A Defensive "Coat"

Iron-based amorphous alloys can be applied as thermal spray coatings to protect materials exposed to harsh environments such as (counterclockwise from top left): oil- and gas-transmission pipelines, tunnel-boring machines (courtesy of the Department of Energy), and aircraft carrier decks (courtesy of the Department of Defense).

for Materials under Attack

Thermal spray coatings made with amorphous metal alloys enhance protection of ships and containers in corrosive environments.

FROM complex polymers and plastics to more common items such as window glass and candle wax, amorphous materials abound. These noncrystalline solids are not only prevalent in everyday life but also are an important research area at Lawrence Livermore. By varying the composition of different elements, Laboratory scientists have created novel materials such as amorphous carbon films to prevent wear and friction on computer hard disks (see *E&TR*, August/September 1994, pp. 4–5) and complex nanolaminates with unusual ductility (see *S&TR*, November/December 2008, pp. 10–16). In the last few years, Livermore researchers working on the High-Performance Corrosion-Resistant Materials (HPCRM) project have developed amorphous metal alloys, also known as metallic glasses, that can withstand corrosive environments.

Established in 2003, the HPCRM project was cosponsored by the Defense Advanced Research Projects Agency (DARPA) and the Department of Energy (DOE). The project's goal was to develop ultrahard, iron-based amorphous alloys for use as coatings to protect materials in harsh environments. For DARPA and the Department of Defense, such materials improve the corrosion resistance of ships and other military vehicles that spend most of their service life in saltwater and abrasive sand. For DOE, the coatings reduce the long-range expense of protecting spent nuclear fuel (SNF) containers while offering enhanced neutron absorption and criticality control.

Livermore chemical engineer and corrosion scientist Joe Farmer, who initiated and led the HPCRM project, is no stranger to high-performance, corrosion-resistant materials. In the early 1980s, he worked with a DOE team developing alloy C-22, a crystalline, nickel-based alloy designed to reinforce containers for long-term storage of nuclear waste. "Much of the Laboratory's early work with the nickel-based alloy was the first of its kind," says Farmer. "For example,

Iron-based amorphous alloys can be applied as thermal spray coatings to protect materials exposed to harsh environments, such as containers used for the long-term storage of spent nuclear fuel.

our thermochemical modeling showed that alloy C-22 had sufficient stability to survive the storage periods required for an underground repository, where containers would have to withstand temperatures near the boiling point in nearly saturated geothermal brines.” The HPCRM team applied many of the same techniques learned during the repository studies to the DARPA challenge, thus providing the nation with additional benefit from the original investment.

DARPA approached the Laboratory in 2003 for help with a new iron-based material the agency had developed. Although this material was harder, stronger, and more wear resistant than virtually any known steel, it lacked corrosion resistance. “DARPA asked us to manipulate the material’s composition to improve this essential property,” says Farmer. Shortly thereafter, DOE’s Office of Civilian and Radioactive Waste Management joined the effort as a cosponsor because the materials could be used for DOE mission work.

Together with colleagues from Livermore, other government laboratories, universities, and private industry, the HPCRM team developed and tested more than 40 compositions of iron-based amorphous alloys before determining the two most promising ones—SAM2X5 and SAM1651. “These materials are four to five times harder and more wear resistant than the best stainless steels and nickel-based alloys,” says Farmer. “Tests showed the corrosion resistance of these two alloys was far superior to that of stainless steel and comparable to or better than that of the nickel-based alloy C-22, the gold standard for the SNF container.”

SAM2X5 and SAM1651 are also less expensive, costing about $15 per kilogram ($7 per pound) compared with up to $80 per kilogram ($37 per pound) for alloy C-22. In addition, the high-boron alloys could absorb three to four times more thermal neutrons than the borated stainless steels commonly used for criticality control.

A Winning Combination

In a crystalline alloy, atoms form a three-dimensional lattice, but those in an amorphous solid are disordered and have no crystalline structure. Some materials are naturally amorphous, but others must be processed to maintain their glassy state. The cooling rate of this processing must be fast enough to prevent the atoms from forming a crystalline structure.

For amorphous metals and alloys, the minimum, or critical, cooling rate to prevent crystallization is extremely fast, as high as millions of degrees per second. Materials with lower critical cooling rates are thus much easier to process. As with corrosion resistance, the critical cooling rate can be controlled by carefully manipulating an alloy’s composition. “For example, adding yttrium to some formulations will increase melt viscosity and slow the crystallization kinetics, which reduces the critical cooling rate dramatically,” says Farmer.

