sealed in a silica tube as shown (top right). The tube assembly is placed in a furnace and heated so all the elements melt. The temperature is then lowered closer to the melting point of the solution element, allowing the target crystal to form. In the Ce-Sb in Sn flux example, the initial temperature is roughly 1,000 degrees Celsius, then lowered to 600 degrees.



Once a crystal has formed in the growth crucible, this assembly is placed in a centrifuge. Excess liquid is captured in the catch crucible. The glass wool then traps the liquid, leaving the crystal in the growth crucible.

To then separate the liquid tin from the Ce-Sb crystal, the tube assembly is removed from the furnace and immediately placed in a centrifuge, which spins the remaining liquid tin off into the catch crucible, leaving the crystal behind. The centrifuge delivers up to 100 times the force of simple gravitational decanting, resulting in "cleaner" crystals.

"When you develop new materials, you need to have some familiarity with the ingredients and the techniques at hand," said Canfield. "With solution growth, we can go from looking at superconductors and ferromagnets, to spin glasses, to quasicrystals—go from one material to another to another—just by changing elements or growth conditions. Over the course of 20 years here, we are closing in on 10 thousand different growths."

Frozen in a Flash

RAPID SOLIDIFICATION KEEPS MATERIALS ON COOLING FAST TRACK

BY KERRY GIBSON

If the single crystal growth techniques described in the previous article sit at one end of the materials synthesis spectrum, then rapid solidification techniques fall at the opposite end of the scale. The former promote the growth of the material's equilibrium crystalline structure. Rapid solidification techniques promote the opposite effect, cooling the material so quickly from liquid to solid, that the crystals formed are small, or in some cases non-existent, becoming amorphous or glass-like with no discernable crystalline pattern to their overall molecular structure.

It's also a way to form composite materials whose constituents have widely varying "freezing" temperatures.

"If you take a molten metal and cool it, what wants to form will vary depending on its chemistry," said Ames Laboratory scientist and Division of Materials Sciences and Engineering Director Matt Kramer, "because what wants to form is not always a homogeneous solid."

For example, if you freeze a mixture of water and alcohol, the water will solidify first—turning to ice—while the alcohol remains liquid, leaving a slushy mixture until the temperature is lowered to the alcohol's freezing temperature.

"So when you cast a molten alloy, small crystals will form quickly on the surface of the mold, you get segregation of the materials and the remaining liquid becomes enriched," said Kramer, who is also an Iowa State University adjunct professor of materials science and engineering, "which results in a heterogeneous bulk material."

Rapid solidification allows the material to cool extremely quickly so as to suppress or even eliminate the segregation. Techniques range from strip casting, which cools materials at about 1,000 Kelvins per second to splat quenching which, as the name implies, squashes a droplet of liquid material between two plates. Splat quenching can cool the material as high as 10^8 Kelvins per second.

"Why is that important? Because there's an intimate relationship between temperature and the time at which materials cool," Kramer said. "We call it TTT—Time-Temperature Transformation."

It takes a certain finite amount of time for the initial crystals to form, a process called nucleation. The molten material has to organize itself into crystals only a few 10s of atoms across and then those crystals need to grow.

"There's a very non-linear relationship between time and temperature transformation," Kramer continued. "Solidification occurs over a broad range of temperatures. At too high a temperature, it stays molten. At a temperature just below the melting temperature, the material solidifies slowly, and in cases where constituents have different melting temperatures, significant segregation in the casting can occur if cooled slowly

Rapid solidification techniques allow researchers to bypass the time-temperature transformation so a molten metal alloy forms without a crystalline order, creating a metallic glass.

"Glassy metals have some very unusual properties," Kramer said. "On average, they tend to have very good strength, but not much plasticity, so they are hard to mold into shapes."

However, by first forming a metallic glass, then heating the material back up, researchers can achieve metastable phases of the material that aren't attainable by other methods, such as casting. And these intermediate phases may have desirable properties such as strength, ductility, resistivity, or conductivity.

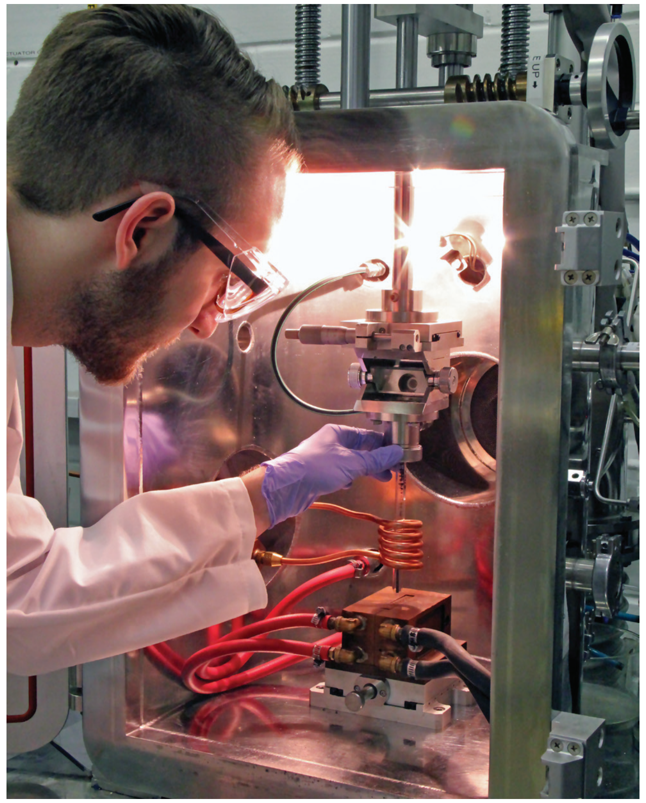
"Manipulating the phases, their sizes, the degree at which we can control their growth, and even their morphology, or shapes, are all buried in the details of the classical time-temperature transformation," Kramer said. "A lot of the work we're doing is trying to understand the relative balance of cooling rates to phase selection process. How can we predict and control those so we can move beyond an Edisonian approach."

Ames Laboratory scientist Brandt Jensen loads a sample into the melt spinner. The induction coil melts the sample, which is then forced in a stream onto the spinning copper wheel.

