

**NPL REPORT
DEPC-MPE 032**

**Non-Invasive Methods for
Monitoring Microstructural
Condition of Materials**

W R Broughton and J Nunn

NOT RESTRICTED

September 2006



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Engineering and Process Control Division**

ABSTRACT

A critical evaluation has been carried out on non-invasive techniques for the detection of damage and the characterisation of microstructural changes that occur during the life cycle of materials from processing through to in-service operation. The techniques were grouped into 8 different categories. This review does not present the theory and full operation of the techniques in great detail, but notes their strengths and weaknesses and their range of application. This review is carried out from a generalist's point of view and keeps foremost in mind the likely usefulness of individual techniques to the current and projected work carried out in the Division of Engineering and Process Control of the National Physical Laboratory. A short list comprising one candidate technique for damage assessment and four candidates for microstructural evaluation is presented.

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1 INTRODUCTION

There is increasing demand for more sophisticated methods for non-invasive characterisation of microstructural changes that occur at the surface and within the bulk material as a result of processing or in-service operation. In response to this demand, there have been rapid advances in the development of non-destructive evaluation (NDE) or non-destructive inspection (NDI) techniques for examination and analysis of materials and manufactured components and assemblies for design, quality control and in-service inspection purposes. These techniques can provide quantitative information on the size, shape, distribution and location of particulates, grains and defects, and surface chemistry and morphology. It is expected that the introduction of new techniques will reduce the need for expensive materials preparation prior to testing, and provide a technology solution for online process control. Additional benefits expected to include improved quality control and reduction in product wastage, and early detection of adverse material changes due to processing enabling remedial steps to be carried out early in the lifetime of the product, and in-service component failure enabling timely servicing and maintenance. Reduction in the need for time consuming metallographic preparation of samples by enabling online measurements, will lead to significant cost savings for material producers and equipment manufacturers, as well as cost savings in future NMS projects.

This report critically examines non-invasive techniques for monitoring microstructural changes and damage formation during the life cycle of a material or component (i.e. processing and in-service). These techniques have been assessed as to breadth of application, sensitivity, resolution, ease of use and cost, for identifying and quantifying microstructural changes. Consideration is given to their suitability for industrial applications (i.e. production and service inspection) and material types (e.g. metallic, polymer, ceramic, semiconductor and composite). The review provides recommendations on the techniques to be investigated. This is a necessary step to guide and inform the experimental programme. The report forms part of a review for the DTI funded underpinning research project “**SM07: Assessment of Damage and Microstructural Condition of Materials Using Non-Invasive Techniques**”, which aims to investigate the potential of non-invasive techniques for characterisation of microstructural changes and mechanical damage that occur during the life cycle of materials/components. Diagnostic tools will be developed within the project to facilitate the application of novel non-invasive techniques to subsequent projects in National Measurement Systems (NMS) Materials Programmes.

The techniques are presented broadly in groups by the principles used, but unavoidably there are some techniques, which straddle classification and as such could belong in two or more categories.

2 VISUAL INSPECTION

Although the number of non-destructive testing techniques available to the materials scientist and engineer is very large, the most universally applied is still visual inspection. It is often a preliminary visual inspection that leads the test engineer to locate the most likely place to find damage, degradation or microstructural changes of interest or concern.

2.1 DYE PENETRANT

The unaided eye is frequently unable to detect micro-cracks until they become relatively large, by which time the component has long been critically dangerous. In order to aid visual inspections of surface and subsurface fractures use is made of dyes and penetrants.

The dye penetrant method consist of painting the surface of the material to be tested with a low viscosity dye which is then attracted to microscopic surface fractures through capillary action (see Figure 2.1). The excess dye is removed and fractures which otherwise might have not been detected through optical or microscopical inspection become easily visible.



Figure 2.1: Use of dye penetrant to highlight small cracks.

It is frequently necessary to grind the material surface flat, to remove any porous surface corrosion that would otherwise attract the penetrant. The technique is not suitable to highlight any sub-surface defects.

This technique is suitable for detecting the presence of voids and solid inclusions (e.g. backing film) in the bondline. Thin debonds and delaminations are difficult to detect because the presence of these defects has minimal effect on the absorption characteristics of polymeric materials. The use of penetrant fluids can enhance the imaging process, however, these fluids can adversely affect the short-term properties and fatigue performance of polymeric materials. Penetrants should not be used to assist damage monitoring in those tests where the test data is to be used for design or quality assurance purposes. Small tensile loads or the use of a vacuum pump can be used to promote fluid penetration.