The iron-based alloys developed by the HPCRM team combine several elements, each of which performs an important function. Iron gives the materials strength at an affordable price. Chromium, molybdenum, and tungsten are the necessary ingredients for enhanced corrosion resistance. Boron promotes glass formation and is an outstanding thermal neutron absorber, an important attribute for criticality control in various DOE applications. In fact, an unusually high level of boron is homogenously dispersed throughout SAM2X5 to make it an effective neutron absorber.

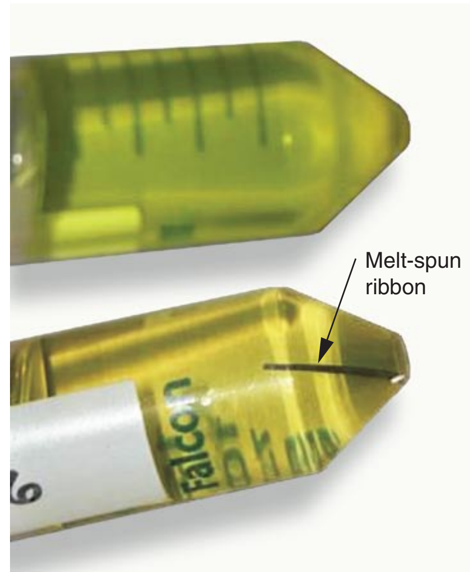
Eliminating the Competition

The 40-plus candidate materials underwent accelerated testing for periods of months to years to measure such characteristics as passive film stability, corrosion resistance, hardness, wear resistance, strength, fracture toughness, and absorption of thermal neutrons. Results for candidate materials were then compared with those of more conventional stainless steels, nickel-based alloys, and borated steels. “We conducted our tests using the quality assurance standards established for SNF repositories, which increased the confidence of external stakeholders in our work,” says Farmer. “Test results showed not only that we were meeting the performance requirements established by our sponsors, but also in many cases, we were doing much better.”

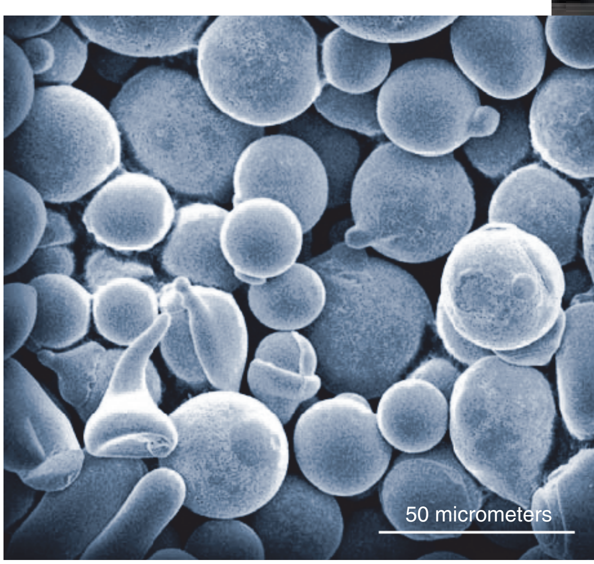
The testing series conducted by the Laboratory was similar to a competition with elimination rounds, where only the best performers progress to the next stage. In the first round, each material was made into a melt-spun ribbon. In this process, the liquid form of the amorphous material is dripped onto a supercooled copper wheel, which quenches the metal and transforms it into a solid ribbon a few millimeters wide and only 150 micrometers thick. “This method is the easiest way to make a metallic glass because it requires the least amount of material and prep work to produce a workable sample,” says Farmer.

Formulations that passed the first stage were used to create drop-cast ingots. These tube-shaped casts, which were larger and thicker than the ribbons, were fabricated at Oak Ridge National Laboratory. Tests with the ingots allowed the researchers to determine if thicker sections of the material could be cooled fast enough to maintain a glassy state. Winners of the ingot “competition” then moved on to the next round, where gas atomization transformed each formulation into a fine powder.

