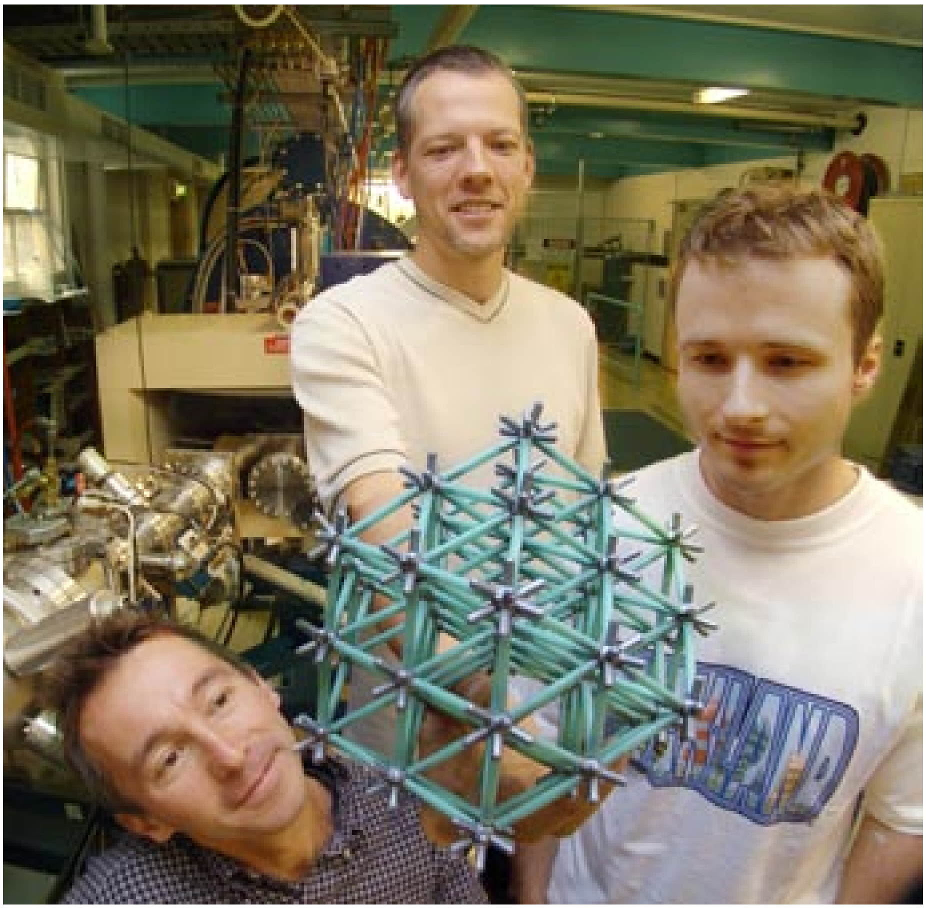
CSEM's
# Materials Monthly
February 2006 Making materials matter


(From the left) Mark Ridgway, Patrick Kluth and Bernt Johannessen gaze at the beautiful symmetry in a model crystal lattice. Their challenge has been how to break this order in pure metal to yield new material properties. (Photo by Tim Wetherell)

**After centuries of fine honing our understanding of crystalline metals, materials scientists are now turning their attention to their unstructured cousins – amorphous metals. ANU research is suggesting that if you want a pure amorphous metal, ion implantation on nanocrystals might be the way to go.**

# Blasting out supermetals

**Researchers are demonstrating that if you want to make pure amorphous metals you need to think (nano) small.**

## The challenge of disorder

It's been discovered in recent years that the highly disordered structure of amorphous metals give them a suite of interesting and, in some cases, superior properties from their conventional crystalline counterparts. The reason that we're only now paying them attention is because up until recently they've proved fiendishly difficult to fabricate.

When a molten liquid metal cools it's atoms naturally move towards an ordered crystalline arrangement. To form an amorphous metal you need to cool it rapidly to freeze a random atomic pattern in place before crystallisation occurs. The disordered structure is said to be 'quenched in'. Achieving such a structure, however, has proved quite difficult (see the box on bulk metallic glasses). It was first done by rapidly cooling thin layers of molten metal.