Researchers at Ames Laboratory use several techniques including melt spinning, injection casting, and high-pressure gas atomization (covered separately on pages 6-7) to produce small-grained and amorphous materials.

MELT SPINNING

This technique involves shooting a stream of molten material onto a spinning copper wheel where it solidifies quickly, forming a ribbon of metal. The copper wheel is typically water cooled and depending on the speed at which it spins, up to 30 meters per second, the molten metal is quenched up to 10^6 Kelvins per second.



Jacob Fischer, undergraduate research assistant, loads a sample into the injection casting system. The melted material is injected into water-cooled copper molds.

“There are limits to the process,” said Ames Laboratory scientist and ISU associate professor of materials science and engineering Jun Cui. “The copper wheel must be perfectly balanced to spin at such high speeds. And beyond a certain point, the material no longer flows in a ribbon but breaks apart.”

There is also a variation in the process where the copper wheel has small grooves cut across its surface. These grooves intentionally break the cooled metal into short strips, which Cui said are easier to work with in some applications.

INJECTION CASTING

As the name implies, injection casting forces the molten material into a copper mold, typically a small cylinder that will produce short rods one to four millimeters in diameter. The mold is held inside a larger water-cooled copper mold providing quench rates fast enough to produce amorphous (glassy) samples in some alloys.

“Small samples—usually less than five grams—are placed in a graphite or quartz nozzle and rapidly heated by induction to several hundred degrees above the melting point,” said Matt Besser, Ames Laboratory scientist and manager of the Laboratory’s Materials Preparation Center. “We then drop it out of the heating zone and pressurize the system so the material squirts into the mold.”

By using different shaped molds, material can be cast in plates, or wedges. Besser said thermocouples can be placed along the length of the wedge to measure the difference in cooling rates from the fastest at the thin tip to the slowest at the thicker end.

“We’re able to fabricate samples to fit specific needs,” Besser said, “and it’s convenient because we can produce small samples, especially when the alloy contains expensive materials.”

Seeking explanations for solidification puzzles

One of the most common and robust ways to create a new material, particularly a metallic alloy, is to melt two or more constituent materials, mix them in the liquid state, then freeze or “solidify” them under certain controlled conditions. While seemingly simple, solidification processing can produce an incredible variety of material structures with important features on scales from nanometers to centimeters, giving rise to a host of remarkable properties ranging from enhanced strength and stiffness to unusual magnetic, thermal, electrical, and photonic properties.

But the make-up and structure, and therefore the properties, of that end result can vary greatly depending on a variety of conditions present as the material transitions from liquid to solid. Ames Laboratory scientist Ralph Napolitano works to explain and predict what takes place at that liquid-solid interface and how those various interactions result in certain structures, chemistries and properties.

“When a material goes from a liquid to a solid phase, a lot of things must happen as part of that transformation,” said Napolitano, who is also an Iowa State University professor of materials science and engineering. “Nominally speaking, an amorphous or non-crystalline liquid phase has to reconfigure itself into some kind of crystalline packing. But many other simultaneous events are taking place to make that happen. Indeed, it is the way that the different transport processes and different structural entities enter into that equation that really influences what that final structure may look like.”

If equilibrium yields the normal or expected result, there are all kinds of deviations that can shift the result from equilibrium. Some of them are very small deviations, such as slightly different chemical compositions or slightly different concentrations of different kinds of crystalline defects. Deviations can also be very large—completely different crystalline packing or composition or even an array of multiple phases that you might never see closer to equilibrium.

“What dictates how far away from the final equilibrium state you might be is what happens along that pathway from the equilibrium liquid to this far-from-equilibrium structure,” Napolitano said. “Varying the composition of a material and the rate at which we cool it has dramatic influence over final phase or assembly.”

“Beyond just the phase—the particular crystalline structure—conditions during freezing greatly influence the growth morphology,” he continued. “Any given phase will grow with a certain morphology that is dynamically optimized with respect to all of the different processes—such as the redistribution of heat, chemical species, and configuration of crystalline defects—making the overall transformation more efficient. Composition and cooling rate, along with the phase itself and the energies of the crystal defects and interfaces, all play a role in this collective dynamical optimization, ultimately resulting in the selection of the final state, which may look nothing like the equilibrium state.

Ralph Napolitano

“This far-from-equilibrium synthesis provides a portal or pathway to structures, chemistries, and properties that aren’t accessible through conventional methods,” Napolitano said.

To complicate matters, these pathways may include several other steps —before and after solidification, so that the complex freezing structure may only serve as some intermediate stage, along the way to a desired structure.

Cooling rate provides a high level of control in certain windows. At the low (slow) end, cooling rate can be controlled very carefully, and even cooling rates from isothermal treatments to 100 degrees per second can be controlled reasonably well.

“We can go to cooling rates of 10^3 to 10^4 degrees per second with techniques like melt spinning, but within that window, process control is challenging and local variations exist,” Napolitano said. “We have investigated such variations, and our understanding has certainly increased. Even so, with relatively few ‘process knobs’ to turn (e.g. melt temperature, wheel speed, wheel material, injection rate and stream diameter) precise quantitative control remains a real challenge.”

As a strategy to reveal a clearer picture of the complex behaviors, Napolitano’s group has chosen to focus on a few select two-component or “binary” systems. In particular, binary systems, such as copper-zirconium and aluminum-samarium, provide great opportunities to investigate far-from-equilibrium transformation. These systems exhibit complex competitive solidification, glass formation, and crystallization, forming a host of non-equilibrium phases and multi-scale growth structures. At the same time, with only two components, analytical and computational treatment of the thermodynamics and kinetics become more tractable, compared with multi-component systems.

“With both of these systems, there’s a composition range over which the liquid forms a glass rather easily so you can cool it at rates that are achievable experimentally,” Napolitano said. “Once the alloy is glassy, other treatments can be used to crystalize the material at low temperature. In this regime, conditions can be controlled carefully, and reactions can be slowed substantially, even permitting in-situ real-time investigation. Of course, having an accurate and comprehensive picture of the system thermodynamics is critical. Whether you’re solidifying the material directly from a liquid, or first quenching to a glass and then heating to crystallize the material, you still have that same thermodynamic playing field.”

