

UP CLOSE: An ICAM researcher from the University of Cambridge analyses a sample alloy.

Hub of discovery

Tapping expertise from industry and academia, a collaborative research programme is uncovering valuable information about corrosion and developing advanced materials for oil and gas applications, including a new hydrogen-resistant steel alloy, as **Russell McCulley** reports.

he University of Manchester Institute of Science & Technology and the Victoria University of Manchester in the UK produced some of the 20th century's most notable achievements in atomic theory, chemical engineering, computer science and advanced materials. One aim of the 2004 merger of the two institutions was to ensure that the tradition carries on in the 21st.

The university was an appropriate choice, therefore, to serve as a hub for the BP

International Centre for Advanced Materials (BP-ICAM), a research partnership established in 2012 with a \$100 million, 10-year grant from the UK supermajor. The "spokes" in the partnership are the University of Cambridge, Imperial College London and, giving the partnership its international dimension, the University of Illinois at Urbana-Champaign in the US. Each institution has a particular strength to bring to the project - metallurgy and alloy design at Cambridge, corrosion and imaging expertise

in Manchester, membrane technology from Imperial, and groundbreaking research in self-repairing materials from Urbana-Champaign.

In addition to funding, BP provides "mentors", company scientists and engineers who share knowledge and guidance. The centre has 26 programmes under way involving around 90 researchers and more than 40 BP mentors.

Research focuses on four areas — structural materials and metallurgy, separation, protection, and surface interactions. The first is an effort to "extend the operating envelope of carbon steel", says Robert Sorrell, BP's vice president of public partnerships, Group Technology. Scientists are also looking at new applications for composites, novel alloys, and two-dimensional materials such as graphene, the atom-thick carbon material discovered in 2002 by University of Manchester physics professor Andre Geim.

Separation research will draw on Imperial's membrane expertise to develop more effective enhanced recovery

ADVANCED MATERIALS



VISUALISATION: Katie Moore, a BP-ICAM research fellow in Manchester, with the NanoSIMS 50L, one of the university's imaging tools.

technologies, while research in surface interactions could have the most impact on downstream processes and products such as engine lubricants. Protection mainly deals with coatings research, where a number of studies are under way.

The initiative was launched around the same time as BP's Project 20K, which is developing processes and equipment for the company's high pressure, high temperature deepwater oil and gas prospects. But Project 20K is only one business area that stands to benefit from BP-ICAM research, Sorrell says.

"When we looked across all of our businesses, we realised that there are substantial materials challenges, from upstream to refining," he says. To address such a diverse range of challenges, the company determined early on that it needed a more collaborative model than the traditional arrangement of working with a single research institution on a limited scope.

"This gives us the opportunity to leverage a staff of 200plus scientists at BP into the



COOL COATING: A sample of self-healing material is removed from cold storage at The University of Illinois at Urbana-Champaign.

academic community across the four partners in the BP-ICAM," he explains, with Manchester serving as a sort of centre of gravity for the wide-ranging effort.

Imaging power

Among the many benefits the Manchester campus brings to the programme is an array of state-of-the-art imaging techniques. Access to the technology has allowed BP-ICAM researchers to study carbon steel and corrosion at the atomic level.

Philip Withers is a professor of materials science at the University of Manchester and director of BP-ICAM. He joined the university in 1998 and set up a programme to investigate residual stress and damage characterisation, originally focused on materials used in the nuclear and aerospace sectors. Some of the same materials are being adapted for the oil and gas industry as exploration moves into ultra-deepwater and highpressure, high-temperature reservoirs.

Corrosion, Withers says, has a toll on the global economy of some \$2 trillion per year. A significant portion of BP-ICAM research is geared to understanding corrosion at the "nano" level.

"If we can understand the nature of corrosion, and we can understand the nature of how to protect against corrosion, we can offer important benefits in terms of the longevity of parts. And these are parts that are very difficult to replace."

To that end, Manchester has an arsenal of imaging tools to deploy, including the NanoSIMS 50L, a machine that uses a beam of high-energy ions to "disrupt" a very thin layer of a metal sample. The process generates secondary ions that can be extracted and separated according to mass. The information is used to produce a chemical map of the sample, which researchers then use to analyse the movement of trace elements, isotopes

>>

ADVANCED MATERIALS

Photo: BP



SMART MATERIAL: A researcher prepares a liquid containing fluid-releasing microcapsules for testing.



"This steel was designed with manufacturability in mind. There was no point in having a fantastic steel that we can't use."

> Philip Withers, BP-ICAM

and light elements, such as hydrogen.

Hydrogen is of particular interest because it can significantly weaken steel over time, a process known as hydrogen embrittlement. SIMS (secondary ion mass spectrometry) allows scientists to observe the location of the hydrogen and identify locations to which it segregates.

