CSEM's
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April 2007 Making materials matter

Clean in an ultrafast flash

Using ultrafast lasers for materials conservation

For most people a pulse length of a billionth of a second would seem fairly short. For laser physicists at ANU interested in materials conservation, however, it's way too long. They're investigating what's possible in terms of cleaning precious materials when you apply ultrashort laser pulses – pulses measured in pico- and femtoseconds. Preliminary results suggest they're onto a winner.

Laser cleaning of cultural objects is not a new concept; lasers have been used to clean the surfaces of buildings and sculptures since the late 1980s. However, materials conservators have remained cautious about the use of lasers when it comes to cleaning smaller, more delicate objects because the conventional approach simply isn't precise enough.

Laser induced removal of surface layers (or 'laser ablation') has a lot to offer when it comes to cleaning the surfaces of valuable cultural materials. It has the potential to remove dirt, overpainting and other surface contaminants without the treated surface being physically touched or having chemicals applied. Laser ablation and micromachining of surfaces is already in widespread use in the semiconductor, automotive, and aerospace industries due to its lower costs, higher throughput and reduced toxicity problems compared to other cleaning methods. Correctly applied, laser cleaning can minimise or avoid both mechanical and chemical disruption of historic surfaces and, in certain circumstances, can selectively remove contaminating dirt or coatings.

A nanosecond is too long

Until now, lasers used to perform conservation tasks have had pulse durations of nanoseconds or longer, and the wavelength, intensity and pulse length have had to be carefully chosen to tailor the laser to different materials and tasks. Nanosecond pulse laser ablation works by evaporating surface layers by breaking molecular bonds through heating or photochemistry.

However, the ablation process with nanosecond pulses tends to heat and crack the bulk of material under the surface, due to the formation of shock-waves or heating of the surface. This represents an undesirable degradation of the material being cleaned and

continued on next page

Inside this MM

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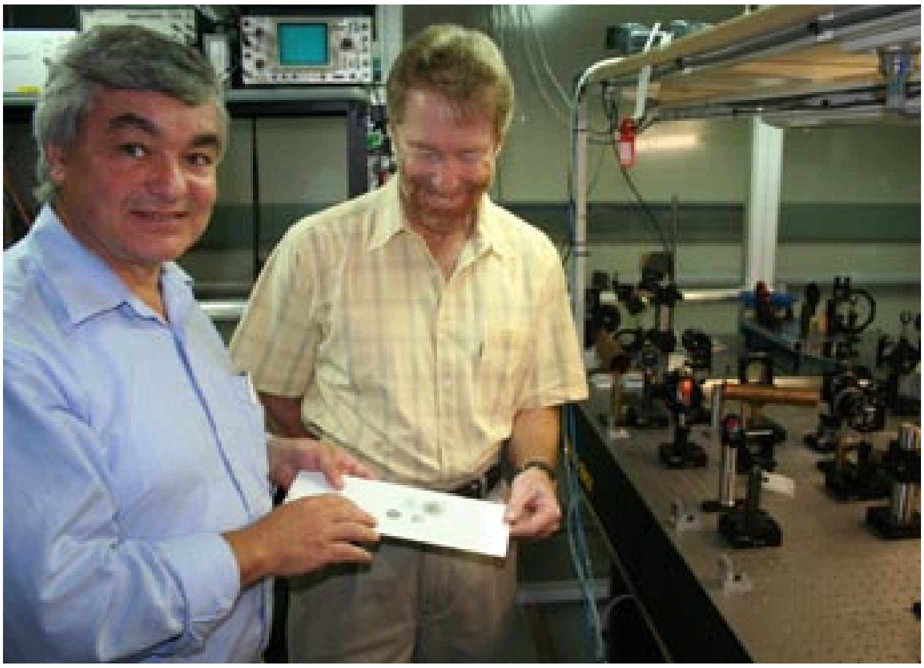


Dr Andrei Rode (on the left) discusses a sample of a laser cleaning experiment with Dr Ken Baldwin in the Laser Physics Lab. "The laser is powerful enough to remove the surface layers of paint, indeed it actually produces a plasma layer, which looks like a flame," says Dr Rode. "However, because the laser was fired in such short pulses, none of the heat penetrates deeper than the surface."