The aluminum-samarium work is being expanded to a larger range of binaries, including other aluminum-rare earth alloys. In general, those systems are expected to exhibit similar behaviors, though Napolitano warns that very subtle effects can dramatically tip the balance between phases and growth structures. Very small energetic differences exist between the competing phases. Under high driving forces, these differences are often negligible and the kinetic pathways control the outcome. Even changes in chemical composition on the order of a percent or less can dramatically change the final state.

“This kind of study is only possible by bringing together many different approaches in theoretical condensed matter physics, materials science, computational thermodynamics, materials synthesis, and state-of-the-art characterization,” Napolitano said. “There is no doubt that this work requires the full gamut of experimental and computational capability and a team of investigators with a broad range of expertise.”

To that end, the new electron microscopy equipment at Ames Laboratory’s Sensitive Instrument Facility (SIF) will play a vital role.

“It’s important not only in terms of spatial resolution, but some of the in situ capabilities as well,” he said. “Hot-stage transmission electron microscopy with atomic scale resolution will allow us to look at some of the early stage dynamics that really are watershed events that tend to send the material down a whole different trajectory. So absolutely, the SIF is critical to moving forward in this area.”

An array of ball milling canisters and stainless steel balls Vitalij Pecharsky's group uses to process materials in their solid state.

Solid-State Processing:

New paths to new materials

BY KERRY GIBSON

Creating materials in their solid state can be tricky, but offers some advantages over other methods. It typically involves subjecting the component elements to some type of mechanical force—such as stress, shear or strain—to drive a reaction.

"You eliminate the need for solvents, so it removes potentially harmful substances from the waste stream," said Ames Laboratory scientist and Iowa State University Distinguished Professor Vitalij Pecharsky, "and it offers greater selectivity so you can steer it toward a specific reaction. Most processing is done at room temperature so energy inputs are reduced and the resulting end products may be meta-stable as well."

It also offers a pathway to materials that aren't typically possible by other methods. One example is the work Pecharsky has done using ball milling. Using this mechano-chemistry technique, you can create a homogeneous mixture—a consistent blend throughout the entire sample—even though you start with a mixture of components that can be 99.9 percent of one component and only 0.1 percent of the second component.

"You can get complete dispersion," Pecharsky said, "something that would be very difficult to achieve by melting the two components together."

Because it doesn't require solvents and often can be done without heat and with relatively low energy inputs, solid-state processing costs less than other methods. In many cases, it's also scalable to industrial/commercial applications.

MECHANO-CHEMICAL BALL MILLING

As the name implies, ball milling uses metal balls in a closed canister to shake, rattle and roll a chemical reaction that turns individual chemical components into a compound. Pecharsky said the impact of the balls with the container and each other, with the material mixture getting smashed between them, transfers the mechanical energy of the rattling balls into chemical energy that in turns drives the reaction.

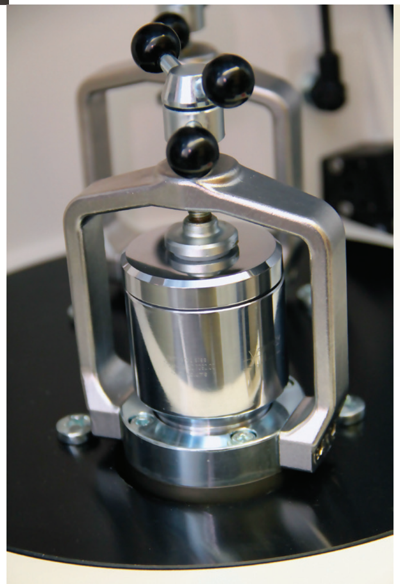
The shear, stress and strain fractures the normal molecular structure of the component materials, allowing them to combine in ways that normally require a solvent to break the molecular bonds and let the reaction take place.

Pecharsky's group is using the technique to investigate creation of metal hydrides to serve as a hydrogen storage medium. The group recently added a low temperature ball mill that allows processing of materials that are plastic or ductile.

"These materials will deform, but don't fracture at room temperature," Pecharsky said. "By lowering the temperature to that of a liquid nitrogen bath, like most things, they become brittle and we're able to process them using this technique as well."

FRICTION CONSOLIDATION

A brand new area for Ames Laboratory, friction consolidation uses high pressure and friction to grind, tear and press new materials into existence.



A canister containing elements and stainless steel balls is clamped in place in a ball mill in preparation for shaking.

"It's very fundamental," said Ames Laboratory scientist and ISU associate professor of materials science Jun Cui. "We put material in a die and apply pressure with a rotating plunger. The friction from the rotating plunger creates shear stresses within the materials. They eventually heat up, soften and flow homogeneously. It's a violent and chaotic process, but there's also a certain amount of order to it."

The process typically uses powdered metals which are easily consolidated because of the small initial size of the particles. Similar to ball milling, friction consolidation allows creation of microstructures not possible by other means.

"For example, you can take copper and process it with carbon nanotubes and wind up with a nanocomposite material that has greater mechanical strength than normal copper without any reduction in electrical conductivity, " Cui said, "or may create a magnesium-titanium alloy that is corrosion resistant."

Once the material has been consolidated, it can then be extruded or processed by a number of standard industrial methods.

Ames Laboratory researcher Shalabh Gupta loads material into a cryogenic ball mill used to process ductile or plastic materials. A liquid nitrogen bath cools the materials, making them brittle enough to be mechano-chemically milled.

GLEEBLE THERMOMECHANICAL SYSTEM

Another new technology for Ames Laboratory is a Gleeble system that allows laboratory simulation of any number of commercial materials processing techniques. The new equipment recently installed in the Laboratory's Metals Development building lets researchers precisely control and measure what happens to materials during an array of industrial processes from casting and forging to sintering and extrusion.

"It allows us to do the precise measuring and monitoring of physical simulations of complex processes," said Pete Collins, Ames Laboratory associate scientist and Iowa State University associate professor of Materials Science and Engineering, "as opposed to computational simulations. However, the two really go hand in hand —our measurements can validate and inform modeling simulations, and modeling can suggest the physical simulations we need to run."