The University of Manchester is also home to a plasma focus

ion dual beam microscope one of only two in existence, Withers says — and an electron microscope that allows scientists to examine metal and corrosion at the nanometer level. "It lets us see on both sides of the grain boundary," he says, referring to the region that separates two adjacent crystallites, or grains, in a polycrystalline material such as carbon steel. The grains are identical in structure and chemical composition but



COLLABORATION: Sheetal Handa and Robert Sorrell discuss research under way at BP-ICAM headquarters in Manchester.

deviate from the crystal lattice pattern, creating defects at the boundary that are susceptible to hydrogen ingress and corrosion.

"Hydrogen embrittlement is a very significant issue for the industry," Sorrell says. "But that's not the only area of corrosion we are working on." The Manchester campus includes the BP Research Laboratory in Corrosion & Materials, where researchers are also investigating corrosion from carbon dioxide, hydrogen sulfide and fatigue, among other sources.

The lab holds a number of tools that allow scientists to perform forensic work in corrosion and stress testing, using electrochemical measurements gathered in stress-free or applied stress laboratory tests. Researchers have been able to compare the ductility of metal samples exposed to an inert environment and in an environment rich in hydrogen,

ADVANCED MATERIALS



TEAMWORK: Michael Odarczenko (centre) and fellow researchers discuss an experiment on a plate coated with a self-healing material.

» which is known to reduce ductility.

The laboratory equipment also allows close study of small pits in steel created by corrosion. Tests identify what Withers calls the "critical default size", where metal develops cracks under pressure - similar to the point at which an inflating balloon with a tiny pinhole will burst. The knowledge can help inspectors determine how urgent it is to repair or replace an affected piece of equipment, predict how it will behave over time if left untreated, and how to devise appropriate inspection schedules based on the modelling.

The research, says Sorrell, "will inform existing models, or let us create new models that will enable us to improve how we do things, so that we better understand stresses and strains on metal and the failure mechanisms. We'll be able to engineer things better, going forward, and have greater confidence in the materials that we have."



"We'll be able to engineer things better, going forward, and have greater confidence in the materials that we have."

Material success

The lab also has the capacity

it passes through metal. The

techniques are being used to

developed by Harshad Bhadeshia

in Cambridge through BP-ICAM.

study the new alloy, HT 10,

The alloy has been shown to

to track hydrogen dispersal as

Robert Sorrell, BP

"trap" hydrogen and slow its movement within steel, making it much more resistant to hydrogen embrittlement than F 22, the industry standard steel, according to BP-ICAM.

"We are testing strength, corrosion resistance, hydrogen resistance and weldability," says



ON ALERT: Michael Odarczenko, a BP-ICAM PhD student at the University of Illinois at Champaign-Urbana, holds a sample of an experimental coating that indicates damage by changing colour.

Steve Ooi, formerly a research fellow at BP-ICAM, who now serves as deputy director of SKF University Technology Centre for Steels at the University of Cambridge. A patent application has been filed for HT 10, the first of many that officials expect the BP-ICAM programme to produce.



CARBON CAPTURE: Philip Withers explains how researchers can use imaging tools to create a 3D image of an area of damage in a steel sample.

Tests have shown that hydrogen moves through the alloy at one-tenth the rate that it penetrates traditional carbon steel, Ooi says.

The Cambridge team has created a 100-kilogram billet of the material. "The first was only 60 grams," Ooi says. Researchers used computer modelling to refine the properties of the steel alloy in order to scale up the sample. "We characterised it by measuring the hardness, checked the microstructure properties, checked whether we see the key nanoprecipitate that we need in this steel." Verification gave them the green light to cast the 100-kilogram billet. "Now we are talking about producing a oneton (billet) so we can do further evaluation on this material, such as weldability studies," he says.

The results of weldability studies will be critical to HT 10's future use. As Withers explains: "It's often very easy to make small precipitates in steel in very small quantities." Precipitates are formed through a rapid cooling process that produces uniformly dispersed particles in the metal's grain structure, thereby strengthening it. "When you have a small amount of steel, you can cool it very quickly and create very small precipitates. If you cool it less quickly, those precipitates often grow and you don't have that effect. So one of our specifications was, can we make the steel in a way that we can cool it and make thick sections economically," he says.

"That's one of the advantages of tying an industrial perspective with an academic perspective. This steel was designed with manufacturability in mind. There was no point in having a fantastic steel that we can't use."

Second skin

Rapid progress is also being made in the field of selfprotecting and self-healing materials, a specialty of the US division of BP-ICAM. The goal is to develop new chemistries and strategies for autonomous



detection, protection and healing in materials and coatings.

The key ingredient in work done to date is a microcapsule with a liquid core embedded in a coating or other protective material. The microcapsules' contents are released when

"We're seeing a new set of environments that we haven't seen before, and trying to understand how the current materials may behave under those conditions."