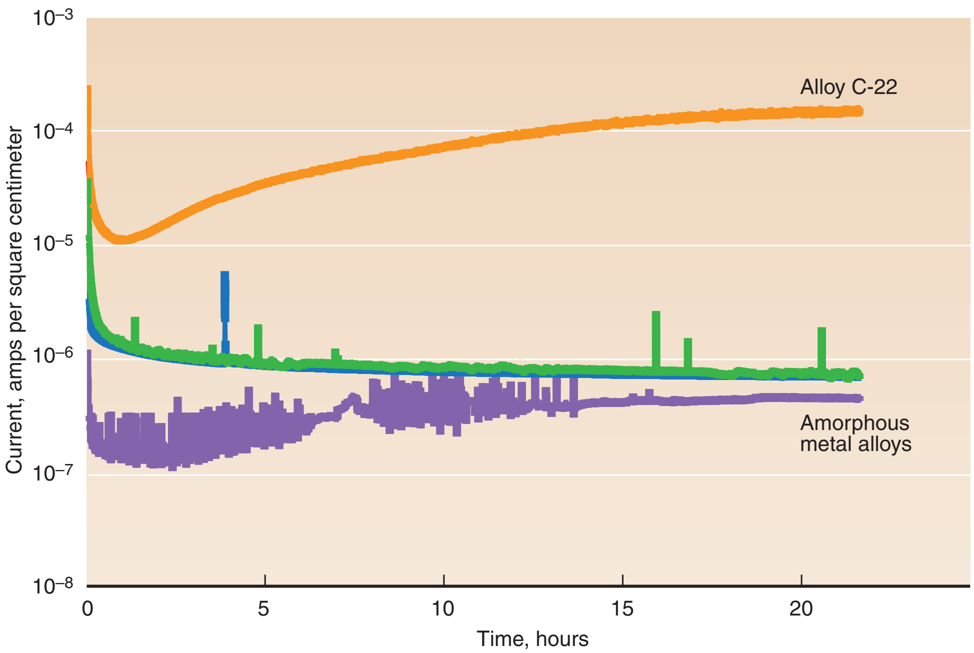
At this stage, the Livermore team used characterization tools such as scanning



In tests using melt-spun ribbons, alloy C-22 (top) easily dissolved when submerged in a boiling acid solution. A formulation of the new iron-based amorphous alloy (bottom) remained intact, even after long-term exposure.



In one test, the Livermore team used a high-velocity oxy-fuel process to melt amorphous powders (left) for use in a thermal spray coating. The coating was applied with a hypersonic torch at extremely high pressures to a half-scale prototype spent nuclear fuel container (above).



Polarization tests subjected the iron-based alloy SAM2X5 and the nickel-based alloy C-22 to a constant applied potential for prolonged periods. The increase in current for alloy C-22 (orange curve) indicated a breakdown in its passive film. SAM2X5 remained stable as a melt-spun ribbon (purple) and in course (blue) and fine (green) powder form.

electron microscopy, x-ray diffraction, and transmission electron microscopy to measure each powder's particle crystallinity, size distribution, and morphology. Powders that met the desired specifications were applied as thermal coatings to stainless-steel substrates using the high-velocity oxy-fuel process. Finished coatings ranged in thickness from 375 micrometers to 2 centimeters.

The melt-spun ribbons, drop-cast ingots, and coated substrates were subjected to a battery of tests to determine each material's physical, mechanical, and thermal properties. X-ray diffraction experiments provided data on any residual structures, such as crystalline precipitates, which might reduce a material's corrosion resistance and effectiveness in the targeted applications.

The team also used energy-dispersive x-ray spectroscopy to determine a material's exact elemental composition. Through differential thermal analysis and differential scanning calorimetry, the researchers measured material changes in response to temperature and identified glass transition and crystallization temperatures, melting points, and other important characteristics.

When the iron-based alloys are exposed to aqueous environments, such as hot geothermal brines, seawater, or salt fogs, passive oxide films form a protective layer on a material's surface, which prevents corrosion. In wet, salty environments, such as the ocean, this protective layer can break down in the presence of aggressive elements such as chloride. The rate of breakdown depends on film quality, exposure time, and temperature. Higher temperatures accelerate the rate of attack.

To determine corrosion rates, passive film stability, and the effects of thermal aging on corrosion resistance, the Livermore team immersed the sample ribbons, ingots, and coated substrates in concentrated brines near the boiling point and in natural seawater at elevated temperatures for periods ranging from days to months. "We applied standard electrochemical techniques to evaluate the corrosion mechanisms and rates as functions of alloy composition and environmental conditions," says Farmer. "Electrochemistry is an extremely sensitive tool that allows us to study material degradation processes in situ, without having to periodically remove the sample from the harsh test environments. More recently, we have extended such measurements to high-temperature molten salts and have made in situ observations of alloy degradation at temperatures up to 1,000°C."