2.2 MAGNETIC PARTICLE PENETRANTS

This technique is similar to the dye penetrant, but the liquid contains small ferromagnetic magnetic particles. The material is then magnetised strongly, and any surface or sub-surface features (e.g. defects or inclusions), which affect the local magnetic permeability will cause the magnetic field to be diverted towards the surface.

The small ferromagnetic particles will be attracted to region of increased magnetic field strength and so highlight their positions. Clearly this fault location and enhancement technique is only applicable to ferromagnetic materials.

3 OPTICAL TECHNIQUES

This section examines a number of techniques for producing visible images of structures or details too small to be visible by the human eye, using an optical microscope (or other magnification tool). Microscopy involves either the diffraction, reflection, or refraction of radiation incident upon the subject of study and the subsequent collection of this scattered radiation in order to build up an image of the surface being inspected. This process may be carried out by wide field irradiation of the sample (e.g. standard light microscopy) or by scanning of a fine beam over the sample (e.g. confocal laser scanning microscopy).

3.1 OPTICAL MICROSCOPY

Following visible inspection by eye, optical (or light) microscopy is generally the next approach used for inspecting changes in microstructure. It involves passing visible light that has been either transmitted through or reflected from the subject through a series of lenses to be directly observed by the eye, or imaged on photographic film or captured digitally. Optical microscope consists of the entire system of lenses, imaging and lighting equipment, and sample stage. There are a number of limitations associated with optical microscopy. These include:

- The technique can only image dark or strongly refracting objects,
- Maximum resolution is $\sim 0.2 \mu\text{m}$ on very idealised objects, normally the resolution is limited to $0.5 \mu\text{m}$.
- Image clarity is reduced by out of focus light from points from outside the focal plane. At the highest magnifications (where the maximum resolution is possible) the depth of focus is of the order of $1 \mu\text{m}$.

Contrast enhancement can be achieved through staining different structures with selected dyes (e.g. biological samples), however care is needed to ensure that staining does not introduce artefacts. These limitations have to some degree been resolved through the development of microscopy techniques designed to examine specific materials or microstructures (see micrograph in Figure 3.1), or to obtain specific information about optical or other properties of the specimen. A number of these optical microscopy techniques are briefly described below.

3.1.1 Bright Field Optical Microscopy

This is the simplest of all the light microscopy techniques. It may be carried out either with transmitted illumination (i.e. sample illuminated below and observed from above), or with reflected illumination (i.e. the sample is illuminated via the same objective that images the object). No sample preparation is normally required, although limitations due to working distance may dictate that the object be sectioned so that particular pits or depressions can be brought into focus.

The two main disadvantages are that there is often very low contrast, which is not particularly suited for biological samples, and low apparent resolution. A useful image enhancement technique involves the use of coloured or polarizing filters on the light source to increase visibility of features under white light. Other enhancements include the use of oblique (sideways) illumination, thus giving a three dimensional (3-D) appearance and highlighting features that may otherwise appear invisible. The main advantage of using bright field optical microscopy is the simplicity of set-up with only basic equipment required. No sample preparation is required. Figure 3.1 shows typical images obtained using bright field optical microscopy.