Clean in an ultrafast flash

(continued from previous page)

materials conservators, therefore, have been wary in applying the technique to valuable items or objects made from a mixture of materials.

But the limitations of the nanosecond lasers may well be over come by using ultrafast lasers. In the last decade lasers have been developed that are capable of delivering laser pulse lengths of picoseconds down to femtoseconds (a femtosecond is a millionth of a nanosecond – see box on how long is a femtosecond). The manner in which these ultrafast lasers interact with matter is fundamentally different to nanosecond lasers. They can ablate matter with high precision and virtually no effect on the surrounding material.

Ultrafast lasers at ANU

Dr Andrei Rode from the Laser Physics Centre at the Research School of Physical Sciences and Engineering has been working with ultrafast lasers for a many years and together with Dr Ken Baldwin from the Atomic and Molecular Physics Laboratory is investigating the potential of ultrafast lasers for use in laser cleaning of heritage art objects.

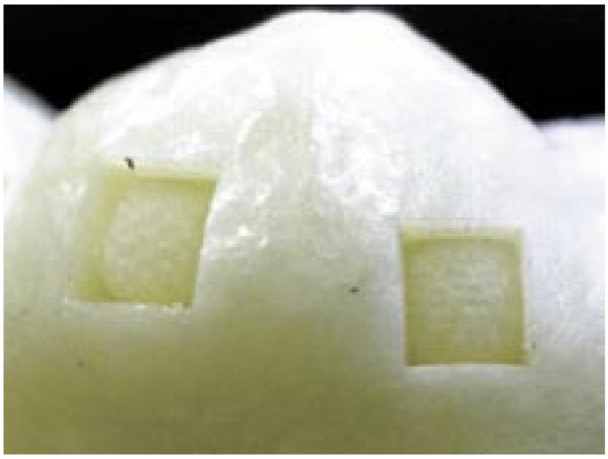
"The investigation arose from discussions I had with local art conservators on the interaction of lasers with matter," says Dr Baldwin. "They expressed an interest in learning more about what might be possible with ultrafast lasers and the conversation grew to include a number of cultural institutions from around Australia.

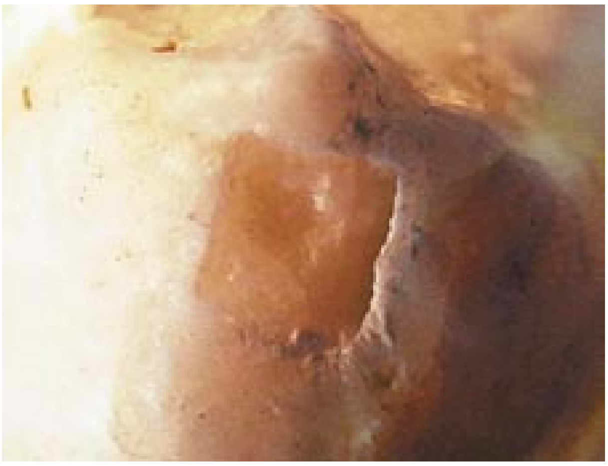
"At ANU we have a suite of lasers that provide a wide range of pulse lengths ranging from nanoseconds (10^{-9} seconds) all the way down to a hundred femtoseconds (1 fs = 10^{-15} seconds). We're in a unique situation because we can use conventional laser cleaning techniques which involve longish pulses, by that I mean nanosecond pulses, and compare the results from those with the very short pulse techniques that have been developed here by Andrei and his colleagues Eugene Gamaly and Barry Luther-Davies. Ultrafast lasers allow us greater control on the removal of layers of materia down to molecular layer thickness."