Nanocrystallites can form in amorphous alloys at elevated temperatures, causing the alloys to lose their corrosion resistance. To determine when the materials start to crystallize, the team heat-treated, or annealed, melt-spun ribbons at various temperatures. Subsequent electrochemical testing established the upper limit of the operating temperature. The researchers also used indentation methods to measure material hardness as a function of temperature and impact testing to establish the damage tolerance of the coatings. They also determined how well the coatings resist abrasion and wear.

After initial tests identified SAM2X5 and SAM1651 as the most promising materials, coating processes based on the two formulations were increased to commercial-scale production. Coated prototypes underwent salt-fog testing at a facility used by the Marine Corps in Fredericksburg, Virginia. Salt-fog testing is a standard method used by the automotive industry to measure corrosion resistance. In these tests, researchers evaluated SAM2X5 and SAM1651 coatings on various steel substrates, including half-scale prototype SNF containers and criticality control assemblies. In addition, they performed seawall tests using sail cover plates from submarines, and they applied coatings to panels inside air ducts aboard amphibious ships for testing during deployment.

"We demonstrated that the new alloys could be produced in significant quantities under industrial conditions, and we tested their performance in realistic scenarios," says Farmer. "Under a wide range of harsh conditions, we found no significant corrosion—the materials appear to have passed the Admiral's test with flying colors."

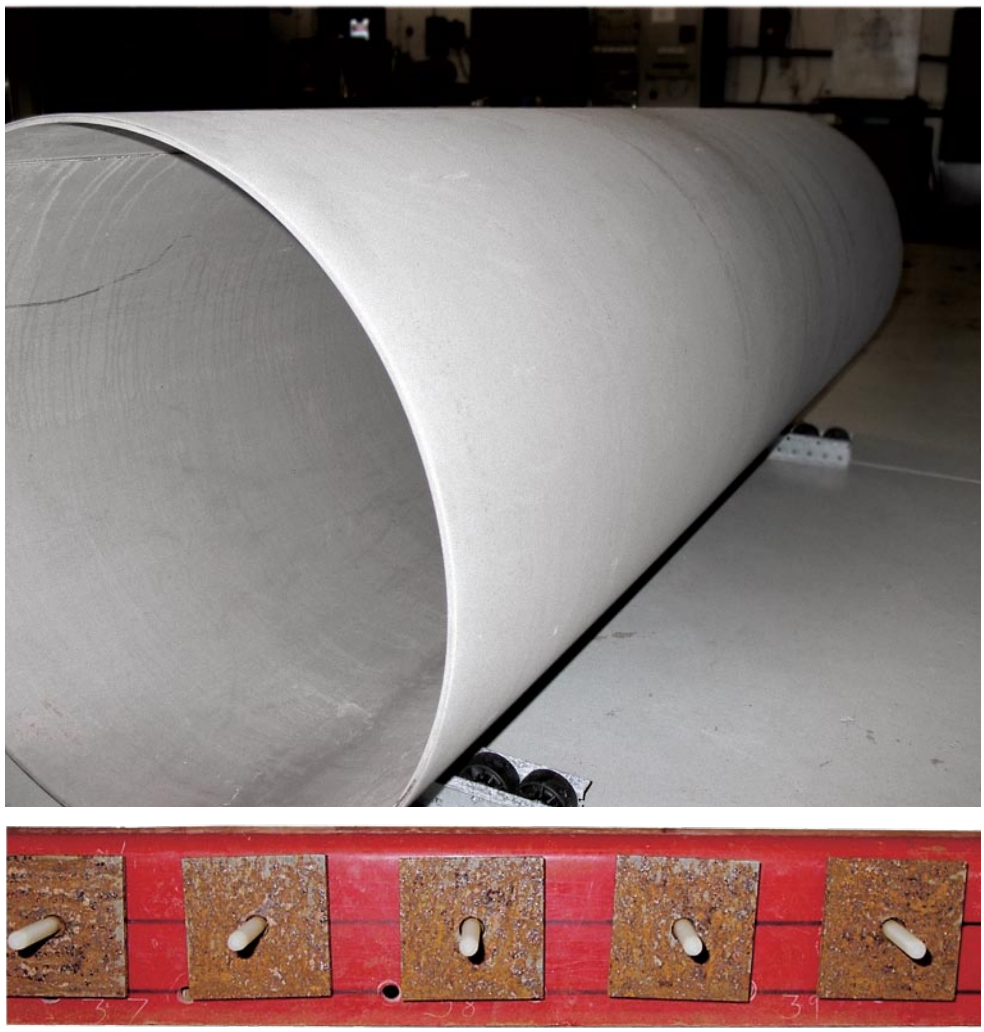
In the final round of experiments, the research team exposed several families of the SAM2X5 and SAM1651 alloy compositions to intense neutron irradiation in the 1.5-megawatt TRIGA reactor at McClellan Nuclear Radiation Center operated by the University of California at Davis. These tests demonstrated the phase stability of the materials at neutron irradiations corresponding to between 4,000 and 10,000 years inside an SNF container—the most realistic conditions that could be found for the applications of interest to DOE.

