# **Secondary Science Review**

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## Materials for the future The science of stuff

Stepe Science Enhancement Programme



The cover image shows Katherine Inzani, a Materials Science postgraduate student at the Norwegian University of Science and Technology (Photo: Geir Mogen/NTNU)

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### Stuff for the future

This issue of CATALYST has a materials science and engineering theme. It is impossible to estimate the number of different materials we make use of every day. Some are traditional, such as wood and pottery. However, we are increasingly reliant on new materials, designed by materials scientists and put to use by materials technologists and engineers.

While materials scientists may be interested in the materials they work on in their own right, they usually have an eye on the uses which these materials will find in the future. There is constant demand for new materials which make more efficient use of raw materials and which can be produced to demanding specifications. The first five articles in this issue give just a hint of the great variety of materials which are currently under development.

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## Wearing electronics

The demand to make technology increasingly smaller and more integrated into our lives has driven the development of 'wearable technology', which refers to electronic devices that can be worn on the body, or integrated into clothing or accessories.

Wearable technology is a broad term which can include smart watches and fitness trackers to medical sensors and navigational aids, such as shoes with built-in GPS. Most of the existing products are for protection and the military clothing sector but it is thought that sport and fitness, and health and medical applications will see the fastest development in the next few years.

Electronic devices typically operate with a rigid circuit board, which can be seen when these devices are taken apart. But now, alternative, flexible materials for circuits, such as textiles, are being developed. Within this research-sector there is a push towards making this technology truly wearable by integration of electronics into the clothing you wear every day. These may be described as smart fabrics or electronic textiles. One way to achieve wearable electronics is by having



Stretchable nylon fabric with a conductive coating

#### Key words textiles electronics conduction health

Nanoparticles are between 1 and 100 nanometres in diameter. A nanometre is 10<sup>-9</sup> m, one billionth of a metre. electrically conductive fabric, which researchers at the National Physical Laboratory (NPL) and Coventry University are currently investigating.

There are different ways of making fabrics conductive, for example, by sewing in conductive silver threads or by printing a conductive ink. The trick is to produce something which is reliable and robust enough to handle our daily life stresses, such as bending, stretching, washing, sweating and weather, whilst retaining the typical handle and drape of the fabric. Conductive threads can fray and ink printed onto a flexible substrate can crack when flexed.

Another approach would be to use a coating of a conductive polymer, such as polyaniline or polypyrrole. These polymers have a delocalised electron structure (like graphite) which allows them to conduct even though they are not metals. However, the conductivity and processability of these organic polymers isn't typically as good as that of metals.



A circuit board design printed onto fabric

#### Making a fabric conduct

A process developed at the UK's National Physical Laboratory (NPL), and being optimised with Coventry University, involves making a fabric conductive once it's already in its final form, in other words already a garment. This is a multi-step, additive process involving a range of interesting chemistry. It has been done successfully with both natural fabrics (e.g. cotton) and synthetic ones (e.g. polyester).

The process starts by depositing a catalytic seeding layer onto a fabric (a catalyst is something that initiates or speeds up a reaction). This seed layer is typically an unreactive metal such as silver, used as tiny nanoparticles.

The nanoparticles can be generated in a solution and applied to a fabric pre-formed, or they can be formed directly on the surface of the fabric. To make silver nanoparticles, a silver salt is reduced to silver on the fabric in the reaction:

$$Ag^+ + e^- \rightarrow Ag$$

The chemical which reacts with the silver ions to turn them to silver atoms is called a reducing agent.

The size of the nanoparticles is influenced by the choice of reducing agent. Choosing a relatively strong reducing agent, like sodium borohydride (NaBH<sub>4</sub>), results in smaller particles which are more effective as catalysts. The fibres of the fabric are therefore coated with silver nanoparticles, as seen in the electron microscope images.



Electron microscope images of cotton fibres coated with silver nanoparticles visible in the close up

Although the catalyst itself is a metal, it is not of sufficient thickness on the surface to make the surface very conductive. The electrical resistance at this point in the process is, therefore, still very high. To improve the fabric's conductivity requires more metal to be deposited and this is done using a process from the printed circuit board industry. The silver nanoparticles act as the catalyst for this step.



The electroless copper plating bath

The technique used is called electroless metal plating and involves a series of electrochemical and chemical reactions taking place in an aqueous solution. The end result is a metal being deposited ('plated') on top of the silver catalyst layer. The fabric is immersed in the electroless copper plating bath, and the plating occurs where the silver nanoparticles are.

The plating bath contains formaldehyde, which reduces a copper salt to metallic Cu in the reaction:

$$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$$

It also contains sodium hydroxide, to increase the pH of the plating bath to >11, since copper deposition is more favourable at higher pH. The metal will only plate where there is a silver nanoparticle catalyst on the surface, allowing researchers to be selective with which areas are made conductive. Whole areas of fabric can be made conductive, or tracks can be produced using a technique such as inkjet printing to deposit the catalyst.



A conductive track connected to a battery and LED

Once the surface has been coated with this first layer of copper, the plating continues to build up the metal layer as a self-catalytic process on the copper surface. The resulting fabric is now coated with enough metal to be conductive.

Finally, the fabric surface needs to be coated to prevent the copper from oxidising in air and turning back to copper ions. This can be achieved with a silver immersion treatment, where silver atoms form a thin layer on the fabric by replacing some of the copper. An organic polymer finish is an alternative. At present all preparation is done in the lab but process scale-up is being explored which will allow this technology to be used in commercial products.

#### Smart clothing

This technique could make integrating electronics into all types of clothing simple and practical by enabling lightweight circuits to be printed directly onto complete garments. There is a growing market for wearable 'smart' electronic devices and the NPL technology could find applications across a range of sectors, such as remote healthcare development. Integrating electronics and sensors that can measure and monitor physiological properties, such as your heart rate or a wound swelling, could allow medical professionals to detect problems early and reduce the number of hospital admissions. Ideally the technology would be integrated so discreetly that its wearer is not conscious of it and it is not visible to other people. An interesting property of the fabrics produced using this method, and with others available on the market, is that the conductivity varies with stretch. This opens up possibilities of using the fabric as a stretch sensor.