The ultrashort advantage

"The interaction of ultrashort laser pulse with materials is very different to the way in which the conventional, long-pulse lasers interact with matter," says Dr Rode. "The boundary between the short laser pulses and the long laser pulses is a clear physical quantity for each particular substance which determines if the heat wave and shock wave generated by the laser pulse can penetrate into the bulk of the material. If the pulse is short enough so that there is no time for the heat wave to propagate into the bulk of the material during the ultrashort laser pulse then you don't have any heat load or shock wave load in the layers underneath the surface layer, the so-called skin layer, where the laser light is absorbed. If the pulse is shorter than this we call it an ultrashort pulse.

"Ultrashort laser pulses interact with matter in a non-equilibrium way meaning that there is no temperature equilibration between the electron component and the ion component. What happens is that the laser can remove material from the surface with ultra short pulses but there is no heatwave or shockwave propagating into the bulk, which stays untouched without any detrimental effect to the underlying layers and without any collateral damage to the surrounding material.





What a difference a moment makes: Optical microscope images of 1 mm2 craters on a tooth surface ablated with 150-fs laser pulses (top) and 60-ps pulses (bottom). There is no damage to the area around the fs-laser ablated cavity; the edges are sharp and the crater floor is smooth; the temperature rise is in the range 2.4°-3.6°C. On the contrary, cracks and thermally affected boundaries are clearly seen around the 60-ps ablated cavity; the temperature rise is above 50°C. Average laser power ~1W, ablation time 2 minutes in both cases.

"I have to say that we have only just started this investigation on laser cleaning of objects of art, however, we have done some preliminary experiments that show us that the process actually works. Now we need to put a lot time and effort into adjusting it. We're currently developing hardware for the experiments."

When do you stop?

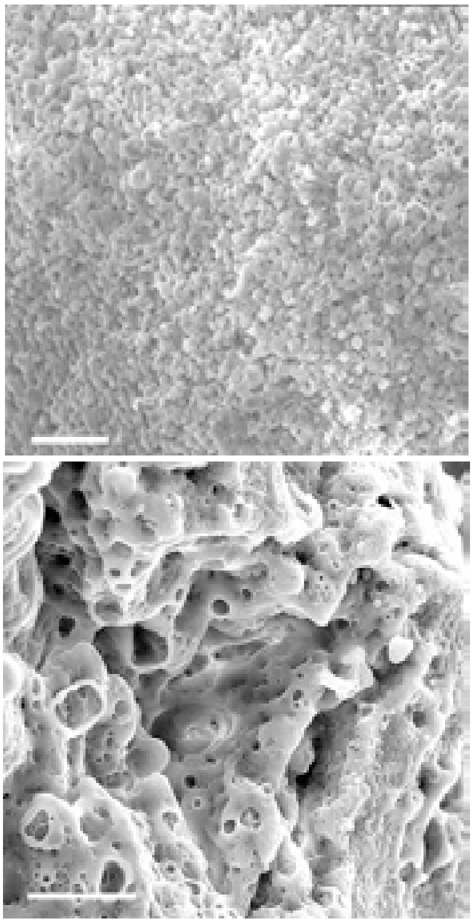
"A major challenge is to arrange a feedback that tells you when you've finished removing the dirt from the surface and you start touching the

How long is a femtosecond?

Ultrafast lasers generate very short, powerful pulses which are measured in femtoseconds (fs). A femtosecond is a millionth of a billionth of a second (1 fs = 10^{-15} s), a time period so incredibly short it's impossible to conceptualise it in relation to everyday life. There are more femtoseconds in one second than there are seconds in 30 million years. This is 10,000 to 100,000 times shorter than the nanosecond pulses produced by lasers currently used in conservation. When nanosecond (long-pulse) lasers interact with matter, they do so under normal equilibrium conditions. When ultrashort laser light pulses interact with matter, it results in non-equilibrium conditions allowing them to ablate matter with high precision and with virtually no effect on the surrounding material.

original material," comments Dr Rode. "For example, when do you know you've reached the underlying painting or metal?"