The equipment uses resistive heating to bring samples quickly to high temperatures needed to simulate melting, casting and welding—thousands of degrees in a few seconds. The electrical demands—enough power to run two or more average homes—were a primary reason for locating the equipment at Ames Laboratory. The equipment was part of Collins' research startup agreement when he accepted the faculty position at Iowa State.

"It also made sense from a materials processing standpoint to have it located near the (Laboratory's) other additive manufacturing tools, such as the LENS™ (laser engineered net shaping) 3D printer," Collins said. "The Gleeble can be an important component of a high-throughput suite of capabilities, so we can rapidly test the array of alloy samples that the LENS™ system can produce. In addition, we now have the capability to assess other powder consolidation techniques. We can also take metals powders and simulate how those powders are processed under pressure and temperature to optimize the conditions for the best results."

Ultra-high vacuum equipment provides a clean, stable, and controllable environment for building 2D materials and investigating them through scanning tunneling microscopy.

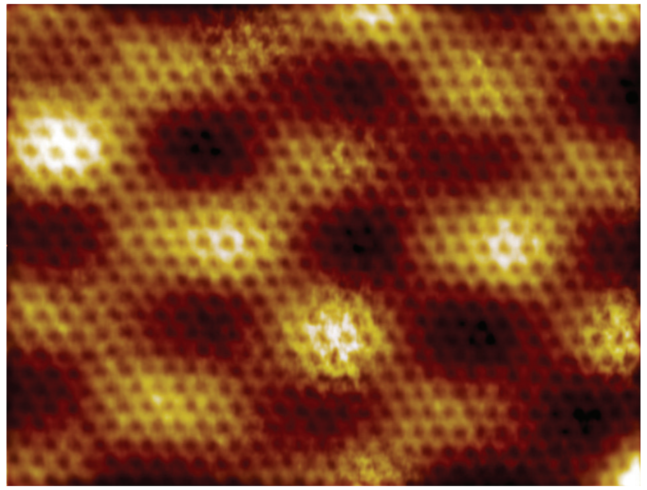
Exploring Mysteries on the Surface:

2D MATERIALS REVEAL SURPRISING PROPERTIES

BY LAURA MILLSAPS

Two-dimensional materials are a bit of a mind-bending concept. Humans live in a three-dimensional world, after all, where everything observed in our natural world has height, width, and depth.

And yet when graphene—a carbon material unique in its truly flat, one-atom-deep dimension—was first produced in 2004, the mind-bending concept became reality and an unexplored frontier in materials science.



A scanning tunneling microscopy image of graphene.

Ames Laboratory scientists Pat Thiel and Michael Tringides are explorers on that frontier, discovering the unique properties of two-dimensional (2D) materials and metals grown on graphene, graphite, and other carbon-coated surfaces.

"Our work is somewhat of a miracle, if scientists can talk about miracles," said Tringides, who is also a professor of physics at Iowa State University. "Only a few decades ago, no one would have believed that we could see individual atoms, but our capabilities now not only allow us to see them, but manipulate them, like a child building with Lego® bricks. We're able to create these materials from the bottom up, ones that could never happen in nature."

They're created in a controlled laboratory setting, in an ultra-high vacuum environment, and investigated with the aid of scanning tunneling microscopy. After heating the substrate to high temperature all impurities and defects are removed. The substrate is cooled and atoms of interest are deposited one by one from specially designed sources. By tuning the temperature and deposition rate, the researchers search for the Goldilocks-like condition: atoms move not too fast and not too slow so a truly 2D material forms.

While their research groups create a variety of surface materials in their work, the fabrications methods all have one thing in common: attempting to confine the assembly of the atoms to the 2D plane. That's difficult, because it's counter to what atoms naturally want to do under most conditions, to assemble in three dimensions.

Pat Thiel

Michael Tringides

"Atoms are chaotic by nature; we are fighting this randomness in everything we do," said Tringides. "In our work, atoms are precisely arranged on a highly reactive surface in a vacuum. Every aspect of the environment is controlled. Our work is to fabricate very small, very clean, and very perfect. Working on materials in the nanoscale demands it."

Learning how these materials behave is paramount. Because 2D materials are all surface with no bulk, a host of unique nanoscale properties—chemical, magnetic, electronic, optical, and thermal—can be attributed to them.

"There's a rule book for the properties of bulk, or three-dimensional materials—and it contains big chunks that are universally understood and accepted," said Thiel, a physical chemist, materials scientist, and Distinguished Professor at Iowa State University. "But the rule book for 2D materials is largely unwritten. There are lots of things we don't know. We get lots of surprises, and then we must explain them."

Writing the rule book to the behavior of these materials is only the first step in a larger goal; creating tunable materials that could be potentially useful in a host of tech applications, including ultrafast microelectronics, catalysis, and spintronics.

It's the reason that Thiel's and Tringides' research has focused upon growing metals on 2D substrates over the last four years, turning it into a major strength of Ames Laboratory's materials research.

Graphene has gained a lot of enthusiastic attention in both scientific research and the tech industry because electrons travel very fast along its surface, explained Tringides. But to create functional devices, it necessitates patterns of nanoscale-size metal contacts on its surface, designed specifically for a desired function.