More recently it's been discovered that certain alloys such as Vitreloy (a mix of zirconium, copper, nickel, titanium and beryllium) have a very high viscosity and can freeze into amorphous states even at quite modest cooling rates. This paved the way for the commercialisation of bulk glassy metals, often referred to as supermetals because of their hardness, strength and elasticity.

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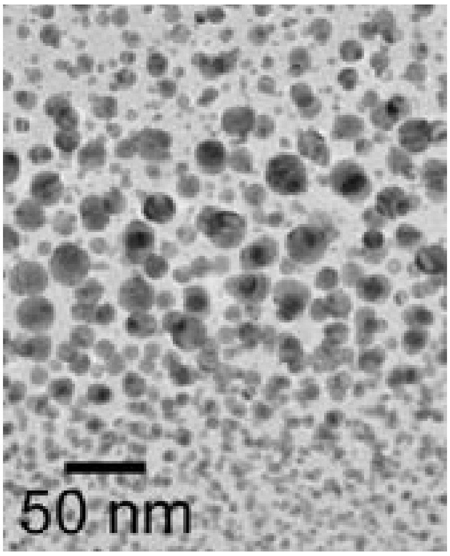

*A transmission electron micrograph showing gold nanocrystals embedded in a thin layer of silicon dioxide (the scale bar represents 50 nanometres). The size and distribution of the nanocrystals are determined by the energy and number of gold ions implanted into the silicon dioxide, and the degree to which the sample is then heated (annealed).*

## Inside this MM



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THE AUSTRALIAN NATIONAL UNIVERSITY

## Blasting out supermetals

(continued from previous page)

There's been large amounts of publicity surrounding these new super materials with flashy claims about their ability to form superior products such as the heads of gold clubs and baseball bats.

While it might be possible to form amorphous metals from some alloys, the same has not been achieved for pure metals. It's simply impossible to cool the molten metal fast enough to yield the desired amorphous structure. That might be about to change thanks to research by materials scientists in the Department of Electronic Materials Engineering (RSPSE). Rather than attempt to freeze disorder into molten metal as it cools, they are attempting to introduce disorder into crystalline metal using ion bombardment.

### Ion bombs

Scientists have long experimented with ion implantation to create disordered metals. The process involves accelerating ions to high velocity and smashing them into the material with the aim of displacing atoms and transforming the metal structure from a polycrystalline to an amorphous state. However, to date, this hasn't worked when using ions of the same element as the target, for example copper ions bombarding copper, because the disorder or amorphous zones produced by the ion rapidly recrystallises.

The process does work when using ions of a different species to the metal being bombarded, for example oxygen ions into copper. These 'foreign' ions, when introduced in sufficient quantities, alter the chemical composition of the target metal and can inhibit recrystallisation. Foreign implanted ions, however, also introduce undesirable impurities which themselves alter the properties of the metal. But now scientists at EME believe they have found a way round this problem.

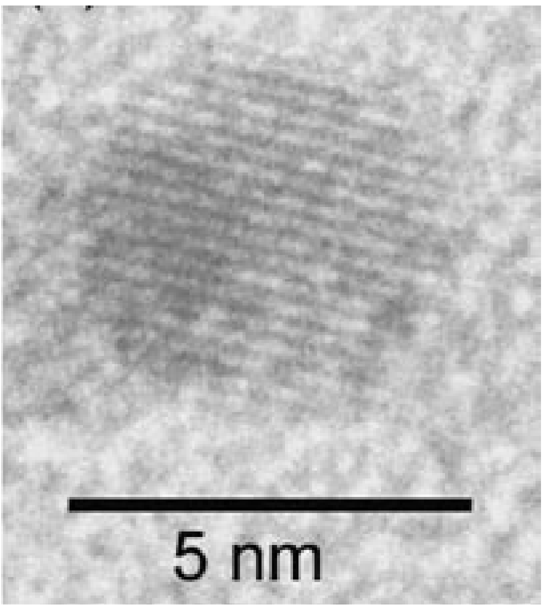
"The solution, we believe, lies in working with nanocrystals of metal rather than with bulk samples of the metal," says Dr Patrick Kluth, the scientist leading the research.