"Consider, for example, if you have a fabric with a gold thread and you want to clean the thread without touching the fabric. Lasers could do this but you would have to know the chemical composition of the material you want to clean and



Scanning electron microscope images of the cavity floors shown on page 2. In the case of 150-fs pulse ablation (top) and 60-ps pulse (bottom). The 150-fs ablated floor is smooth, while the 60-ps one shows cavities and a "boiling" surface, indicating a lot of heat at the surface. The scale bars are 10-μm long in both images.

the dirt you want to ablate. One of the major tasks of our project is to develop a feedback control by spectral analysis of the ablated material so that we can choose exactly the moment when we have the right and wrong spectral lines appear in the spectra. This provides a feedback to stop or continue the laser scanning over the surface for cleaning.

"Such feedback control using the spectra of the ablated species is already in use in some medical and dentistry applications so we have an idea of where to start with this. With laser drilling in dentistry, for example, they can separate the spectra of caries from the spectra of healthy enamel. Caries is a demineralisation of the tooth surface caused by bacteria, it's the products of decay. They use the spectral characteristics of the ablated plume so we have a general idea of where to start with this. Of course, the chemistry and the processes we're dealing with in materials conservation are completely different."

A powerful femtosecond laser has recently been purchased and set up in the Laser Physics Lab.

"This new laser can generate up to 10 watts of laser power with a repetition rate up to 250 kilohertz and the pulse duration is about 150-160 femtoseconds," says Dr Rode. "It's a commercial laser worth several hundred thousand dollars and it's actually being used for work on about five different projects."

"We're also using another powerful high-repetition laser that fires pulse lengths of 10 to 12 picoseconds. It's a unique laser which has taken us over three years to put together. There is no other laser like it. While it produces pulses that are about 100 times longer than our new femtosecond laser, the repetition rate is much higher and the average power is much greater. We have 50 watts of energy and we can change the repetition rate from approximately 150 kilohertz through to 28 megahertz so the time duration between the pulses can be as short as 30 nanoseconds. This laser is more useful for ablation and deposition of thin films."

New frontiers

While ultrafast lasers hold a lot of potential for materials conservation, the scientists are keen to point out that it's still early days.

"So far, ultrafast lasers have only been used in experimental research labs," says Dr Baldwin. "At the moment they are still prohibitively expensive and not adapted to the industrial environment. They simply aren't available as a convenient conservation package – in fact, almost no conservators have access to them.

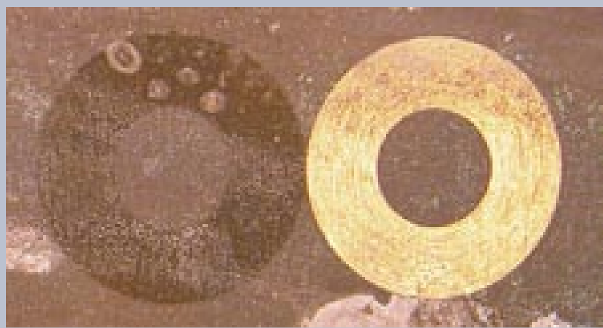
continued on page 6

Gone in a flash

How does an ultrashort laser pulse remove surface material from an object? The electrons at the surface of a layer take up the laser energy and use it to break bonds within the immediately surrounding molecular structure. Ions, however, are much heavier – their inertia does not allow them to move quickly enough to follow the fast oscillations of the laser wave, so the laser energy stays within the ion and does not get propagated to surrounding molecules. The electrons are therefore heated to tens of thousands of degrees, while the ions remain cold. This is a non-equilibrium (and very transient state) of matter.

The term 'ultrafast' thus represents laser pulses shorter than the time of equilibration of energy in the material. This time depends on the particular material, but in general is shorter than 10 picoseconds.