Through this extensive testing program, the Livermore researchers verified the corrosion resistance and mechanical properties of each formulation. They then worked with several industrial partners to prepare the powders to specifications for real-world applications. Carpenter Powder Products of Pittsburgh, Pennsylvania, optimized the SAM1651 gas atomization process, and Caterpillar in Peoria, Illinois, developed the SAM1651-based high-performance coatings. The NanoSteel Company in Idaho Falls, Idaho, produced the SAM2X5 powder, and Plasma Tech, Inc., in Torrance, California, developed those coatings.

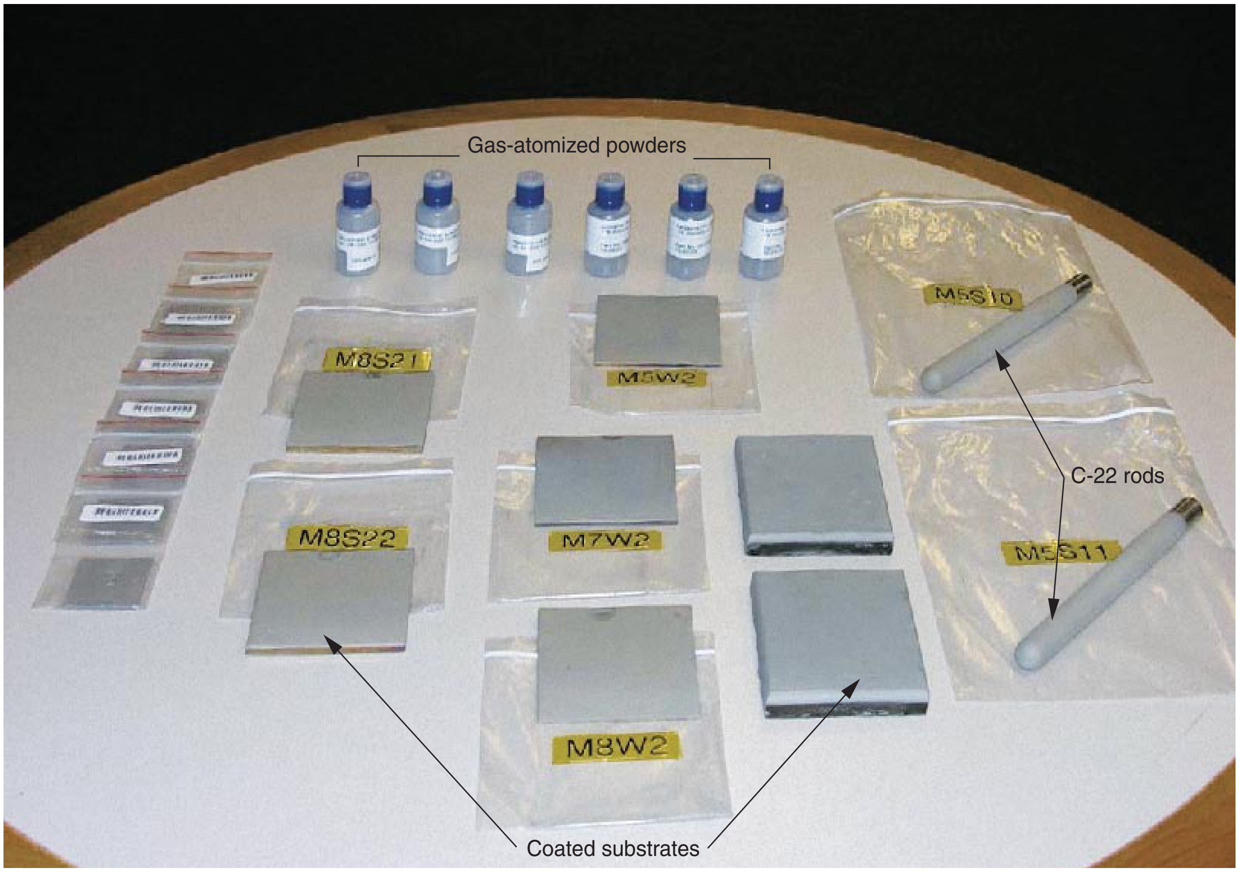
Meeting the Sponsors' Needs

In the future, the high neutron absorption capability of alloys could be exploited for advanced reactor systems with complex geometries, such as the Laboratory's Laser Inertial Fusion Energy engine. (See *S&TR*, April/May 2009, pp. 6–15.) Systems that can achieve a high burnup of fission fuels present particularly challenging problems because materials must withstand intense neutron bombardment over long periods. Much of the neutron damage affects the crystal lattice. One intriguing question is whether materials without lattices would be less prone to such damage. Perhaps future investigations will lead to even more resilient alloys for nuclear energy conversion applications.

The extreme hardness and abrasion resistance of iron-based amorphous alloys also makes them valuable for DOE's tunnel-boring operations. In collaboration with Oak Ridge, the Colorado School of Mines, and Herrenknecht USA, the HPCRM team conducted several tunnel-boring experiments after applying the amorphous materials to disc cutters. "In laboratory tests at Colorado, the coating showed no signs of spalling even after more than 100 cuts on granite," says Livermore scientist Frank Wong, who led



In salt-fog tests, a steel container coated with SAM2X5 (top) had remarkably better corrosion resistance than plates of uncoated carbon steel (bottom).



Test samples of the iron-based amorphous metals included powders, coated rods, and substrates.

the disc-cutter collaboration. "These tests marked the first time in 25 years of tunnel-boring research that a coating of any kind could survive rock impact."

Field experiments with a Herrenknecht tunnel-boring machine were equally impressive. The coatings survived under dynamic cutter loads that are typical of hard rock excavation. Compared with the measured wear on standard cutters, the amorphous alloy reduced wear on the discs by 15 to 20 percent for normal load-bearing operations and 10 to 28 percent for the severe loads of transition boring.