"The nanocrystals are first formed using an ion implantation process," he explains. "We bombard layers of silicon dioxide with a range of metal ions, for example copper or gold to produce a supersaturation of the metal in the thin glass layer. Afterwards these layers are annealed to ensure sufficient thermal movement of the metal atoms such that they can form small metal clusters. The result is the formation of a layer of metal nanocrystals of varying sizes depending on the dose of ions and the subsequent annealing temperature. If you look at a cross section of the layer using a transmission electron microscope the nanocrystals look like tiny grains or pebbles embedded in the silicon dioxide."

### Nanocrystals of metal

"Now these nanocrystals have often a very similar crystalline structure as the bulk material but exhibit different properties because of their finite size and their far greater surface area to volume. In the nanocrystals of the size range we are looking at between 10% and 50% of all atoms are located at the surface. These differences are critical because the crystal structure is easier to disorder, and this disorder is more difficult to reform.

"To introduce disorder into these nanocrystals we bombard them with more ions, this time high energy ions that pass right through the nanocrystals. For example, we've been using high energy tin ions. The disorder is created as the ions pass through the nanocrystals and




*A high resolution transmission electron micrograph of a single gold nanocrystal. The lines represent rows of gold atoms sitting in a crystal array. To create amorphous nanoparticles of gold these nanocrystals are bombarded with high energy tin ions. As these ions pass through the nanocrystals they knock gold atoms out of their crystalline positions.*

*In these nanocrystals we are looking at between 10% and 50% of all atoms being located at the surface*

knock atoms out of their crystalline positions in collision cascades. The ions themselves, however, lodge deeper in the surrounding matrix of silicon dioxide. In this manner we get the disordering effect of the implantation without the problems of impurities being introduced into the nanocrystals because the tin ions are not actually lodging in them.

"Though technically speaking they're no longer nanocrystals because we've disordered their crystalline structure. It would be better to refer to them now as nanoparticles of gold and copper."

Dr Kluth is carrying out the research with Dr Mark Ridgway and Mr Bernt Johannessen. The researchers have been fine tuning the process such that the implantation disrupts all trace of the normal face-centred cubic crystalline structure whilst leaving the particle size intact.

### The value of nanoparticles

"We're not fabricating bulk metallic glasses but we are producing nanoparticles of pure amorphous metal," says Dr Kluth. "Whereas the bulk metallic glasses are known for their physical properties of strength and hardness, we anticipate our nanoparticles will exhibit some very interesting electrical and optical properties. Indeed, the whole field of metallic nanoparticles embedded in a dielectric matrix such as silicon dioxide is rapidly opening up. Their nonlinear optical properties give them enormous potential for applications in optical filters, memories or switching devices. And because ion implantation has widespread commercial application it's possible that what we're learning can be readily taken up by the electronics, photonics and metallurgical industries."

Dr Kluth believes the

Department Electronic Materials Engineering is a excellent place to undertake these investigations on amorphous metallic nanoparticles.

“It’s a great place for this work,” he says. “At EME we have both the know-how in materials fabrication and processing, in particular ion implantation, and the expertise in the advanced synchrotron-based characterization techniques that are necessary to examine these small particles. Only these techniques are capable of resolving the fine structural differences which we often see in nanoparticles like changes of the interatomic distances as compared to bulk metals of less than 1%. This combination of processing and characterization is fairly unique and incredibly important when it comes to working in an area such as amorphous metallic nanoparticles as it draws on the pure science and the applied.”

### Nanoparticles and synchrotrons

An important part of the story has been developing a capacity to study these materials at the nanoscale.

“The key to our success has been developing a thorough understanding of structural perturbations at the nanoscale,” says Dr Mark Ridgway. “And that understanding is based on our capacity to characterise these particles in terms of size, structure, shape and distribution using a range of techniques including electron microscopy, ion backscattering, x-ray diffraction and scattering, and extended x-ray absorption fine-structure (EXAFS) spectroscopy.

“Some of these techniques involve working with a synchrotron and we are fortunate to be able to access some of the world’s most advanced synchrotron facilities such as the Photon Factory in Japan and the Advanced Photon Source in the USA.”

Dr Ridgway has long played a leading role in developing Australia’s synchrotron research capacity and is looking forward to the opening of an Australian facility in the coming years.