As with any new technology, the properties of these fabrics need to be measured in various situations to understand their reliability, and how long they're likely to last. Such tests include measuring how the electrical conductivity of the fabric changes with stretch, which is measured using a stretch rig. A washing machine is used in the lab to see how the conductive coating withstands a laundry cycle with detergent. So far cotton has performed particularly well, with the conductivity of the fabric remaining more or less the same after 100 wash cycles.

There are other innovative applications of conductive fabrics, and one company called Footfalls and Heartbeats has developed a knitted technology where the fabric itself is the sensor. It is used in compression bandages for venous leg ulcers to monitor the applied compression by measuring a change in electrical resistance as the fabric stretches. This can let the medical practitioner know if the bandage has been applied appropriately. They currently knit in conductive silver yarns that act as the connecting wires, but they are looking into printing circuits to make the product more robust.

Interest in conductive fabrics is increasing and they will play an important role in the future of wearable technology. Although there is still research and optimisation to be done on the process, this is an exciting technology which could benefit the healthcare sector in years to come through the incorporation of sensors into garments.

Kathryn Wills works for NPL and Coventry University as a Knowledge Transfer Partnership associate, Roya Ashayer-Soltani works as a Higher Research Scientist at NPL and Chris Hunt is a Principal Research Scientist at NPL. Metal plating has been used over the years to produce a number of items such as silver plated cutlery.

#### John Stacey

Key words biomimetics evolution natural selection technology

## **Biomimicry** Materials that imitate life

Biomimicry means imitating life. Why should we do this? All living things have developed methods of overcoming problems and they have had many generations to do so. Humans, by comparison, have only been solving problems for a few generations.

The science of biomimetics is defined as 'the study and development of synthetic systems that mimic the formation, structure or function of biologically produced substances, materials and processes'. An everyday example is the development of the hook and loop tape called Velcro. In 1941, coming back from a hunting trip in the Alps, the engineer George de Mestral noticed that the fruits of the cockle burr were very difficult to remove from his clothing and his dog's coat. Inspired by nature, he developed materials of hooks and loops that worked the same way as the plant fruits. The plant evolved the hooks as a means of dispersing fruits containing seeds over a wide area. They are especially good at attaching to mammalian fur.



The hooks of burdock inspired the invention of Velcro

#### **Kingfisher train**

The first Japanese bullet trains only travelled at 210 km/h because they made too much noise and created a sonic boom when leaving tunnels that could be heard by local residents 400 m away. One of the engineers, Eiji Nakatsu, happened to be a keen birdwatcher and wondered how a kingfisher could dive so fast from air into water with ease. The shape of the kingfisher beak was investigated and found to be optimum: a rotational parabolic body or a squashed diamond shape.

The shape was used to design the nose of the next generation of bullet trains. Along with other modifications the result was less noise, more efficient power consumption and speeds up to 300 km/h.



The beak of the kingfisher gave engineers insight into high-speed train design.

#### Non-reflective eyes

The compound eye of an insect is built of thousands of identical structural units called ommatidia. These are packed together to form a large round compound eye. Every ommatidium has an outer surface made of a substance called chitin. In some species of moth the outer surface is not smooth when viewed under an electron microscope but rather composed of very large numbers of small bumps. These bumps, called nano-nipples, reduce reflection to allow as much light as possible to enter the insect's compound eye. This adaption allows moths to fly in low light conditions.



A scanning electron micrograph of nano-nipples on the surface of a moth's eye

How does this work? When light passes from one transparent medium to another, a fraction of it is reflected. This is because of the change in refractive index n – that's why we see reflections in shop windows (for glass n = 1.4, for air n = 1.00). The refractive index of chitin is n = 1.57, so an even greater fraction of light is reflected.

The nano-nipple surface means that the refractive index changes gradually from 1.00 to 1.57 and so very little light is reflected.



Reflection and refraction: **a** The eye of the Monarch butterfly has a smooth surface so 5% of light is reflected. **b** The Mourning Cloak butterfly has nano-nipples on its eye surface so reflection is greatly reduced.

So how did the surface of insect eyes develop nano-nipples? Within a population of any species there will be natural variations of structure. This means that the surface of some eyes will not be as smooth as others. If there is a selection pressure that favours eyes that reflect a little less light (due to the rough surface) then these individuals have a better chance for passing on the trait for the rough surface. If this selection pressure is maintained for generations then the eye surface becomes rough as chitin is laid down with nano-nipples. This is the process of natural selection.

Monarch butterflies have a smooth eye surface. As they fly during the day there is no advantage to preventing light reflection. As energy and more organic molecules would be needed to make the nano-nipples these structures do not develop unless there is a selection pressure.

Anti-reflection surfaces have been developed to improve readability in sunlight. They reflect as little as 1% of incident light. Solar panels can be made with a moth eye surface coating to capture more light energy. So the evolution of a biological structure can be mimicked to improve the efficiency of sustainable energy supplies.

#### Slithering snakes

How do snakes slither so easily? There is no obvious difference in the structure of snake scales on their upper and lower surfaces. However the scales of the lower surface produce less friction. This allows the snake to move across rough surfaces without damaging its skin.



A California kingsnake

Under an electron microscope the scales of the California kingsnake have a coating of lipid molecules. These are arranged in rows and columns only on the lower scales. The snake may be moving on the tips of these molecules and this layer may have self healing properties. More research is being done to find out whether the lipids just keep the scales from drying out or they are the source of the reduction of friction. Low friction lubricants modelled on this lipid layer may reduce wear on moving parts in all types of mechanical devices.