The electrons expand away from the surface, pulling the charged, ionised atoms (which were created by the cascade of electron liberation), out of the surface by electrostatic attraction - a process known as electrostatic ablation. In contrast to the equilibrium conditions of laser ablation at longer timescales, where atomic motion allows heat and shock waves to propagate into the underlying material, non-equilibrium conditions cause the laser-heated surface material to vanish before any heat or shock wave can propagate into the surrounding bulk.



Brass coated with paint and wax after laser cleaning with varying energy levels. The experiment demonstrates the control over single layer removal achievable by appropriate selection of incident laser fluence

On silver, art, copper and firescale

Eileen Procter is a materials conservator, researcher and artist. Her work on the properties of a range of silver alloys was recently recognised with the awarding of the 2006 CSEM Prize for Applications of Materials, and she believes there's a lot to be said for mixing a bit of research with a bit of hands-on practice.

"My education in materials began with a degree in materials conservation at the University of Canberra," says Ms Procter. "I've been applying this knowledge as a materials conservator at the Australian War Memorial since 1994. However, I've found the studies I've done in the Gold and Silversmithing Workshop at the ANU School of Arts have given me new perspectives on working with metal, especially silver.

"In the conservation course you get a lot theory about metals but it doesn't give you any practical experience of working with them – there's no fabrication, no raising or hands-on metal work. Now I've researched the properties of a range of silver alloys and applied this knowledge in silversmithing.

"I've taken this experience back to my conservation work and I find I'm better prepared to work with metals in a number of ways. As one example, the latest travelling exhibition at the War Memorial is called 'Sport and War' and includes the display of many trophies. There is one particular trophy where they had soldered the letters 'Australia' on the outside of the cup, and it was really discoloured. From my research in the workshop I knew instantly that this discoloration was firescale, they hadn't bothered to clean it up properly afterwards, so I knew that in future I can polish it and it'll look pretty spiffy for the first exhibition but it'll keep coming back because the problem is in the metal. That's something you learn from being a practitioner."

And when it comes to spotting firescale, Ms Procter is now something of an expert as this was a central focus of her work on silver alloys.

"My research in the Silversmithing Workshop looked at new silver alloys available on the market and how their properties compare with that of traditional Sterling Silver. Fine silver (that's 99.9% commercially pure silver) is too soft for hard-working items such as spoons, bowls and vessels. It's alloyed with other metals to augment its wear resistance – to increase its strength without losing its ductility, colour, brilliance or formability.

"Sterling silver is the international standard for alloys containing 92.5% silver. The remaining 7.5% is undefined within the standard but traditionally the metal has been copper. However, the addition of copper to the silver brings a new problem – firescale.

Eileen Procter and Johannes Kuhnen hold up objects created using silver alloys. "It's important from a practitioners point of view to know the plastic and elastic properties and limits are of a particular alloy," says Ms Procter. The object she's holding is a vase titled "Aqua Vitae" that she made from Sterling silver. The coffee pot held by Mr Kuhnen was created by the artist Robert Foster and was made with Sterling silver and epoxy resin.

"Firescale forms during heating, when oxygen reacts with the copper on the surface of the alloy. With increased and prolonged heating this can diffuse into the alloy. While surface oxides can be removed by soaking the object in 10% sulphuric acid, the sub-surface oxides remain. The presence of these oxides is revealed only with the removal of metal during finishing stages and is evidenced as a dark grey stain on an otherwise silver surface. This stain is not only unsightly but also weakens the structure of the metal by causing splitting or delamination along the metal/oxide layers.

"With the traditional silver/copper Sterling alloy, there are several ways in which firescale can be limited but not altogether avoided. You can remove the surface oxides by annealing in a salt bath, by using a protective atmosphere during all heating operations or by coating the metal with various chemicals prior to heating the alloy; however, all of these treatments takes time and resources.

"In recent years many new alloys have been made available to silversmiths that reputedly eliminate firescale by either replacing the copper with one or more other metals (such as zinc, platinum or cadmium) or by replacing a small amount of copper with germanium (up to 1.6%). Germanium is a metalloid that was used in transistor radios before silicon was available. During heating, the oxygen reacts with germanium in preference to copper. The germanium oxide layer then prevents oxygen from reacting with copper, thereby preventing firescale."