"Coatings were clearly visible on the crown of all the test cutters even after 14 meters of tunnel advance," says Wong, "and the coatings remained effective for up to 23 meters." In comparison, no other coating had previously survived more than 1 to 3 meters of tunnel advancement. By using the iron-based amorphous materials on essential components, DOE could potentially reduce the overall maintenance expense and extend the life of tunnel-boring equipment.

Because many applications of interest to DARPA involve ships, the Livermore team collaborated with colleagues at the Naval Research Laboratory. Prototype parts collected from various naval shipyards were refurbished and coated with the amorphous alloys for testing under realistic conditions. For example, submarine sail cover plates coated with the amorphous metal alloys were exposed for several months to the standard seawall testing at a naval facility in Key West, Florida, to determine how well the alloys performed in warm, wet, salty conditions with abundant sea life.

The Navy is particularly interested in improving antiskid surfaces on decks of littoral, or close-to-shore, combat ships. Exhaust from jet engines during takeoff can torch epoxy antiskid coatings on the upper decks. Lower decks are periodically flooded by seawater and exposed to heavy traffic from troops, tracked vehicles, and chains. "Our team learned to texture the coatings, just like the conventional epoxy coatings, to provide better traction in these mission-critical areas," says Farmer. Trials are still in progress, but testing thus far has been very successful.

The Department of Transportation is evaluating the metal alloys in coatings applied to rebar and other structural components to reinforce steel bridges. Annual maintenance and repair costs for bridges throughout the U.S. are estimated at billions of dollars. If new coatings could strengthen existing components and slow the progress of corrosion, bridge repairs could be safely scheduled less frequently, thus reducing the overall maintenance cost.

Branching Out

The HPCRM team is finding many potential applications for alloy-based coatings. For example, they could prevent wear on the bearings and shafts of wind turbines and improve the corrosion resistance of offshore drilling platforms and oil- and gas-transmission pipelines.