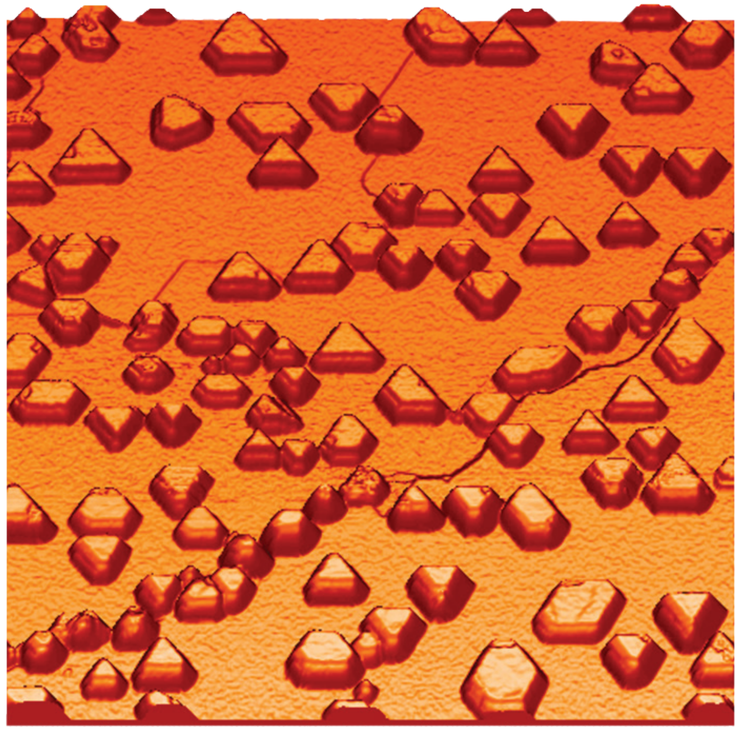
"Whatever material we are trying to create, uniformity of the surface is the key to a functional device, and that is where our 'perfect' research comes in. That perfection makes us slow, but it's a trade-off," said Tringides. "If we can gain a thorough understanding of how these contacts can be produced under ideal conditions in a controlled environment, then these methods can be optimized eventually for commercial production and use."

> "If we can gain a thorough understanding of how these contacts can be produced under ideal conditions in a controlled environment, then these methods can be optimized eventually for commercial production and use."

Thiel and Tringides' most recent success is the intercalation of dysprosium onto graphite layers. Intercalation is the introduction of a material into compounds with layered structures. That's a real challenge with graphite, since its purely 2D surface results in "slick" layers with no good way to form bonds between them.

"It's like a stack of blankets on a bed," said Thiel. "The blankets themselves are structurally sound, but two blankets stacked on top of each other slide around, slip off the bed, and are easily peeled off in layers."

But the team has recently discovered the conditions under which they can create different types of intercalated metal-and-graphite systems, bonding those sliding blankets of material together two-dimensionally. It's a promising new way to form a thin coating of a metal protected by a carbon skin, and could lead the way to materials with unique magnetic or catalytic properties.



Dysprosium was found to make triangular-shaped crystalline islands on graphene. Characterizing the unique structures of materials grown on 2D surfaces helps researchers better understand their possible electronic, magnetic, or catalytic properties.

With such a narrowly focused and highly controlled experimental focus in basic science, it could be tempting to assume that their research, like their experiments, occurs in a vacuum. But Thiel credits the success of surface science at Ames Laboratory to the close collaboration of varied research groups.

"Ames Laboratory is a fertile environment for surface science experiments because we have the opportunity to collaborate directly with many scientists in diverse areas of expertise addressing the same problem from a different viewpoint," said Thiel, including specialists in photonic band gap materials, optical physics, theory, and materials fabrication. "While that collaboration model has been adopted by other institutions and is the norm now, Ames Lab's intimate size and community culture really started it all, and our achievements in surface science have benefited greatly from it."

Inorganic Chemists

Take a Team Approach to Science

BY STEVE KARSJEN

When Cynthia Jenks talks about Ames Laboratory's scientific accomplishments in inorganic chemistry, she's quick to credit any successes to the team of specialized scientists who are part of the Laboratory's Chemical and Biological Sciences (CBS) program and the Division of Materials Science and Engineering.

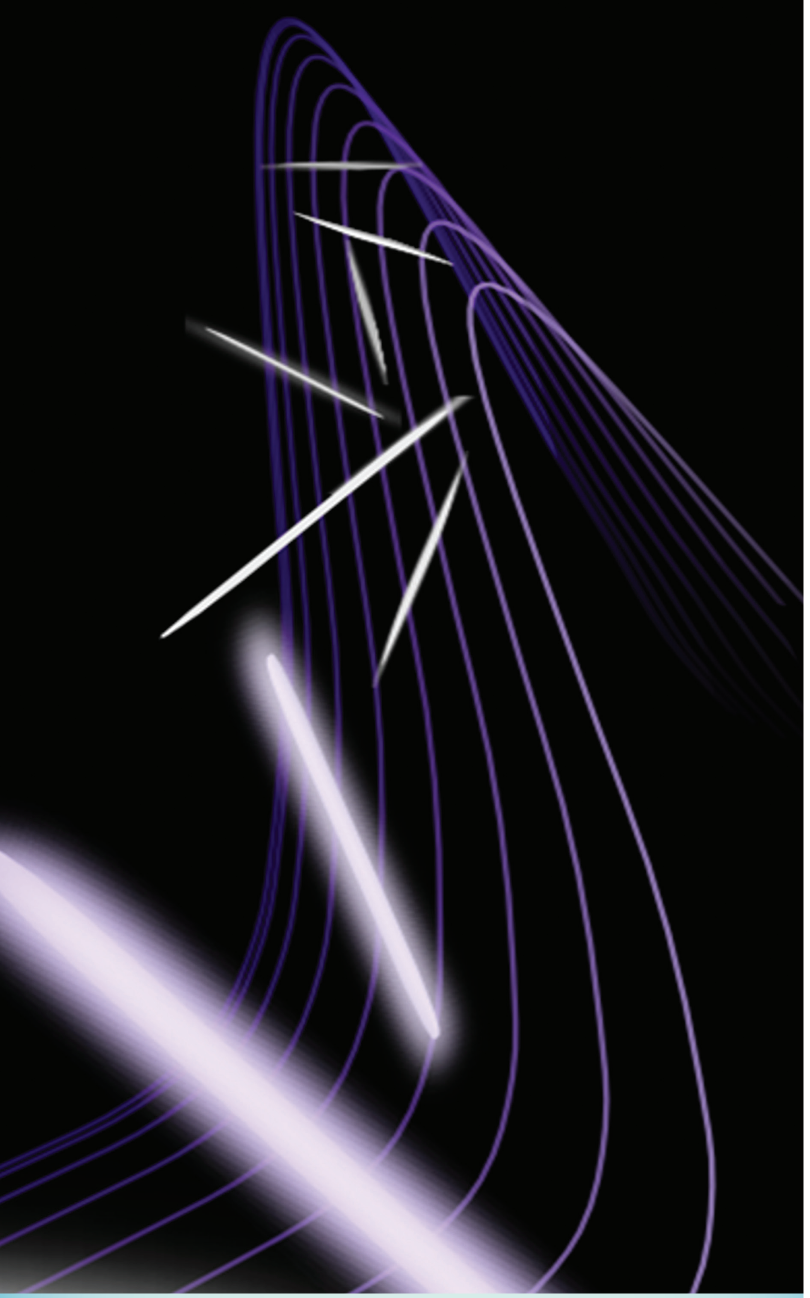
"Whether designing new nanomaterials, devising new homogeneous catalysts, interfacing between homogenous and heterogeneous catalysts, or developing ionic liquids, our work involves scientists with a diverse skill set in inorganic chemistry," said Jenks, assistant director of Scientific Planning and division director for Ames Laboratory's CBS program.