#### Biology branching out

There are many other examples of large and smallscale biological solutions to problems that have already been identified. Organisms have developed solutions over millions of years by the mechanism of natural selection, design by evolution. The study of biomimetics is a new branch of biology that has the promise of providing better solutions to existing problems.

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**Key words** polymers durability self-repair Plastics and polymers are long-lasting but plastic can break. This article explores research to make polymers which will fix themselves. This could be useful in a wide range of applications.

Polymers are molecules containing thousands or even millions of atoms linked together into chains. They are fundamental to our lives in two quite different ways. Life itself is based entirely on the self-programmed synthesis of polymers such as the nucleic acids DNA and RNA. Nucleic acids, in turn, direct the synthesis of proteins - high molecular weight polymers that are not only biological catalysts (enzymes) but also form structures such as hair, skin, cartilage and indeed most other types of living tissue. When tissues are damaged, information stored as a sequence of different chemical sub-units in DNA is called upon to program the synthesis of new protein molecules, and these gradually replace the damaged material. Many parts of the body can thus effectively repair themselves.

The development of synthetic polymer chemistry over the past hundred years has led to the discovery of new materials that are also fundamental to modern life and society, but now in terms of their value in *technology*. Medical devices ranging from dental fillings to prosthetic limbs to replacement heart valves are all based on synthetic polymers, as are many structural components of computers, televisions, smartphones and cars. Even aircraft (apart from the engines) are no longer built from metals, but instead are produced mainly from carbon-fibre reinforced polymers, which are extremely strong and very much lighter than metals – lighter even than the lightest aluminium alloy.



Aircraft are now built mainly from polymers reinforced with carbon fibre. Such composite materials were tested extensively on this research aircraft (the British Aerospace Experimental Aircraft Programme) and are now employed in nearly all modern airliners and military planes.

However, continuous exposure of synthetic polymers to environmental stresses (abrasion, impact, pressure, chemical attack and high temperatures) can lead to progressive loss of physical strength and, eventually, to complete mechanical failure of the structure. If polymers could be designed to repair themselves when they get damaged, then such materials would show greatly improved durabilities and lifetimes in use. The development of such self-repairing polymers is currently a topic of intense investigation by scientists around the world.

#### Ready to repair

The problem has been approached from many different directions. Ideally, the damage itself would trigger a repair response, and such materials have indeed been developed. These generally comprise polymers containing embedded microcapsules of liquid monomer. When the polymer is damaged, the capsules are broken and the monomer is released. It then flows through the damaged region, making contact with a catalyst that causes it to polymerise and thus repair the fracture. However, this is obviously a one-shot solution to the problem, because the monomer capsules at the site of the repair are used up. A second damage-incident at the same site would not result in any repair.

Without going to the extremes of molecular complexity found in genetically-programmed biological systems (which are still well beyond the scope of synthetic polymer chemistry), it would clearly be preferable for a repair mechanism to be somehow built into the structure of the polymer itself *at the molecular level*. That would – in principle – allow the polymer to self-repair repeatedly, at the same site, no matter how many times the damage was inflicted. Remarkably, over the past ten years or so, polymer chemists have been able to design and synthesise new polymer systems where this idea really does work in practice.

The basic principle behind all these systems is to use relatively short-chain polymers, having perhaps only tens of monomer repeat units rather than the hundreds or thousands needed to provide high mechanical strength in conventional synthetic polymers. Short-chain polymers normally have only poor mechanical properties, because the chains cannot entangle to the same degree as higher molecular weight chains. However, if the end-groups of a short-chain polymer are designed to associate together in some sort of reversible way, then good mechanical properties can still be achieved. Moreover, mechanical failure of this type of material will generally occur by dissociation of the chain-ends, rather than by breakage of the covalent bonds in the polymer chains themselves. The short-chain polymer molecules (not being highly entangled) can then flow easily under a stimulus such as heat or light to repair the damage. The chain ends can later re-associate to generate the original polymer structure and so restore the properties of the material.

#### Four hydrogen bonds

A good example of a reversible interaction is the hydrogen bond. This results from the attraction between an atom that is a tiny bit negative and a hydrogen atom that is a tiny bit positive. A hydrogen atom has only a single electron, and when hydrogen is bonded to certain elements such as oxygen or nitrogen this electron is pulled away, enabling its partly-exposed and positively charged nucleus (a proton) to attract a negatively charged atom in a neighbouring molecule.

A single hydrogen bond does not produce a tremendously strong attraction between polymer chain-ends but, in 2002, work by Meijer and colleagues at the Eindhoven University of Technology led to the discovery of an end-group (called the ureido-pyrimidinone unit) that forms *four* strong hydrogen bonds, simultaneously, to another end-group of the same type. Attaching this unit to both ends of a short-chain polymer results in the chainends associating strongly, but still reversibly, and produces materials that show excellent self-repair characteristics. They flow very easily on heating, to repair damage, and some polymers of this type will even repair themselves spontaneously at room temperature after being broken.



A low molecular weight polymer in which the ends are designed to associate strongly and specifically by quadruple hydrogen bonding between ureidopyrimidinone end-groups. This gives properties (such as mechanical strength) that are usually associated with high molecular weight polymers. These materials can also show self-repair, when broken, by re-forming the hydrogen bonds.

#### **Complementary molecules**

Our own work at the University of Reading has focused on a different type of interaction between molecules known as 'p-p-stacking'. This type of attractive force arises when the flat surfaces of two different molecules come into contact. Some groups attached to the p-system pull electrons away from it which leaves a partial positive charge (just as with hydrogen in the hydrogen bond). Other p-systems can develop a partial negative charge. These two units are therefore described as complementary, in that one is electron-rich and the other is electron-poor. When their flat surfaces come into contact (the situation known as p-p-stacking) the molecules are held together, reversibly, by the attraction between the positivelyand negatively-charged carbon atoms in the two complementary molecules.