While new Sterling Silver alloys are available for silversmithing, no-one has actually compared their properties for this type of work so Ms Proctor set about testing five of them – Argentium, Bright Silver, Lustre Silver, Oxantis and Sterilite Silver – against those of spinning silver and traditional Sterling Silver. She tested each alloy for hardness, tensile strength, elastic and plastic deformation, ductility, compression and raising characteristics.

"It's important from a practitioner's point of view to know the plastic and elastic properties and limits of a particular alloy," she says. "In

Ms Procter with a set of silver samples stretched by the Department of Engineering's Instron machine to test the ductility of the various alloys.

raising you start with a flat plate and move it up, changing the angle but not the thickness, and the elastic limit is important to this process. But, if you're forging or sinking (where you let a flat sheet slump into a space), you're stretching the metal and that's where plastic deformation comes in. What I've found is that Lustre Silver has very short area of elasticity but a huge plastic quality so it's great for forging and sinking but not so good for raising. What it means is that you can't hit it as hard or for as long as, say, Stirling Silver."

"Having industry developing new alloys is very beneficial but they all come with side effects," says Johannes Kuhnen, Head of the Gold and Silversmithing Workshop. "With research such as Eileen is carrying out we're better placed to say what we feel are the best, most appropriate silver alloys for specific jobs. Her work provides us with some sound data with which we can go back to the manufacturer and suggest how an alloy might be produced in a form that we can use, or maybe suggest directions for other mixes."

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For more info on the Gold and Silversmithing Workshop, please see the March 2007 issue of Materials Monthly, available at the MM archive: www.anu.edu.au/CSEM/newsletter.php

A diversity of materials at the AWM

The Australian War Memorial has a number of conservation laboratories housed at the Treloar Conservation Centre (in Mitchell). Conservation activities include technical and scientific studies on objects, stabilising the materials and structure of damaged objects, performing restoration work where damage to an object has made it structurally unsound or difficult to display, and establishing the environment in which artifacts are best preserved.

At the Memorial, conservators care for large technology, small objects, textiles, photographic, paper and art collections. There are also staff working in the fields of conservation science and preventive conservation. An analytical chemistry laboratory provides additional support for research programs, which investigate the vast range of deteriorating materials found in objects in the collections as well as new ways of conserving them.

Eileen Procter is based in the Small Objects laboratory, and faces new challenges everyday.

"We used to be called the metals lab but you don't just get metals; it's metals and wood, metals and plastic, metals and anything," she explains. "We're sort of a catch-all area. What ever doesn't fit into the other sections, like food and pharmaceuticals, comes here.

"Of course, when we're talking about food we're mainly talking field rations for soldiers. The earliest form of rations we've had were from the Boer War in 1895. It was a small metal tube bearing a used-by-date of 05, which is of course meant 1905, not 2005. There was pin-hole corrosion at one end of the tube so we decided to cut it open, take the rations out, treat the corrosion and then solder it back together for display. The food it contained which turned out to be two different meals separated by a thin division. One was a soup like powder and the other was chocolate cake, which is what caused the corrosion.

"And then there's our biscuit research, an area in which the AWM has been quite active. A lot of First and Second World War biscuits were described as hard tack, and they really do mean hard tack. I think the soldiers had to soak them in tea to soften them up though many men actually used them to write on and sent them home as letters. The last biscuit I treated was written on with a felt tipped pen and the ink didn't bleed out at all so the material had little moisture in it. Fifty years on they're still quite intact.

"The day to day challenge of this work is dealing with a wide variety of objects, most of which present a complex mix of materials. For example, at the moment I'm working on a German decontamination kit, though what it decontaminated and how it was used is unknown. We simply don't know what chemicals it contains. It's leaked in the time its been stored and the first thing I have to ask myself is 'what do I have to do protect myself when handling it?'