Jenks said several CBS-based research projects are generating interest from the scientific community. For example, inorganic chemist Javier Vela is researching ways to design more efficient solar cells using a family of materials known as perovskites. Chemists Aaron Sadow and Igor Slowing are working on a project to design more energy-efficient catalysts using earth-abundant materials, and solid-state chemist Gordon Miller is using theoretical/experimental investigation to identify new organic materials that show promising chemical and physical properties.

One project involving teamwork at Ames Laboratory is a so-called "Big Idea." This project, which includes scientists and engineers at 12 DOE national laboratories, resulted from a Big Idea Summit sponsored by the Department of Energy in 2015. Ames Laboratory's part includes finding new catalytic technologies that can efficiently produce biofuels from diverse waste streams, including industrial waste, farm waste and municipal solid waste. Since these potential feedstocks are distributed, modular reactor designs offer the potential for economically converting them into useful fuels and chemicals.

Cynthia Jenks

> "When we all bring our expertise to bear on scientific challenges... the result can often be the creation of exciting new science."



This is a rendition of a one-dimensional, needle-like nanocrystal, such as the one prepared by Javier Vela in collaboration with Emily Smith and Jacob Petrich. Vela's team has prepared a family of highly luminescent perovskite nanocrystals with shape correlated emission.

"If you want to do something like one of these 'big ideas', it's never going to be a single person who will be able to solve these problems. It takes a team of scientists, from inorganic chemists to engineers to those who understand separations and modular design," said Jenks. "When we all bring our expertise to bear on scientific challenges and study the foundations of the roadblocks to their success, the result can often be the creation of exciting new science."

MATERIALS SYNTHESIS

Ames Laboratory associate scientist Javier Vela's research focuses on the development of new optical nanomaterials, heterostructures, and devices for applications in catalysis, energy conversion, and biological imaging.

Javier Vela

"In my laboratory, we're very good at making things, in our case, nano-sized particles of different compounds," said Vela, who likens his work to that of a high end, scientific cook.

Like any good cook, Vela begins with raw materials, which for him include different compounds, either crystalline or molecular. Then he consults his toolbox of available reagents and mixes in the appropriate amount of ingredients to make the appropriate material. It sounds easy, but according to Vela there's little room for error.

"We have mastered the art of knowing how to combine these reagents in the right proportions and under the right set of conditions to achieve the desired materials in the formulation and with the right properties we're interested in," said Vela, who is also an associate professor of chemistry at Iowa State University. "In the world of synthetic chemistry, whatever we make has to be reproducible; nothing can be by luck."

Recently, Vela's group of synthetic inorganic chemists has been cooking with two other Ames Laboratory and ISU scientists, Emily Smith, analytical chemist, and Jacob Petrich, ultrafast spectroscopist, who, like Vela, study organo lead-halide perovskite semiconductors. These tiny semiconducting optically active crystals are known to display intriguing electronic, light-emitting, and chemical properties.

"My part of the work is to understand the synthesis issues going on inside these perovskites, which has led to several interesting phenomena," said Vela. "With our increased knowledge, we are developing a rational, predictable approach to modify their structure and to enhance their properties to make them better."

Ultimately, Vela said, better organo lead-halide perovskites could lead to better construction materials for solar cells with 20 percent solar power-conversion efficiency.

CATALYSIS

According to Ames Laboratory associate scientist Aaron Sadow, much of today's chemical manufacturing involves catalysis—the acceleration of chemical reactions. Many of these processes involve mixed-phase heterogeneous catalysis, but Sadow said there are also a large number of processes that use single-phase homogeneous catalysis, most commonly solution-phase catalysts.

> "The interesting thing for me is these materials provide the opportunity to access new mechanisms and new pathways, and if we can understand those pathways, we can use these earth-abundant metals in interesting processes that could one day have an impact on industrial catalysis."

Sadow, who is also an ISU associate professor of chemistry, has been partnering with computational scientists at Ames Laboratory to understand what happens at interfaces between liquids and catalytic solids.

"We're trying to measure the rates of reaction, understand mechanisms and then use those to guide site synthesis," Sadow said.

His group is involved in cutting-edge research involving the design of both homogeneous and heterogeneous catalysts using earth-abundant materials. These materials, like zirconium or magnesium, are cheaper and more plentiful than commonly used catalysts like platinum, rhodium and palladium.

"The interesting thing for me is these materials provide the opportunity to access new mechanisms and new pathways, and if we can understand those pathways, we can use these earth-abundant metals in interesting processes that could one day have an impact on industrial catalysis," said Sadow.

Aaron Sadow

INNOVATIVE AND COMPLEX METAL-RICH MATERIALS

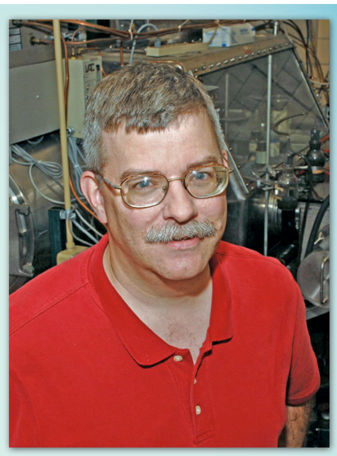
Ames Laboratory associate scientist Gordon Miller is both a theorist and experimentalist, two diverse areas of expertise he combines to identify new inorganic materials that show promising chemical and physical properties.