A hydrogen bond is an example of an intermolecular force or bond which acts between molecules.



Association of two polymer chain-ends by mutual, complementary p-p-stacking (above). This type of interaction is strongly reminiscent of the handshake often used in ancient Rome – a mutual grip of the wrist (below).



A blend of two low molecular weight polymers, one with electron-rich pyrene end groups that intercalate into chain-folds of the other polymer to form multiple p-stacks with its electron-poor naphthalene-diimide units. Fracture results in dissociation of the p-stacks, but these can re-form and so repair the damage.

It was relatively easy to attach the negative groups to the end-positions of a polymer. The resulting low-molecular weight polymer was then blended with a polymer with segments containing two positive units. These segments are designed to double upfold and so allowing double p-pstacking. This doubling up increases the strength of the interaction between the polymer chains substantially, in much the same way that Meijer's quadruply hydrogen-bonded system multiplies up the strength of interaction between chain ends.

#### Self-healing polymers

The polymer blends with p-p-stacking were very good at healing themselves inat temperatures up toof about 90°C. We knew that this was entirely due to the aromatic p-p-stacking interactions, because we also usedtested a control blend of the same two polymers, but without the p stacking end-groups,s and it and this failed to show any signs of self-repair at all under the same conditions.



False-colour scanning electron microscope images of polymer blends on heating from room temperature to 100 °C. In the left-hand series a polymer blend with extensive p-p-stacking interactions shows essentially complete self-repair over this temperature range. On the right, a similar blend but without this type of interaction shows no repair at all.

Self-repairing polymers are now becoming available to industry in small quantities to allow development. The lessons learned from research in this area are therefore being directly applied, for example, in car paints that repair their own surfaces when scratched, and in the development of new self-repairing, high strength composite materials reinforced with carbon nanotubes.

Howard Colquboun and Wayne Hayes are professors of chemistry at the University of Reading.



## Materials for space travel

Imagine that you are in a spacecraft, orbiting the Earth. You're travelling at 27 000 km/h through the vacuum of space. You're above the Earth's atmosphere; the beautiful Blue Planet lies below your feet.

#### Density

To get into space, a rocket packed with fuel is needed to lift your spacecraft into orbit. Typically, it takes 100 kg of rocket and fuel to launch 1 kg of spacecraft. To make the most of the lifting force available, spacecraft are usually made of low density materials such as aluminium alloys, similar to the materials used for aircraft.

However, it is better to use an even lighter material especially if it remains stiff and strong when very thin. Carbon fibre composites are good for this, and future spacecraft may have very thin outer shells made of carbon nanotube materials.

#### Getting tough

We talk of the 'vacuum of space', but space isn't empty. There are lots of hazards. For example, there is the problem of space debris – pieces of old spacecraft whose orbit crosses yours. You can avoid collisions with the biggest pieces simply by shifting up or down slightly. But the smallest pieces are difficult to avoid because no-one knows where they are.



Each dot represents an item of space junk in orbit around the Earth. Most is close to the Earth while there is a second concentration in geostationary orbit further out into space.

If you collide with a piece of debris the size of a pebble while travelling at high speed, your spacecraft could be wrecked. So any craft must be made of tough stuff. Space engineers are working on self-repairing materials which can automatically 'heal' any damage done by collisions with particles in space. (See the article about self-repairing polymers on page 6 of this issue of CATALYST.)

#### **Testing times**

There's no better way to test materials for use in space than by taking samples up into orbit and exposing them to the space 'weather'. The photograph on pages 10-11 shows NASA's MISSE experiment on board the International Space Station. A suitcase sized panel juts out from the ISS. Its surface is covered in samples of materials, coatings and electronic devices. Eventually these will be returned to Earth where materials scientists will assess their suitability for use in future spacecraft.



Materials engineers examine samples ready for testing in NASA's MISSE experiment

This article continues on page 12.





Samples of materials are exposed to conditions in space in this materials testing experiment attached to the International Space Station (photo: NASA)

#### **Radiation dangers**

Another hazard to human space travellers is radiation. In low-earth orbit the Earth's magnetosphere deflects charged particles (see the article on page 19 of this issue of CATALYST). However, if astronauts travel to Mars they will not have this protection as Mars does not have a magnetosphere or an atmosphere to absorb radiation.

High energy cosmic rays coming from deep in space can penetrate the skin of a spacecraft and harm the crew inside. If a gamma ray strikes the nucleus of, say, a metal atom, the nucleus may split into a shower of charged particles in a process similar to nuclear fission. So materials must be found which are made of lighter atoms – for example, carbon nanotubes – which do not split in this way.



NASA's space weather forecasters predict when intense bursts of radiation from the Sun are heading our way.

#### How much radiation?

Astronauts must accept that they will receive an increased radiation dose whilst in space, although much is done to reduce their exposure. The table shows some typical exposures. The unit used is the millisievert (mSv).

source of exposure	radiation dose
human exposure to background radiation, global average	2.4 mSv per year
full-body CT scan (X-rays)	10 – 30 mSv
6 month stay on International Space Station	80 mSv
6 month trip to Mars	250 mSv
1 year on Mars surface	250 mSv

#### Space suits

In designing a spacesuit, the challenge is to provide protection for the astronaut while allowing free movement. Traditional suits have sufficient pressure for oxygen to dissolve in the wearer's bloodstream. For working outside the spacecraft, the suit has a tough outer layer which protects the wearer against the impact of fast-moving particles of dust or debris. This opaque layer also provides protection against the Sun's ultraviolet rays.

An alternative design is the skintight suit. This is made of an elastic mesh, designed to prevent the swelling-up of flesh when exposed to a vacuum. Tests have been carried out in the zero-gravity environment of a parabolic flight aircraft but it is proving difficult to ensure that all parts of the body are correctly compressed. Would-be astronauts complain that it is very difficult to put such a garment on.