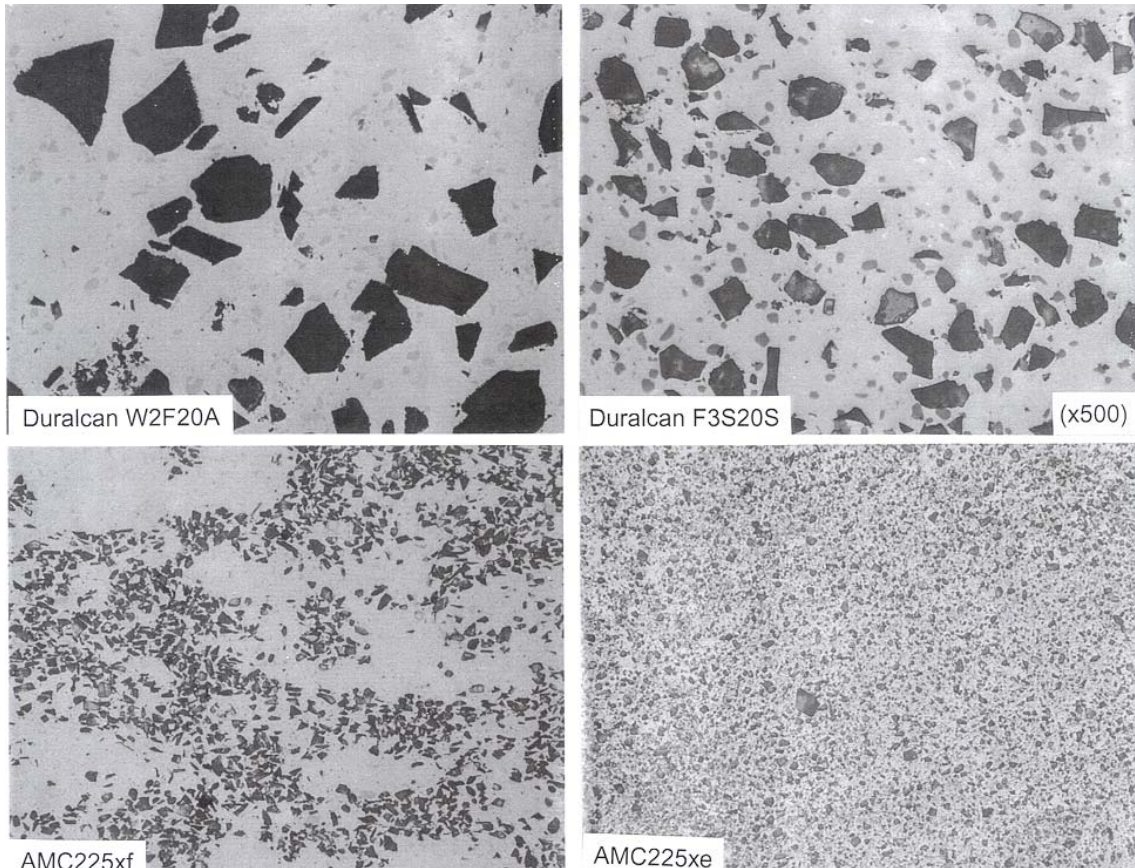


Figure 3.1: Optical images of particulate reinforced metal matrix composites [1].

3.1.2 Dark Field Optical Microscopy

Dark field optical microscopy employs a carefully aligned light source to minimise the amount of directly transmitted light entering the image, and only collected light scattered by the sample. This is achieved by confining the illumination to a ring of light. The advantages associated with bright field optical microscopy in relation to equipment requirements, simplicity of set-up and little sample preparation also apply. Transparent objects in the sample are visible using this technique. Low light intensity and low apparent resolution are limitations still confronting this technique.

3.1.3 Phase Contrast Optical Microscopy

Phase contrast is able to show differences in refractive index as differences in contrast. The optical system consists of a circular annulus in the condenser, which produces a cone of light. The cone is superimposed on a similar size ring within the phase objective. Every objective has a different size ring, and therefore the condenser setting needs to be adjusted for every objective. The ring in the objective reduces the direct light in intensity and most importantly creates an artificial phase difference of about a quarter of a wavelength. The phase change in direct light results in interference with the diffracted light resulting in the phase contrast image. Contrast is excellent, although the technique is unsuitable for thick samples. Another problem frequently encountered is the formation of a halo, even around small objects, which can mask details.

3.1.4 Differential Interference Contrast Microscopy

An improvement on the phase contrast system; a differential interference optical microscope consists of a Wolaston (double image) polarizing prism in the condenser that splits light into two orthogonal, linearly polarized outgoing beams (ordinary and an extraordinary). The spatial difference between the two beams is minimal (less than the maximum resolution of the objective). After passing through the sample the two beams are reunited by another Wolaston prism. A Wolaston prism consists of two orthogonal quartz or calcite wedge-shaped prisms, cemented together on their base to form two right triangle prisms with perpendicular optic axes. The prism separates randomly polarized or unpolarized incoming light. The emergent light beams diverge from the prism, giving two polarized rays, with the angle of divergence determined by the prisms' wedge angle and the wavelength of the light.

For homogeneous samples, there is no difference between the beams, and thus no contrast results. Polarized light is required for differential contrast to work properly. Near refractive boundaries, the difference between the two beams will generate a relief in the image. Two polarizing filters are fitted to the light path, one below the condenser (polarizer) and one above the objective (analyzer). Contrast is very good and the condenser aperture can be used fully open, thereby reducing the depth of field and maximising resolution.