"We concentrate on intermetallic compounds because they are best suited for combined theoretical/experimental investigations," said Miller, who is also an ISU professor of chemistry. "They also offer fundamental opportunities towards understanding relationships among chemical composition, atomic structure, physical properties and chemical bonding in materials due to their elegant complexity."

Miller collaborates with scientists throughout the Ames Laboratory, using a variety of synthetic approaches to produce new materials and then characterizes their atomic structure by X-ray diffraction. He also assesses possible chemical substitutions that can lead to changes in structure and properties. In this way, experiment and theory are engaged synergistically to yield new metal-rich materials.

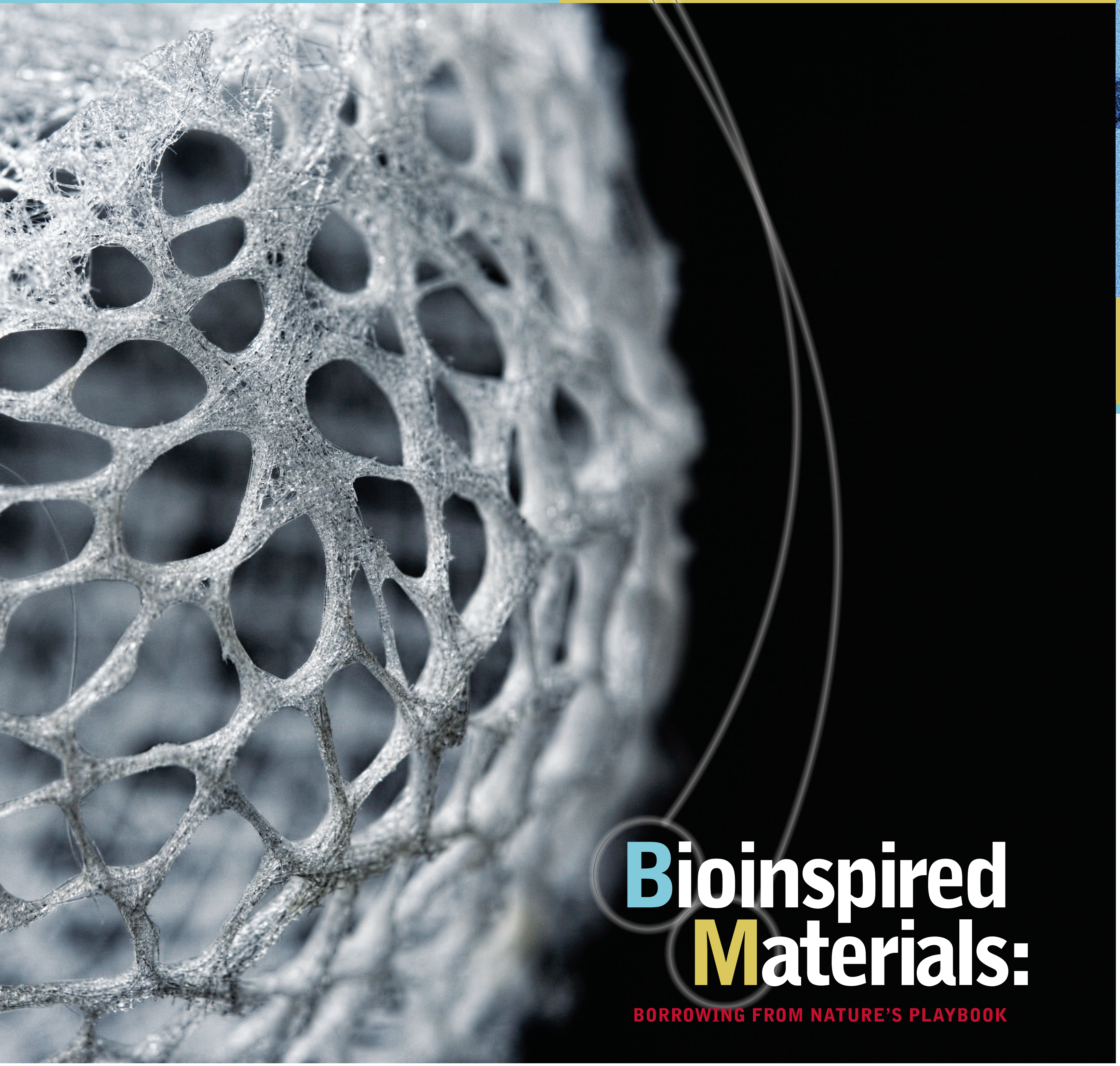
Miller's approach has led to new magnetic refrigerants and quasicrystals. His group's most recent work involves researching cluster chemistry of intermetallic compounds by introducing lithium, research that has resulted in the discovery of new complex structures based on clusters of icosahedra, and shows promise of yielding unprecedented clusters in solids.

Miller feels his greatest outcome has been the students and post docs he's helped teach to approach scientific inquiry using both experiment and inquiry. "The kind of research my group does was not usual when I started 25-30 years ago," said Miller. "The field has really developed over that time."