Skintight spacesuits designed at the Massachusetts Institute of Technology – this type of spacesuit is intended to be worn inside a spacecraft but is more often seen in comic books.



A test sample of fabric used in spacesuits, showing holes made by micrometeoroids (high-speed dust particles)

David Sang is Physics editor of CATALYST.

Divya Vadegadde Duggappa

# Alloys and aircraft

Few people think about what an aircraft is made from, but new metal alloys could be part of the key to make making jet engines quieter and more efficient. At any one time, there are over 500 000 people in the air flying! As Divya Vadegadde Duggappa of Cambridge University explains, one of the things that make this possible is metallurgy.

If you have boarded a flight, you might have noticed large, spinning blades that resemble a big fan. This is a jet engine, which makes it possible for an aircraft to fly. The big fan at the front constantly spins and sucks in large volumes of air from the atmosphere. The compressor blade squeezes the air to 1/50 of its volume. The compressed air is mixed with the jet fuel and an electric spark ignites the mixture creating a small explosion in the combustion chamber. This causes the squeezed gas to expand and shoot out at the nozzle passing through another group of blades called turbine blades, at the back of the engine. This drives the plane forward.

The temperature of the air that passes over the turbine blades is higher than 1500°C. To protect the turbines from such extreme temperatures they are coated with ceramics, which have low thermal conductivity. However, the temperature experienced by the turbine blades is still as high as 1100°C so the materials used in this part of the jet engine need to be able to withstand these high temperatures.

**Figure 1** shows the parts of a jet engine. The fan and compressor blades are made of titanium-based materials and the turbine blades are nickel-based.

Key words metallurgy alloying aircraft engineering



*Figure 1* The parts of a jet engine; the turbine blades must withstand the highest temperatures.

#### Metals for high temperatures

There are metallic elements in the periodic table which have melting temperatures higher than 1500°C. However, they cannot be used in the jet engines because of their other properties such as high density, high cost, high reactivity and lower strength at high temperatures. None of the elements in the periodic table has the combination of the properties desired for high temperature applications. However, the required properties can be achieved by mixing different metals or adding non-metallic elements to metals in a process known as *alloying*. Alloying does not have much effect on the electrical and thermal conductivities, but it has significant impact on the strength, which is the most important property for engineering applications.

#### Metallic structures

Pure metals contain identical atoms arranged in a regular pattern. A two-dimensional arrangement of atoms in a pure metal is shown in **Figure 2**. The positions that are occupied by the atoms are called *lattice sites*. Each atom in the lattice site is attached to the neighboring atoms by metallic bonds. For example, in two-dimensions, the atom labelled 'a' is bonded with atoms 1 to 6. But metals are 3-dimensional and in three dimensions, atoms can be thought as spheres. When layers of spheres pack together there are spaces between them which in a metal structure are called *interstitial sites*.



*Figure 2* The arrangement of atoms in two dimensions in a pure metal.



**Figure 3 a** A shear force pulls adjacent layers of atoms in opposite directions;

**b** After the force is removed, atom 'a' is bonded to a different set of neighbouring atoms.

What happens when a force is applied to a metal? **Figure 3a** shows a force (known as a shear force) pulling part 1 and part 2 in opposite directions. If this force is not enough to break the bonds, the atoms get back to their original position after the force is removed.

When higher forces are applied, the layers of atoms can slide over one another by breaking the existing bonds and making new bonds with other atoms. This is shown in **Figure 3b**, where for atom 'a' the bond has broken with atom '1' and a new bond formed with atom '7'. In this situation, atoms do not get back to their original positions after the removal of the force. There is a permanent change in the shape of the material.

If the forces are continuously applied for a longer period of time, sustained shape change can result in breaking of the metal. So in order to inhibit the shape change, sliding of the layers of atoms needs to be made difficult, which is known as *strengthening*. Alloying can be used to strengthen a metal.

#### Adding extra atoms

A metal can be alloyed with an element of smaller atomic size. If the atoms are small enough, they prefer to sit in the interstitial site as shown in **Figure 4a**. This is why steel, the most commonly used alloy in structural applications, is so strong. Steel is a mixture of iron with less than 0.2% of carbon atoms in it. The carbon atoms are about half the size of the iron atoms. They act as a barrier preventing easy sliding of the layers of metal atoms, thus making it harder to change the shape compared to pure iron. This is because with the carbon atoms present more force is required to break the existing bonds. This is always the case when nonmetallic smaller elements such as boron, oxygen, nitrogen or carbon are alloyed with metals.



Figure 4 Arrangements of atoms in the presence of

- **a** smaller atomic size alloying elements
- **b** larger atomic size alloying elements.

If another element with a larger atomic size is added to iron it will occupy the regular lattice site (Figure 4b) rather than the interstitial site. Brass is one such alloy, a mixture of copper and zinc where the atomic sizes are very similar.

If another element with a larger atomic size is added to iron it will occupy the regular lattice site (Figure 4b) rather than the interstitial site. Brass is one such alloy, a mixture of copper and zinc where the atomic sizes are very similar.

#### **Metal solutions**

In order to form an alloy, a metal needs to dissolve other elements in it to form what is called a solid solution. The ability to dissolve something is known as solubility, the same as it is for a liquid dissolving a solid. The solubility depends on several factors but for the best solubility the atoms should be of similar sizes and the elements must have the same crystal structure and similar reactivity. In addition to these factors, temperature is the most important variable that determines the solubility of elements. For example, nickel cannot dissolve any molybdenum at room temperature. However, it can dissolve 25 weight percent of molybdenum at 1250°C. On the other hand, nickel can dissolve copper completely above 322°C.