“Our work on amorphous metal nanoparticles is materials science at the cutting edge,” he says. “One exciting thing about it is that in 2007 the Australian Synchrotron opens in Melbourne, and we can then carry out these measurements in our own country. Furthermore, our EXAFS beamline should be superior to those we have

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## Bulk metallic glass

In the last decade a new class of wonder materials called metallic glasses have begun to emerge from materials labs around the world. Bulk metallic glasses exhibit properties of incredible strength and elasticity.

Conventional metals have a crystalline structure in which the atoms are lined up in neat, orderly arrays. Most of these metals typically consist of small regions of aligned atoms, called grains, with boundaries between them. In metallic glass, however, atoms are packed together in a somewhat random fashion, similar to that of a liquid.

Research suggests that the prized physical properties of metallic glasses (also known as amorphous metal) arise in large part from their lack of grain boundaries which can serve as points of weakness.

Unlike conventional metals, which are usually cooled until they fully solidify, metallic glasses must be cooled very rapidly and very uniformly to freeze their random atomic pattern in place before crystallisation occurs due to the nucleation and growth of crystal grains. When this phenomenon was first being explored, some 40 years ago, the only way to extract heat fast enough to maintain the metal’s random state was to keep the material very thin. It was produced by ‘splat cooling’ in which droplets of molten metal were quickly frozen on a cold surface.

Continuous amorphous metal ribbons less than 0.1 millimeter thick could also be formed at a cooling rate of 1 million°C per second. The ribbons were wear-resistant and possessed interesting magnetic properties but the high fabrication cost meant it never found any commercial application.

Over the past decade methods have been developed to produce bulk metallic glasses by cooling mixes of zirconium, magnesium, aluminum, and iron. Early approaches to the fabrication of these bulk metallic glasses were mostly trial and error in nature, but researchers gradually began to understand that the correct choice of elements in the mix would allow the formation of amorphous metals being produced with cooling rates as slow as 1 - 100°C per second. These slower cooling rates mean that large parts can be fabricated. Furthermore, many of these metallic glasses remain stable against crystallisation even when heated to temperatures somewhat above their glass-transition temperatures.

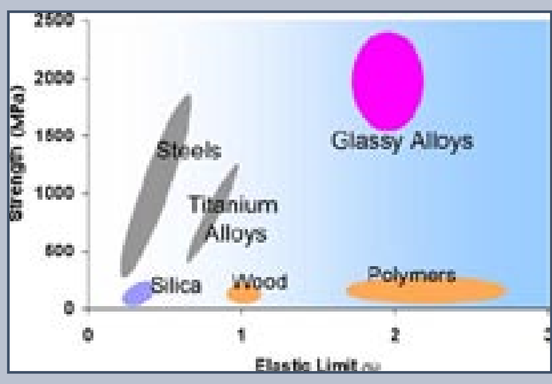
One of the general guiding principles to designing alloys that form bulk metallic glasses is to pick elements with dramatic differences in size. This leads to a complicated structure that crystallises less easily. A beryllium atom, for example, is much smaller than a zirconium atom.

One common mix of these new bulk metallic glasses is two-thirds zirconium, one fifth beryllium, and the remainder split among copper, titanium, and nickel.

These new bulk metallic glasses exhibit high strength-to-weight ratios and hardness, extreme springiness and rebound characteristics, and good acoustic-dampening properties. They’re being considered for a range of applications including golf-club heads, amour piercing ammunition casings and surgical prosthetics.

For example, golf club heads fabricated from amorphous metal “Vitreloy” are twice as hard and four times as elastic as those made from polycrystalline titanium and consequently 99% of the impact energy is transferred to the ball compared to only 70% for titanium.

Unfortunately, the Achilles heel of this wonder material is that it has an extremely low resistance to ‘crack initiation’ – the propagation of a crack once it has formed. When it fails, it fails catastrophically. To fill this hole a range of strengthening materials are being considered to add to the bulk metallic glass (BMG), and one technique being investigated is rods of BMG reinforced with tungsten wire.




*Bulk metallic glasses possess a range of physical properties that distinguish them from other materials. Shown here are typical strengths and elastic limits for various materials. (Figure from www.its.caltech.edu/~vitreloy/development.htm)*

## Blasting out supermetals

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previously used overseas. For example, the photon flux on the sample should be one thousand times greater than that at the Photon Factory beamline."