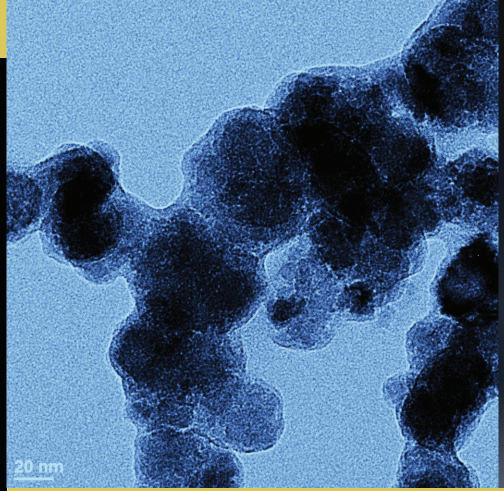
Gordon Miller

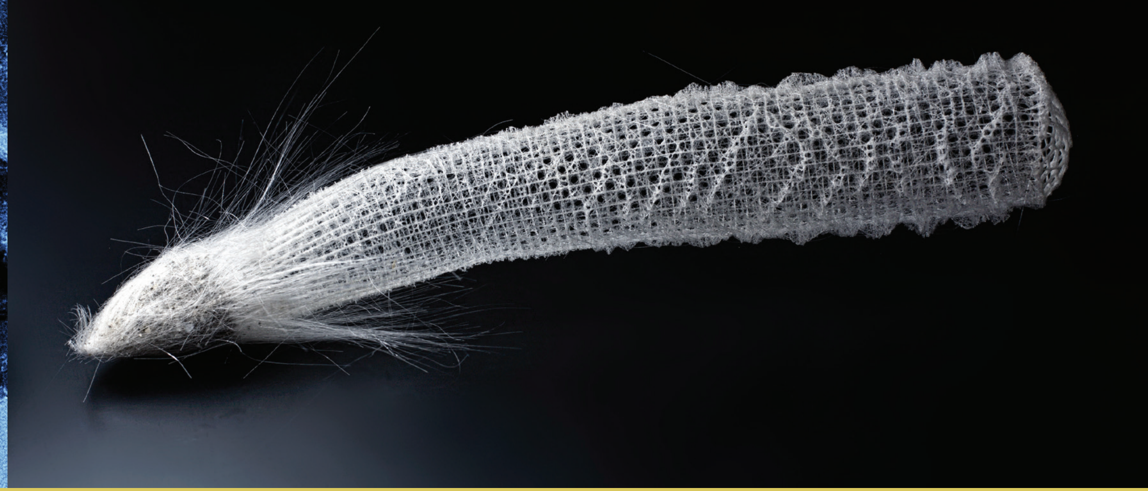
BY KERRY GIBSON



Bioinspired Materials:

BORROWING FROM NATURE'S PLAYBOOK





***Opposite and top right**: A glass sea sponge skeleton showing the complex nature of its structure which provides amazing strength. (Photos by Michael Monn, Kesari Lab, Brown University.*) **Top left**: A micrograph of magnetic nanocrystals grown by Surya Mallapragada's research group.*

**New functional insights into the internal architecture of the laminated anchor spicules of Euplectella aspergillum, PNAS, www.pnas.org/cgi/doi/10.1073/pnas.1415502112*

Nature provides myriad examples of unique materials and structures developed for specialized applications or adaptations. An interdisciplinary group of researchers at Ames Laboratory is trying to unlock the secrets that organisms use to build such complex structures so that power can be used to create materials not found in nature and not capable of being synthesized by conventional means.

"Nature has lots of examples of these hierarchical structures and they're usually organic-inorganic composite materials," said Surya Mallapragada, Ames Laboratory scientist and Iowa State University Carol Vohs Johnson Chair in Chemical and Biological Engineering. "A glass sea sponge skeleton is a perfect example of these structures that are templated by the organic phase. You have inorganic nanocrystals that form and it's a multiscale assembly process, which in most cases happens at mild temperatures and conditions, such as pH."

"So we look to nature for inspiration and as a source of bio-molecules to see how we can recreate some of those processes that create these wonderful materials with hierarchical assemblies or uniform structure," she said.

So far, Mallapragada's team has been able to replicate the creation of magnetite by studying magnetotactic bacteria. These bacteria form magnetic nanocrystals or chains of nanocrystals that they use to orient themselves with the Earth's magnetic field. Using self-assembling polymer templates and proteins from the bacteria, researchers were able to grow magnetite crystals.

"We've used this approach successfully to grow magnetite nanocrystals," Mallapragada said, "but we've gone beyond that, using these techniques to create cobalt ferrite and other magnetic nanocrystals that are not found in nature. That's a great example of templated synthesis."

The group has also worked with calcium phosphate to try to mimic the light-weight strength found in bones.

"In some case, we need to come up with synthetic analogs which can do the same job, but are more robust," Mallapragada said. "In many cases, the biomolecules aren't as robust. Proteins are fragile molecules so if we can do it with synthetic polymers, that gives us a lot more flexibility."

It's one thing to create nanocrystals. Getting those nanocrystals to then organize and form microstructures and then macro-scale structures is something altogether different.

"They're not at the level of complexity we see in nature —that's the Holy Grail," Mallapragada explained, "but that's the inspiration and we're trying to get there with synthetic approaches."

The latest goal for harnessing this natural building process is the creation of metamaterials, so-called left-handed materials, that have interesting optical properties that don't occur in nature.

"We're looking at using organic templates to assemble inorganic particles to get the desired properties," Mallapragada. "We have a very strong collaboration with Ames Laboratory physicists Costas Soukoulis and Thomas Koschny, and they've done some wonderful work with simulations and predictions of structures and developed some lithographic structures, but those are only 2D. So it's really a perfect case for using these bioinspired approaches to self-assemble these metamaterials into 3D structures."

Mallapragada again points to the glass sea sponge for the type of multiscale assembly that's required to build 3D metamaterials.

"The sea sponge has order on multiple scales—nanoscale, micron-scale, millimeter-scale. It's a multi-scale assembly—it looks like the Eiffel tower—and that's why it has a very great strength to weight ratio," she said. "So we need a similar hierarchy. Define the shapes at nanoscale, but then have an ordered arrangement of these nanoscale objects in 2D and then 3D to get the desired properties."

In addition to using self-assembling polymers, which provide long-range order, DNA has also been used because it allows for specificity in the placement of nanoparticles. To create metamaterials, the team is looking at using both to control the placement of gold nanoparticles in a specific pattern, build up layers and then apply a gold film coating to the entire structure to acquire the desired properties.

"It takes a very interdisciplinary approach," Mallapragada said. "We have molecular biologists (Marit Nilsen-Hamilton) for the DNA side, materials chemists (Mallapragada) for the polymer synthesis, Soukoulis and Koschny for the theoretical prediction of the structures and (physicist) Alex Travesset for modeling the kinds of structures can we get."

"We need good characterization so David Vaknin is looking at scattering methods and Tanya Prozorov has been doing transmission electron microscopy work," she continued. "Andy Hillier (chemical/biological engineer) has been involved in metallization, applying the continuous film of gold on those nano structured templates. So it's a multi-level, multi-step, multi-component synthetic process."

Mother Nature should be flattered!

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IN MEMORY

Karl A. Gschneidner, Jr.

"Mr. Rare Earth" - Friend, Mentor, Teacher

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