If an element added to a metal exceeds its solubility limit at a given temperature then it will separate from the original metal and form another state (*phase*) with different crystal structure. For all the elements in the periodic table graphs called *phase diagrams* are available, which show the limit of solubility of each element in other elements at different temperatures. This can be used to design the alloys depending on the application requirements.

#### High temperature alloys

One of the important factors in engineering applications is the temperature at which materials are used. When atoms get hot they become more mobile and sliding of layers of atoms becomes easier, leading to failure of parts. Compared to any other commercially existing alloys, nickel alloys are the best at keeping their strength at high temperatures and hence they are called superalloys. Nickel is one of the elements in the periodic table and it can dissolve many elements. Nickel based superalloys are used for the turbine blades and turbine disks of jet engines. The alloying elements that are normally present in Nibased superalloys are cobalt, chromium, aluminum, titanium, iron, molybdenum, niobium, tantalum, tungsten, ruthenium, and hafnium. Small amounts of boron and carbon are also often included. Apart from strengthening, these alloying elements also help to reduce the alloy's reactivity.



A single jet engine like this can generate a thrust force of 400 000 N.

Research is on-going to increase the efficiency of jet engines. This could be done by burning the air-fuel mixture at higher temperatures, which requires the turbine to sustain higher temperatures. However, nickel based superalloys that are currently in use are operating close to their melting points (1500°C) so part of the research is to try to find alloys which can operate at higher temperatures. This is done by altering the alloying element additions, playing with amount of alloying elements being added and by changing the manufacturing processes. Alloys which can operate effectively at higher temperatures may contribute to the development of aircraft which are more fuel efficient and quieter.

Divya Vadegadde Duggappa is a Post-Doctoral Research Associate at the Rolls-Royce University Technology Centre, Department of Materials Science and Metallurgy in Cambridge. She works on designing new alloys and manufacturing them through advanced fabrication techniques. These offer design freedom, so that complicated designs which could enhance the efficiency can be manufactured. Stefania Hartley

## From prized beauty to outlaw The tale of Japanese knotweed

Several species of knotweed have become invasive pests.

> Key words plants invasive species biocontrol pathogen

Schedule nine of the UK Wildlife and Countryside Act, covers the list of 'plants that may not be planted or otherwise caused to grow in the wild,' with fines of up to £5000 and/or 2 years imprisonment; but why should such a draconian act be needed?

When the Act was introduced in 1981, only giant hogweed, giant kelp, Japanese knotweed and Japanese seaweed were on the list of restricted 'invasive' species. In 1992 nine more joined the club, followed by a further thirteen in 2005 and thirty-seven in 2010. Among the latest additions are two species of rhododendron, the Virginia creeper and the entire *Elodea* genus (the pondweed commonly used in school lab experiments). So, what's wrong with these plants?

According to 2015 estimates, there are currently 2000 non-native species established in Great Britain, and 10-12 new species are added every year. While most of the established alien species cause no disturbance, around 10% of them have a severe negative impact on the local ecosystem; we call these 'invasive'.

Although their number is very small, the damage invasive species causes can be considerable and their cost to the British economy is currently estimated at £1.7 billion per year. In the absence of the herbivores and parasites which keep them in check in their countries of origin, invasive nonnative plants outcompete their native counterparts for space, light, nutrients and pollinators, and ultimately cause a loss of biodiversity. However their effects can be even more devastating than this.



Japanese knotweed in flower



The stem of a Japanese knotweed

#### The knotweed menace

From gold medal winner at the 1847 show of the Society of Agriculture and Horticulture in Utrecht to outlaw bandit in just over one century, Japanese knotweed's story is not uncommon among invasive plants. Many were imported as ornamental beauties and later escaped into the wild. It was very soon after its introduction that Victorian gardeners realised that *Fallopia japonica* (Japanese knotweed) was 'easier to plant than to get rid of' and that it should be treated with caution.

Vational Biodiversity Network

UK records of Japanese knotweed before 1920 (top) and today (bottom)

Japanese knotweed is listed by the World Conservation Union (IUCN) as one of the world's 100 worst invasive species and its total annual cost to the British economy is around £166 million. October 2014 legislation states that failing to prevent Japanese knotweed from spreading to a neighbour's property can result in a community protection notice, on-the-spot fines of £100 or prosecution with fines of £2500 and even imprisonment.

Knotweed is an early coloniser of volcanic soils in its native Japan. It can tolerate extreme temperatures and harsh conditions. In winter it dies back to its roots, but in spring it forms vigorous shoots that can grow through tarmac and concrete at a speed of one metre per month. It eventually forms large stands up to 3-4 m in height, which shades out other plants, ultimately ending up as a Japanese knotweed monoculture. Some building societies have even refused to grant a mortgage to knotweed-infested properties. Its dead canes – which take up to three years to decompose – can clog up flood drains and the extensive system of rhizomes (underground stems) burrows into riverbanks, creating flood risks.

![](_page_18_Picture_6.jpeg)

Work in progress to eradicate the alien and invasive Japanese knotweed in Dundonald, Northern Ireland

One good piece of news is that all the *Fallopia japonica* plants in the UK are females – clones of the infamous Victorian specimen – so the plant can only propagate vegetatively. Unfortunately, a piece of rhizome as small as a fingernail can regenerate a whole new plant. It can only be disposed of with a special licence. Homeowners can attempt to repeatedly cut the plant above ground until the rhizomes' energy reserves are exhausted, but this will take years. Or they can call specialised companies which will extensively excavate and treat the soil chemically or by sifting. Stem injection with herbicides is also possible.

#### Biological control of knotweed

What turns a regular member of the plant community of one country into an indomitable pest in another? Fundamentally, the absence of its natural predators, competitors and pathogens. Strategies for their control can therefore include locating natural enemies. In the case of knotweed, scientists at CABI (Centre for Agriculture and Biosciences International) in Surrey, in collaboration with their Japanese counterparts, scanned through more than 200 natural enemies of the plant in Japan. From this, two promising candidates to bring Japanese knotweed under control in the UK have been identified.