3.1.5 Polarized Light Microscopy

Polarised light microscope provides not only all the information possible using a bright field microscope, but also information on absorption colour and boundaries between minerals of differing refractive indices. It can also distinguish between isotropic and anisotropic materials. Anisotropic materials, unlike isotropic materials that have one refractive index and the same optical properties in all directions, have optical properties that vary with the orientation of incident light with the material axes. Anisotropic materials demonstrate a range of refractive indices depending upon the propagation direction of light through the substance and the vibrational plane coordinates.

Anisotropic materials act as beam splitters and divide light rays into two parts (ordinary and extraordinary beams). Polarized light microscopy exploits the optical properties of anisotropy (i.e. interference of the split light rays, as the beams are re-united along the same optical path) to reveal detailed information about the structure and composition of materials, which are invaluable for identification and diagnostic purposes.

3.1.6 Confocal Laser Scanning Microscopy

Confocal laser scanning microscopy is a relatively new technique, which offers significant advantages over conventional optical microscopy. The microscope enables high-resolution images and 3-D constructions, and enhanced image resolution both laterally and axially. This microscope uses a laser and scans the light across the specimen with the aid of scanning mirrors. The light is then collected through a small pinhole aperture, thereby preventing detection of all light except for that originating from a thin optical section. By collecting a series of optical sections through the thickness of the specimen, images of its 3-D organization can be collected, assembled, and displayed using specialized reconstruction software.

Confocal microscopy is well suited to the examination of thick specimens for which out-of-focus light, using conventional microscopy, would obscure structural details. It is also a useful tool for materials scientists interested in topological characterization of surfaces. The key feature of confocal microscopy is its ability to produce blur-free images of thick specimens at various depths. Images are taken point-by-point and reconstructed with a computer, rather than projected through an eyepiece. It is particularly suited for examining biological samples (e.g. tissue and cells). Confocal microscopes have the capability of observing line/space patterns of 0.12 μm , and measuring the thin transparent films ranging from 1 mm to 1 μm in thickness. Non-contact roughness measurement with the level of $R_{max} = 0.1$ mm are possible.

3.1.7 Infinite Focus Microscopy

The 'infinite focus' microscope is an optical device for 3-D surface measurement. Its operating principle combines the small depth of focus of an optical system with vertical scanning to provide topographical and colour information from the variation of focus. It employs algorithms to reconstruct the image into a single 3D data set with accurate topographical information. Traceable calibration standards allow the verification of measurement results. Vertical or z-direction resolution can be as low as 20 nm making the instrument ideal for surface study of both homogeneous and compound materials. A lateral resolution of 0.4 μm can be achieved at high magnifications (x20, or higher). Field of view ranges between 0.2 mm^2 and 50 mm^2 . Working distance ranges between 3.5 mm and 8.8 mm with working distance being smaller at high magnification.

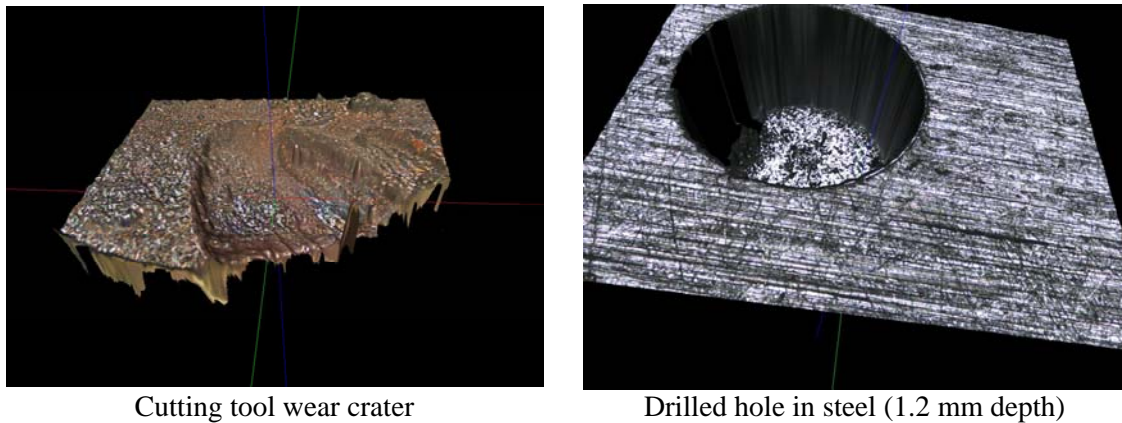


Figure 3.2: 3D optical images (Alicona infinite focus microscope)