Sheetal Handa, BP-ICAM

the coating is damaged scratched, dented or otherwise compromised — and will vary depending on the application. Researchers have created selfhealing coatings, for example, that release a fast-drying, environmentally friendly



»

UNDER THE MICROSCOPE: Christopher Matthews and fellow BP-ICAM researchers at the University of Illinois at Champaign-Urbana are developing self-healing coatings and other "smart" materials.



QUICK RESPONSE: Christopher Matthews indicates the reactive properties of a material used in

self-healing coatings.

²hoto: Russell McCulley

anti-corrosive agent when damaged. The material can "heal" itself before the onset of corrosion.

Scientists at the University of Illinois at Champaign-Urbana have created self-healing coatings in the lab up to 200 microns thick and are preparing to test anticorrosion capsules in real-world environments.

"We have capsules that are ruptured by mechanical damage," says Christopher Matthews, a graduate research assistant at the university. "But there are other stimuli, which is another thing we're working on. A coating can be ruptured by corrosion damage — let's say there's a coating that wasn't painted perfectly, there's something that got coated over, or a water droplet under the coating. That can start corroding, and then you can get flaking.

"However, if you have capsules that are triggered by that corrosion, it could release an anticorrosion agent from the capsule and slow the corrosion before it becomes a catastrophic failure. So it's not just what we can encapsulate, it's also what can trigger these capsules to release their self-protection."

Matthews and his colleagues are also working on "smart" coatings that indicate where the coating has been compromised. The microcapsules may release a substance that changes colour when exposed, or a fluorescent element that would be easy to detect with artificial light, aiding inspection in dark areas.

"The importance of this is to detect and locate damage prior to failure, or before it becomes more expensive to repair," he says. At the moment, the capsules have specific functions. "But we envision in the future capsules that have multiple functions — maybe they will indicate damage, heal the damage, then indicate again when the healing is successful."

Testing the limits

Extreme operating environments — ultradeepwater, ultra-high pressure, remoteness — are driving the oil and gas industry to develop materials that can withstand such conditions, that maintain safety, and can be manufactured at a cost that makes them practical for use. Greater understanding of the properties of steel and its enemy, corrosion, can also help engineers design better infrastructure and accurately predict how it will perform over time.

"At 20,000 pounds per square inch pressure, you're beginning to reach the limits of existing steels," says Sorrell. "So the things that are being done here — trying to really understand the materials structure, assessing strength, strain capabilities, plastic deformation, all the different modes of failure — by modelling this we can get an idea of the limits, and where the failure mechanisms are as you move into these water depths.

"You can go to thicker and thicker steel, but obviously, there you have problems with buoyancy and issues about joining progressively thicker materials."

While the industry has a lot of expertise in such matters, scientists often have little research to help them fully understand what is happening to materials at the molecular level. It is important not just to develop new materials, but to better understand the underlying properties of familiar materials already in use, says Sheetal Handa, research programme director for BP-ICAM.

"We're seeing a new set of environments that we haven't seen before, and trying to understand how the current materials may behave under those conditions," he explains. "Welding structures to withstand high pressure and high temperature, how materials will behave under conditions over time - trying to understand that is the aim of a BP-ICAM project supported by Project 20K. If we can use a material we have now, that's great. If we understand it really well, and know it can withstand those environments, that's great. And if we find that we need some different types of materials, this research gives us tremendous insight."

"It's not all about 20K," adds Sorrell. "What we're doing here



is much broader than that. It's about dealing with the wide range of operating conditions we get. We drill in a lot of different environments. Sand ingress, asphaltenes effectively blocking production lines, how that occurs, why they stick to the walls — these all sound like obvious questions, but actually they're not that well understood.

"So it's back to the fundamentals, because if we

"We are testing strength, corrosion resistance, hydrogen resistance and weldability." Steve Ooi, University of Cambridge

understand these, we can then begin to understand how we can engineer things to manage these issues in the most effective ways. Because if you don't understand, all you can do is mitigate the circumstances you face, rather than make some small changes that could potentially make a difference.

"We don't know what those changes might be yet — we're at the very start of this. But already, some of the insights that are coming in are really interesting."

While BP will seek intellectual property protection for some of the materials and methods developed through the programme, Sorrell insists that BP-ICAM "was not set up to be exclusive". As of mid-2015, the research had produced more than 60 published papers, with the rate of publication expected to increase significantly in the second half of the year.

"This is about collaboration," Sorrell says. "The collaboration we have between BP and the four partners is critical to the success of this programme."

Three years into the project, some of the knowledge gleaned through the collaboration has already enhanced BP's engineering capacity, Sorrell says. Commercial deployment of materials such as the corrosionresistant alloy will take time.

"But we're at the beginning of a journey here," he says. "And we're very excited about the pace at which things are coming through."