In 2010 the insect *Aphalara itadori* was released into the wild (a first in Europe for the releasing of a biological control agent against an invasive plant). This will be monitored until 2016 to ensure that it doesn't affect any other organism than Japanese knotweed. If the experiment is successful, larger scale releases will follow.

The second candidate for the role of 'biocontrol agent' against Japanese knotweed, is the leaf-spot fungus *Mycosphaerella polygoni-cuspidati*. Further studies on this are underway, but first signs are very promising.

![](_page_19_Picture_5.jpeg)

*Leaf spot fungus*, Mycosphaerella polygoni-cuspidati, *on knotweed leaves* 

#### Climate change and invasive plants

![](_page_19_Picture_8.jpeg)

Floating pennywort in a stream in southern England

It is quite likely that climate change will favour the establishment of invasive species. Scientists testing the responses of Japanese knotweed and British native plants to different patterns of fertiliser application found that the knotweed did better than the natives when the application of fertiliser was erratic. As climate change will increase variability of resources and will put native plants under stress, invasive plants might become an even bigger problem.

Stefania Hartley is a science teacher living in Singapore.

Plant	Problem
Giant hogweed Heracleum mantegazzianum	The furanocoumarins in the plant's sap cause damage to DNA which make the affected skin sensitive to sunlight, an effect that can last for years.
Himalayan balsam Impatiens glandulifera	The soil on which these species grow becomes depleted of the fungi on which native species are highly dependent. It can produce up to 800 seeds per plant, which shoot out of the pods up to 7 m away.
Common rhododendron Rhododendron ponticum	Rhododendron will out-compete most native plants. It grows to many times the height of a person, allowing very little light to penetrate through its thick leaf canopy, eliminating native plant species. This leads to the consequent loss of the associated native animals.
New Zealand pigmyweed Crassula helmsii	Forms dense mats and can impede drainage, causing flooding. Displaces other aquatic plant species and reduces amenity use of the waterbody.
Floating pennywort Hydrocotyle ranunuculoides	Grows up to 20cm per day and can regenerate from tiny fragments. Arrived as an ornamental plant in the late 1980s, it is now one of the worst invasive aquatic plants.
Water fern Azolla filiculoides	Forms floating mats up to 30 cm thick which can double in size every 4-5 days.

#### Other invasive plants in the UK

## Earth's magnetic field – what is it good for?

Sunspots are evidence of magnetic activity on the surface of the Sun.

When Mars lost its magnetic field, its atmosphere was ripped away by the solar wind leaving it apparently uninhabitable. Does the same fate await Earth? **Mike Follows** looks at the latest thinking.

In the previous issue of CATALYST (Volume 26, Issue 1) we saw that both the strength and direction of the Earth's magnetic field change, switching direction every 300 000 years or so. This article explores the impact these changes might have for us on Earth in terms of both geomagnetic storms and climate.

#### Not-so-empty space

The Earth is exposed to the solar wind, a plasma composed mainly of electrons, protons and alpha particles which have enough energy to escape from the Sun's corona or surface layer. The solar wind typically travels at 400 kilometres per second. Fortunately for us, the Earth's magnetic field creates the magnetosphere (**Figure 1**), which acts like an umbrella, deflecting charged particles coming our way.

![](_page_20_Picture_7.jpeg)

*Figure 1* The Earth's magnetosphere deflects the charged particles of the solar wind.

The solar wind fills a volume known as the heliosphere. Beyond the furthest planets, the particles of the solar wind gradually lose energy as they collide with the particles of the very low density interstellar medium. The region where they finally run out of energy to push back the interstellar medium is called the heliopause and this is accepted as the outer edge of the Solar System.

As well as the solar wind, the Sun also emits occasional solar flares. These are followed by a coronal mass ejection (CME), when a cloud of up to one billion tons of charged particles is ejected into the interplanetary medium (**Figure 2**). Most head off in the wrong direction to collide with Earth but, when a cloud heads our way, it usually takes between one and five days to reach us. Though our magnetosphere deflects most of these charged particles and the atmosphere protects us from the surge in ionising radiation, CMEs can cause geomagnetic storms on Earth.

![](_page_20_Picture_11.jpeg)

![](_page_20_Picture_12.jpeg)

*Figure 2* A coronal mass ejection: on 31 August 2012 a large bubble of solar material that had been hovering in the Sun's atmosphere, the corona, erupted out into space.

On 6 March 1989, a very large X15-class solar flare was observed. A CME followed on 9 March and four days later a severe geomagnetic storm struck Earth. The storm began with extremely intense auroras at the poles which could be seen as far south as Florida and, because this happened during the Cold War, it is claimed that some people feared that the lights in the sky were due to the detonation of nuclear weapons. Within 92 seconds, the storm had knocked out the Hydro-Québec power grid causing an electrical blackout that left over 6 million people in North America without power for nine hours (**Figure 3**).

#### **Magnetic interaction**

What causes geomagnetic storms? As the CME is a moving cloud of charged particles, it has an associated magnetic field that interacts with the Earth's field, causing it to vibrate. The changing field induces voltages, which drive geomagnetically induced currents (GICs) on the Earth's surface. These currents pass along paths of least resistance, which can include overhead power cables that make up the electrical distribution grid as well as the ground beneath our feet.

![](_page_21_Picture_3.jpeg)

*Figure 3* The areas of the USA where power grid lines were seriously impacted by the 1989 geomagnetic storm.

Most of Quebec stands on rock that has a high resistance, so the current took to the man-made alternative – the 735 kV power lines. This is one of the reasons why North America is so vulnerable to solar storms. In extreme cases GICs can melt the windings of heavy-duty transformers, which can take more than 12 months to manufacture. In the absence of spare transformers, this could have an impact on the long-term supply of electrical energy.