The study of amorphous metallic nanoparticles is a science that is only just opening up. It hasn't yet received the publicity or the hype surrounding the bulk metallic glasses, and it's unlikely that these nanoparticles will be used to make golf clubs or baseball bats. However they could be the seeds of whole new high tech industries. If that happens, the research by Dr Kluth and his colleagues will ensure Australia will be in the thick of it.

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*The high-energy, high-current ion implanter used to create and subsequently disorder the metallic nanocrystals. Negative ions are first formed in the source (far right), then accelerated, converted to positive ions and further accelerated within the accelerator (middle) and then finally rastered across the specimen within the sample chamber (far left). (Photo by Tim Wetherell)*

future materials AWARDS | 2006

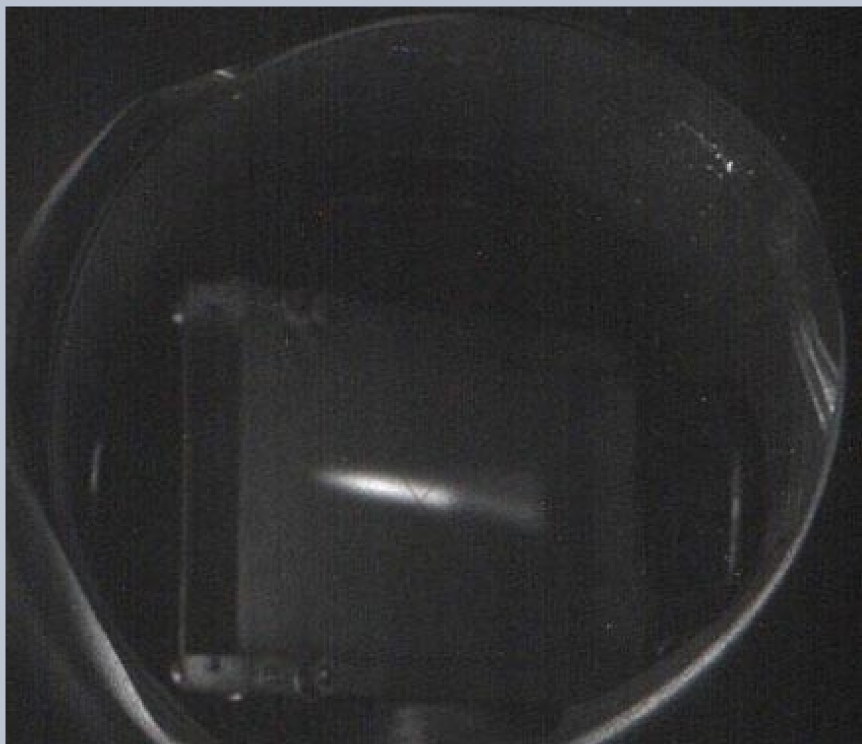
# 2006 FM Awards

Innovations in materials science and engineering lie behind many of the latest products, devices and techniques. Future Materials is proud to invite you to participate in the inaugural Future Materials Awards. Please join us to recognise the innovators in this exciting field.

The Awards are open to companies / organisations with operations in Australia. The innovation must include a materials science aspect. Collaboration with research institutions is encouraged, particularly for SME's, and extra points are awarded for a demonstrated element of risk, either commercially or technically.

Entries close 10 March 2006.

**More info: http://future.org.au/**



# Beam on

As discussed in our feature story on amorphous nanoparticles, materials scientists all around Australia are eagerly awaiting the completion of the Australian synchrotron in Melbourne so they will have better access to a world-class source of synchrotron radiation. Each month there is fresh news on progress as the technological behemoth takes form. Here's an example.

Last month the Australian Synchrotron project delivery team achieved the first electrons emitted from the Linac (linear accelerator) at an energy of 100 MeV. The team managed to get the beam out of the Linac and around the first bend in the transfer line between the Linac and Booster ring (known as the Linac to Booster, or LTB). The image to the right is of a fluorescent screen after the first dipole in the LTB. The thin dark X lines in the bright spot mark the centre of the beamline.

**For more info on the construction of the Synchrotron see http://www.synchrotron.vic.gov.au/content.asp?Document_ID=4300**

# Understanding complex fluids in paper

In his PhD Ray Roberts looked at how simple fluids moved through paper (See MM November 2003). Now he's back at the Department of Applied Maths (RSPSE) as a Visiting Fellow extending the work to investigate how complex fluids move through paper.