The instrument can be used in both the laboratory and near production environment, it can also be operated by semi-skilled technicians where required. Automation of functions and analysis can also be added to make the instrument useable for the majority of surface metrology and inspection requirements. The instrument has the facility for surface contour mapping, and measurement of surface area, volume and surface roughness (according to EN ISO 4287/88 standards). Applications include quantitative analysis of fracture surfaces, crack growth, corrosion deposits, hardness indentation, abrasion and wear, stress and heat deformation, particulate properties (size and orientation distribution) and hole dimensions (see Figure 3.2).

A combined atomic force microscope (AFM) and scanning near-field optical microscope (SNOM) has been constructed to obtain images under liquids. In this combined AFM-SNOM an inverted ac mode configuration is used where the AFM cantilever is driven by exciting acoustic modes of the liquid cell. Optical images of latex spheres on a cantilever have been obtained under perfluorononane, butanol, and water with a lateral resolution of 100 nm. Fluorescence images of latex spheres have been obtained under perfluorononane. The ability to image under liquids opens up a wide range of applications of near field optical microscopy in chemistry and biology.

Limitations to infinite focus microscopy arise from edge shadowing effects. Specimens with tall vertical walls will stop the light either from reaching the surface, or from being collected by the objective after reflecting from a deep surface close to the edge. Image information close to tall edges is frequently lost

3.2 ELLIPSOMETRY

Ellipsometry uses polarized light to measure the thickness and refractive index of thin films. The technique consists of directing a polarised light beam onto surface at an oblique angle of incidence and measuring the rotation of the angle of polarisation of the reflected light. Multiple reflections interfere, as illustrated in Figure 3.3, to provide information about the layer thickness t , optical constant \mathbf{n} (index of refraction) and extinction coefficient \mathbf{k} (a measure of absorption) for each layer interacting with the incident beam. Ellipsometry can yield information about the thickness, morphology and chemical composition of layers that are thinner than the wavelength of the light source.

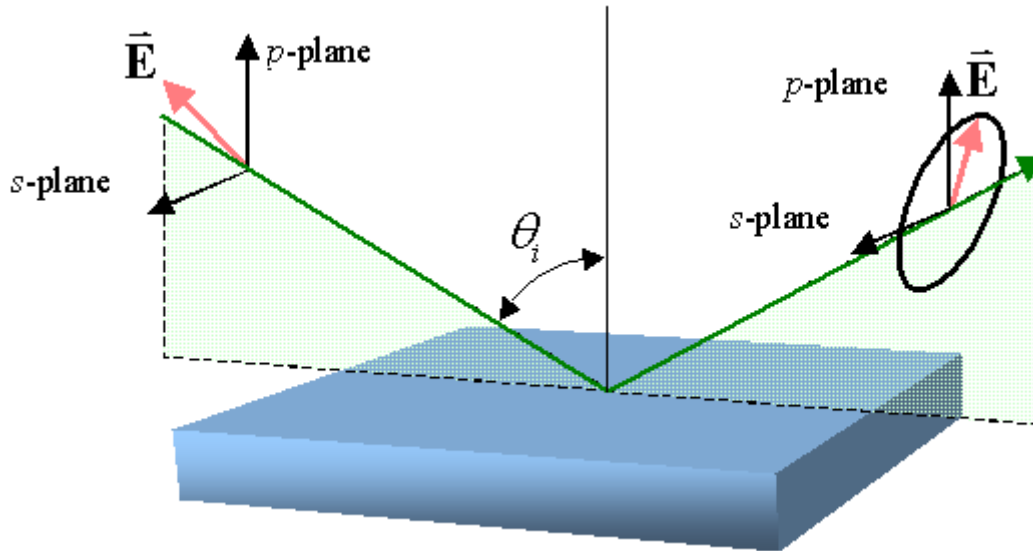


Figure 3.3: Schematic of changes in light polarisation as a consequence of reflection (www.uta.edu/optics/research/ellipsometry/ellipsometry.htm).