On a positive note, Dr Alan Thomson, Head of Geomagnetism at the British Geological Survey, believes that, while the frequency of solar storms will remain the same, GICs will probably weaken in line with the Earth's diminishing magnetic field as we head towards a reversal. But, according to Scandinavian scientists, this may lead the Earth into a mini 'ice age'.

#### Standing guard

Engineers need advanced warning of a geomagnetic storm so that they can disconnect transformers from the grid in order to protect them. This is where Solar Shield comes in. Images from SOHO and NASA's twin STEREO spacecraft will provide a 3D model of the CME and predict when it will reach Earth. A spacecraft called ACE is stationed 1.5 million km upstream of Earth; as the cloud of charged particles sweeps past, ACE will detect its speed, density and magnetic field and give people on the ground about half an hour to take evasive action.

![](_page_21_Picture_10.jpeg)

#### Magnetic fields and climate

There is mounting evidence that the strength of both the Earth's and Sun's magnetic fields may influence our climate. The climate was changing long before humans started burning fossil fuels. Volcanic eruptions and cometary impacts are just two examples. The many causes of climate change make modelling the climate and predicting future climate tricky – there are so many variables to take into account.

In London, 'frost fairs' were held on the frozen River Thames during the 'Little Ice Age' between 1645 and 1715. This period is also known as the Maunder Minimum because the British astronomers Walter and Annie Maunder showed that the number of sunspots was at a minimum (**Figure 4**). Is there a connection? Well, a paper in 1991 by the Scandinavian scientists Eigil Friis-Christensen and Knud Lassen certainly suggests a remarkably strong correlation between the number of sunspots and the Earth's global mean surface temperature (**Figure 5**). But correlation is not the same as causation and their work was largely dismissed because they failed to come up with a causal link. However, their colleague Henrick Svensmark has since suggested the galactic cosmic ray hypothesis.

![](_page_22_Figure_1.jpeg)

**Figure 4** 400 years of counting sunspots: By combining older (red) and systematic modern (blue) observations, the Maunders discovered the period of low solar activity now associated with the Little Ice Age.

![](_page_22_Figure_3.jpeg)

*Figure 5* As the length of the sunspot cycle increases, the Earth's temperature rises.

Galactic cosmic rays, produced by exploding stars called supernovae, are basically protons travelling close to the speed of light. The magnetic fields of the Earth and Sun shield us by deflecting these cosmic rays. The number of sunspots indicates the strength of the Sun's magnetic field. When there are more sunspots, we know that the Sun's magnetic field is stronger, deflecting more of the cosmic rays, leading to a warmer climate.

How does this work? When either or both magnetic fields is weak (as when the Sun sported fewer sunspots during the Maunder Minimum), more cosmic rays reach our atmosphere, creating muons (heavy electrons) that produce the condensation nuclei for cloud formation. An increase in cloudiness results in more sunlight being reflected back into space, making the Earth cooler.

#### The CLOUD experiment

An experiment at CERN is being conducted to try to create the condensation nuclei hypothesised by Svensmark (**Figure 6**). The Proton Synchrotron is being used to mimic galactic cosmic rays by firing high-energy protons at the Cosmics Leaving Outdoor Droplets (CLOUD) experiment, which is basically a chamber of very clean air. Early results are positive.

Svensmark's hypothesis, though controversial, is gaining more advocates. But as Thomas Huxley once said, "Science is organised common sense where many a beautiful theory was killed by an ugly fact." While the theory underpinning geomagnetic storms is understood and accepted, a lot of work still needs to be done in order to forecast when they will arrive and how their impact can be minimised.

![](_page_22_Picture_11.jpeg)

*Figure 6* The CLOUD experiment at CERN. Will high-energy protons, fired into the tank, cause clouds to form?

If we were to lose our magnetic field completely, Earth would become uninhabitable as the solar wind would eventually blow away our atmosphere. As the Earth's field is weakening, engineers will need to develop ways of making satellites and aircraft communications less vulnerable to the solar wind and CMEs. A weakening field might also reduce the intensity (though not the frequency) of geomagnetic storms reducing the need for engineers to protect power grids from GICs. But we might also get global cooling, which would reduce or even reverse the predicted warming due to the enhanced greenhouse effect. The danger is that, if the Earth enters a cooling phase, people might stop believing that burning fossil fuels leads to warming. As we have seen, there is more than one source of climate change operating at any one time, clouding the issue.

Mike Follows teaches and writes about Physics.

#### Look here!

The Geomagnetic Storm of 1989: http://bit.ly/1kdqzQi Cosmic rays and the CLOUD experiment: http://bit.ly/1P7rEoB

# **GOING FOR GOLD**

Gold is a valuable metal, partly for its use in jewellery. But it is also a vital material in electronics because of its electrical conductivity and resistance to corrosion.

![](_page_23_Picture_2.jpeg)

The Super Pit at Kalgoorlie, Western Australia, is 3.5 km long and almost 600 m deep. It produces about 20 tonnes of gold each year, plus 20 million tonnes of spoil. The town has grown to meet the edge of the mine site.

![](_page_23_Picture_4.jpeg)

![](_page_23_Picture_5.jpeg)

![](_page_23_Picture_6.jpeg)

The pouring of gold bars is the final step in a long process. For each gramme of gold extracted from the ore, a tonne of ore must be processed.

![](_page_23_Picture_8.jpeg)

Kalgoorlie is 600 km across the desert from the coast at Perth. Esperance was established as a port for exporting minerals in 1893.

![](_page_23_Picture_10.jpeg)

Kalgoorlie was the centre of a gold rush in the 1890s. Prospectors obtained a licence to 'stake their claim' before searching for flakes of gold in the desert dust.

![](_page_23_Picture_12.jpeg)

Gold can be found in small quantities in many European rivers. This boy is a contestant in a gold prospecting competition, river Gardon, France.