"If you stop and think about it, working with paper and wood particle products is all about understanding how they interact with fluids," says Dr Roberts. "It might be how they absorb liquid that's been spilt (mopping up), display liquid that's been coated on (ink) or protect a product from liquid (packaging).

"The work on simple fluids revealed that they advance through paper as films. It's a pretty basic discovery, and it tells us that the pore space of paper, especially fibre distribution and resultant network of inter-fibre channels, together with local surface energy considerations, are the chief determinants of fluid penetration."

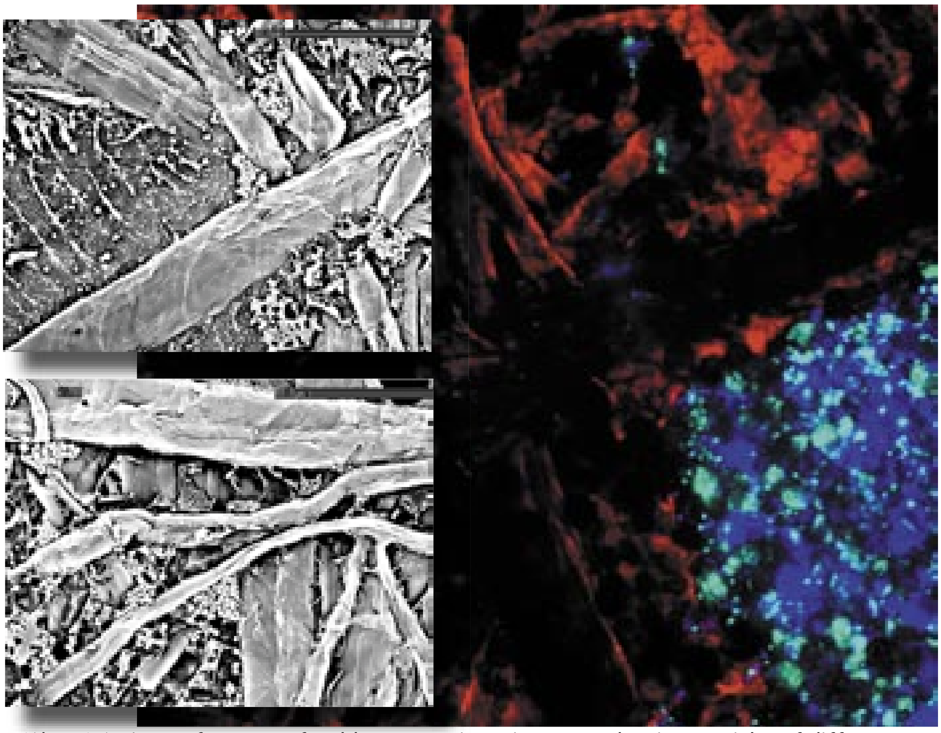
However, in the real world most of the fluids that interact with paper are complex fluids with a liquid and a solid component. Think of most body fluids or ink.

"To understand how complex fluids interact with paper we need to extend the original study to consider what is happening with the particles being carried in the liquid," he says. "Particles don't flow through paper like a liquid. They appear to clump together in narrow pore spaces often leading to damming and uneven distribution.

"My current investigation is attempting to establish methodologies that will help us understand what is happening with different papers and different particle sizes.

"A major obstacle in these studies is finding ways of distinguishing between the liquid and the solid component of the fluid. Cryo-scanning electron microscopy, for example, was a major tool used in studying simple fluids but scanning electron microscopy only visualises surfaces whereas the particles in the fluid are carried beneath the liquid surface. To get around this we freeze the complex fluid as it moves through paper and then ablate away portions of the frozen fluid to reveal the location of the particles.

"We're also using a 2-photon confocal laser scanning microscope from the John Curtin School of Medical Research that can resolve the liquid phase from the solid phase including different sized particles."



*(Above) An image from a confocal laser scanning microscope showing particles of different sizes (red and blue) moving in fluid through paper. (Above left) Two scanning electron micrographs in which the liquid has been frozen and ablated away to show the location of particles among paper fibre.*

The investigation is continuing but early results are suggesting that particle size and size distribution as well as the density of the fibre network play an important role in determining how a fluid penetrates through paper.