"The kit is made of a variety of materials including a metal tin, bakelite, coated cardboard, a plastic ribbon and cotton wool. The tin itself is very badly corroded and the kit came from the Australian Chemical Warfare lab, which no longer exists making it hard to know its provenance.

"We do chemical, electro-chemical or abrasive treatments depending on what we're trying to achieve. With Japanese swords, for example, you try to use the least invasive treatments possible. Sometimes, however, you get corrosion on the blade from fingerprints and occasionally get filigreed corrosion as well. My preference is to apply an abrasive treatment using micromesh emery papers. You use a square the size of your fingertips. Or you could treat it with acids applied with an eyedropper on a spot. Watch it, remove it and neutralise it and then dewater it to make sure you don't go too far. I think that's the whole point of materials conservation – it's about not going too far."

More info: www.awm.gov.au/aboutus/conservation/index.htm

Eileen Procter examines a WW2 German decontamination kit.

Clean in an ultrafast flash

(continued from page 4)

"Close collaboration between scientists and conservators is therefore vital for development of a successful, practical ultrafast laser system for conservation. It's our hope that with investigations such as this it's only a matter of time before ultrafast laser ablation becomes a standard tool in the conservation armoury and a key technique for conserving previously untreatable artworks and heritage objects."

A better tool for cleaning

And the materials conservators are just as excited by the potential of the investigation.

"It's a really interesting project," says Alison Wain, a Senior Objects Conservator at the Australian War Memorial and one of the conservators involved in the project.

"One of the things we're particularly interested in at the Australian War Memorial is using laser cleaning to remove hazardous materials, something which is more common in our work than in most museums and art galleries. So, rather than contaminate gloves and swabs (and yourself) getting rid of hazardous materials, we would like to simply remove them remotely with a laser and suck the ablated material away via a capture head.

"Unfortunately, conventional nanosecond-pulse laser cleaning can cause a lot of damage to the surface, so at the moment their cleaning capabilities are mainly limited to robust materials like metals, ceramics and wood. It's fairly broad brush stuff.

"The ANU investigation into ultrafast lasers, however, promises to overcome these constraints and assist in developing a tool that is incredibly precise about exactly what it removes. Of course, if you're using it for something like paintings that's really important because you might have brush strokes that are very very thin.

"We'll be supplying some test objects and test samples for the scientists to work with. While we know it's still early days in the investigation, it's an exciting project and we're proud that the Australian War Memorial is a partner in the research."

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For more information on the work of the Australian War Memorial, see the story on page 5.

"One of the things we're particularly interested in at the Australian War Memorial is using laser cleaning to remove hazardous materials," says Alison Wain at the AWM.

Partners and objectives

The investigation into using ultrafast lasers for the conservation of cultural materials is a three year project supported by the Australian Research Council, the Australian National University and industry partners including the Australian War Memorial, Army History Unit, Department of Defence (Naval - Spectacle Island), Art Gallery of New South Wales and Artlab Australia. The projects specifically aims to :

• Design and construction of an experimental facility – laser focusing system and computer-controlled scanning system – for laser ablation of surface layers of various materials;

• Design and construction of laser plume diagnostics, including spectral characterisation of the laser plume, monitoring of temperature and spectral composition around the focal spot and video control of the surface layer removal process;

• Building a real-time feed-back laser control system for laser on/off operation depending on particular spectral line characteristics in the plume;

• Experimental tests on removal of surface contamination, testing various scanning patterns to achieve a homogeneous irradiation pattern on the surface;

• Experimental tests on complex profiles, where there are large/sudden variations in the depth profile and/or composition of either the contamination or the underlying material;

• Prior and post-characterisation of the treated surface, including physical profile, Raman spectra analysis, optical and electron microscopy and ion-beam milling to perform cross-section analysis of the treated and untreated surfaces;

•Collaboration with Aix-Marseille II University, Marseille, France, to develop a special decontamination chamber for laser decontamination of radioactive objects.

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