"Our work with these enhanced coatings is a good example of how the Laboratory can transition a mature program into other applicable areas," says Farmer. In addition, the HPCRM project shows how collaborations with industrial partners, other government agencies, and universities can speed development of advanced technologies. The new iron-based amorphous alloys are already proving to be a more effective means of protecting our national and military infrastructure and may soon offer more benefits for our technological future.

—Caryn Meissner

Key Words: amorphous metal alloy, corrosion resistance, criticality control, metallic glass, neutron absorption, thermal spray coating.

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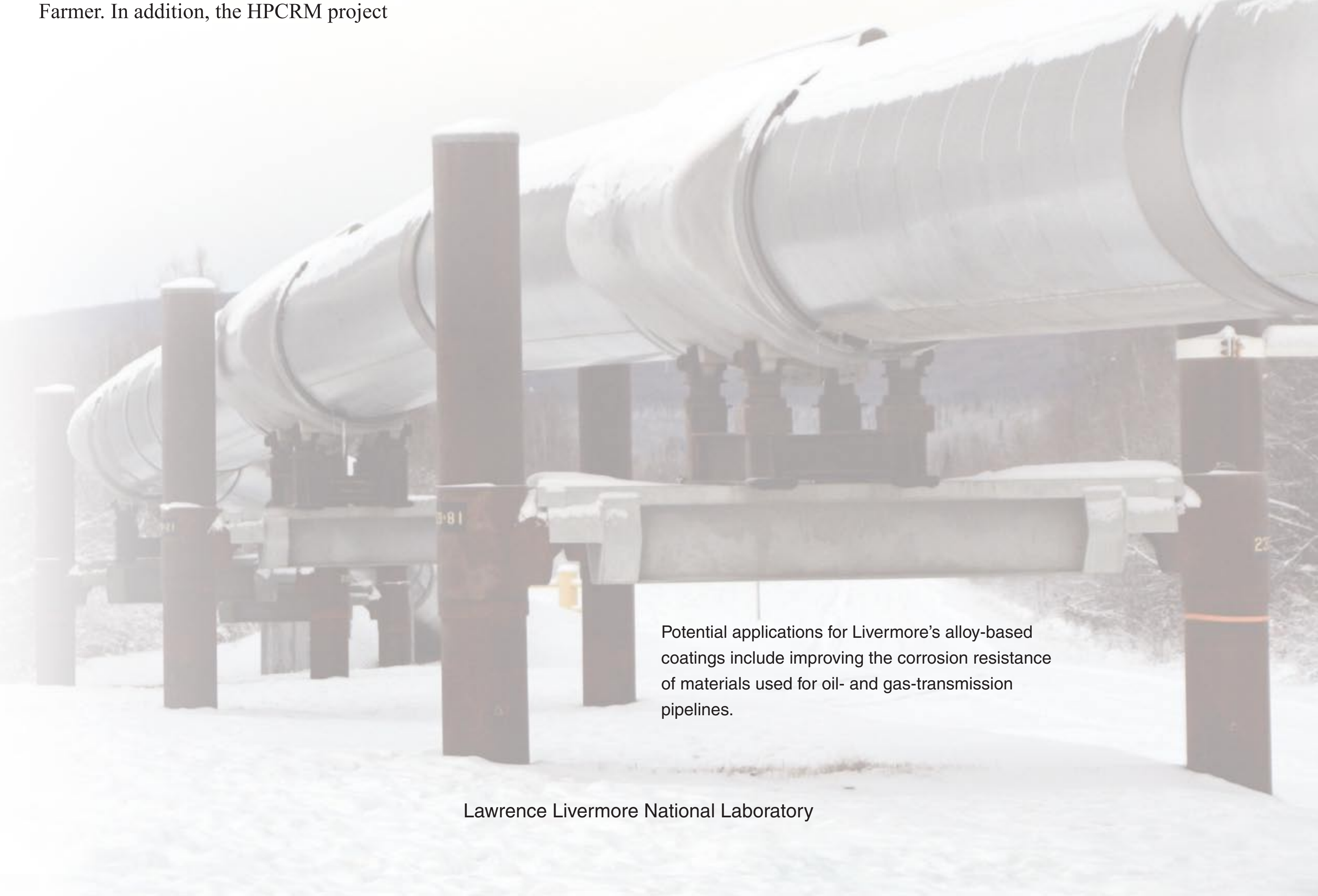

Potential applications for Livermore's alloy-based coatings include improving the corrosion resistance of materials used for oil- and gas-transmission pipelines.