"It would generally appear that the liquid front always moves ahead of the particles with larger particles separating out of the liquid first and only the smaller particles being carried any distance in the advancing liquid films," says Dr Roberts. "However this is not always the case. Sometimes small particles can separate out early in channels that are easily large enough which in turn creates dams that trap more particles of all sizes. We haven't even started to investigate the effects of fillers in paper.

"This is a big field of enquiry with enormous potential. Understanding these relationships and their implications for paper performance opens up vast opportunities for designing paper products with improved characteristics, and more adeptly troubleshooting problems."

As an aside on his research, Dr Roberts is also being employed by the Forests and Wood Processing Research and Development Corporation to investigate industry interest in the establishment of an Advanced Wood Products centre at an Australian university.

"The numbers around the wood products industry in Australia are very interesting," says Dr Roberts. "According to ABARE, the value of turnover of forest products in Australia is over $18 billion. Australia imports roughly $3 billion worth of forest products per year and the industry employs over 78,000 people. For all that, there is no formal partnership between universities and this large industrial sector.

"Canada presents a different picture. It now has a Centre for Advanced Wood Products based at the University of British Columbia, and it has demonstrated its value in terms of providing skilled workers and value adding processes many times over. The departments of Wood Science, Forest Science and Forest Management at UBC have 55 professors ad 650 students. Canada's forest industries are worth over $62 billion per annum and the country exports over $40 billion in wood products each year. The wood products sector directly employs over 250,000 people.

"Imagine what might be possible here in Australia.," says Dr Roberts.

CSEM members might be interested to know that the Canadian Centre for Advanced Wood Products is led by Professor Phil Evans, a former Director of CSEM.

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*The plane built by Rosie Barnes, Aaron Hazelton and Dave Shurey (top left) was named Jabiru and was one of the top competitors in last years' Aero Design Competition in the United States. During the event the plane suffered a catastrophic crash (top centre) however it had already proved itself by then. Rosie Barnes is pictured above with the remnants of the Jabiru in the Advanced Manufacturing Lab (Department of Engineering) where she spent hundreds of hours designing and building the model during its construction.*

# Flight testing materials

As any cook will tell you, 'you've got to break few eggs to make an omelette'. For a materials scientist that might read 'you've got to smash of few models to really know how a material behaves'.

In any event, as the above pictures attest, the model plane put together by engineering students Rosie Barnes, Aaron Hazelton and Dave Shurey was pushed beyond its breaking point in the Aero Design Competition run in the United States last year. However, before it experienced its catastrophic crash it earned the engineering trio fourth position out of a competitive field of 35 entrants from US universities.

"We were competing against some pretty big and well resourced teams from universities all across America," says Ms Barnes, who has recently completed a joint Bachelor of Engineering/Arts degree. "Coming in fourth overall was quite an achievement and we won the award for best oral presentation.

"The competition is to design and make a remote control plane that can lift the most weight. There is a limit on the runway length, and on the wingspan, and it has to have a certain volume in the fuselage."

This is the fifth time that Ms Barnes has competed in the event and this has been her best outcome. Over the years building and competing with model airplanes she has acquired a good understanding of how to best apply carbon-fibre reinforced composites in design and construction.

"It was this experience with carbon-fibre composites that gave me valuable insights in my Honours project on the design and analysis of individual pursuit bicycles where I sought to conceive, design and manufacture an improved bike for competition," she says. "I used carbon-fibre epoxy in my design because of its high specific stiffness and strength. Advanced composites allow for the easy manufacture of complex geometries such as those required in an aerodynamic bike frame."

Such was the quality of Ms Barnes' Honours thesis that she was awarded the 2005 CSEM Prize for best thesis on the Application of Materials. For her efforts she has won a certificate and a cash prize of $2000.

So, it would seem that despite the occasional crash of a model plane, the results of her work with fibre composites are already paying significant dividends.

MM

PS: *Materials Monthly* would also like to congratulate Katy Green from the Department of Chemistry who won the 2005 CSEM Prize for best thesis in the category of Science of Materials. Ms Green's thesis was on the synthesis of a second generation ruthenium-alkynyl dendrimer.

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