There are various ellipsometric techniques available, including single-wavelength ellipsometry (null and phase-modulated techniques), variable angle spectroscopic ellipsometer (VASE), multiple-wavelength reflectometry and spectroscopic ellipsometry, and infrared VASE or IR-VASE.

Many single-wavelength instruments are based on the null technique, which requires that polarisers and retarders be rotated until the effect of the polarisation is inverted and no light is transmitted through the instrument. The light sources used in these instruments are often fixed to a single wavelength. Manually operated systems relying on the human eye are less sensitive and less reliable than automated instruments.

Full ellipsometry analysis requires a baseline set of known properties of the surface and any oxide layers on top, which in the case of aluminium is a single oxide layer. The technique will only measure properties of the additional oxide layer. Modelling the optical properties of multi-layered systems is a complex process, requiring a good knowledge of the optical properties of individual layers, and unless this information is available it is impossible to accurately determine the thickness of individual layers. Better knowledge of the optical properties of the oxide film may help explain differences in results. Although the depth resolution is very good (~10 nanometres) its spatial resolution is poor (a few mm).

3.3 COLORIMETRY

Colorimetry can be used to detect differences between surface treatments and the degree or intensity of the surface treatment (e.g. exposure time). Colour is sensitive to surface morphology and chemical composition. Although instrumented colorimetry systems are available for on-line inspection, interpretation and quantification of reflectance spectra of treated surfaces can be expected to be difficult. The equipment is basically a spectrophotometer that measures the intensity of wavelengths in the reflectance spectra.

The spectrophotometer exposes a small diameter (~10 mm) circular area on the surface to a light source with a daylight colour temperature and compares the percentage reflectance within the visible spectrum (360 – 750 nm wavelength) to that of reference white and black colour tiles.

When monochromatic light falls normally on a surface with an oxide film, several phenomena occur at the interface. Some of the light is reflected back at the film-air interface and does not enter the oxide layer, while transmitted component enters the oxide layer. A portion of the transmitted light is reflected back from the metal-oxide interface. If there is a difference in the phases of the two reflections then different wavelengths will experience different degrees of constructive or destructive interference. A simplistic approach is to assume that the colour of the oxide film is governed only by the wavelength that experiences constructive interference. The thickness of the film is obtained by determining the thickness of an air film between reflecting surfaces that produces the same colour by transmitted light as that observed for the oxide film.

The colorimetry results shown in Figure 3.4 clearly indicate differences in surface reflectance between different levels of chromic acid etch treatment. The reflectance increases with increasing oxide film thickness. As the oxide layer grows, the colour of the surface changes (i.e. becomes whiter).

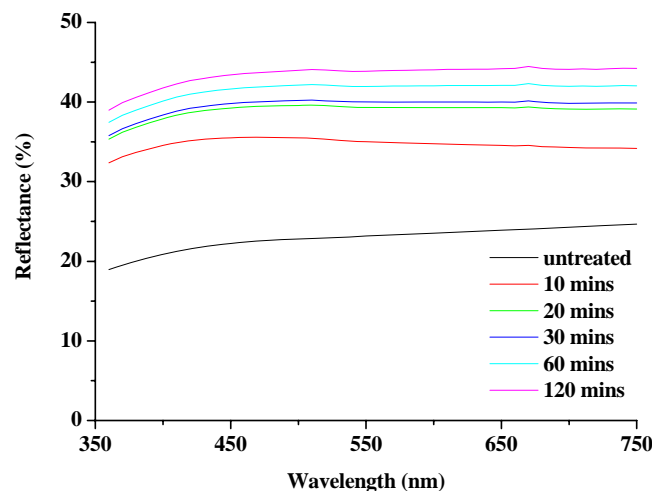


Figure 3.4: Reflectance spectra for untreated and CAE aluminium.

Colorimetry is able to differentiate between untreated and treated surfaces, and between short and long treatment times. It is difficult, however, to differentiate between treatment times that are closely spaced. Also, consideration needs to be given to accurately measuring reflectance of the substrate prior to treatment. Variability in reflectance of surfaces may cause difficulties in data interpretation and quantification. Instrumented colorimetry systems are available for on-line inspection and for maintenance purposes.

3.4 HOLOGRAPHY

Holography is an advanced form of photography that allows an image to be recorded in three dimensions. In principle the production of holograms is simple. The steps to record a hologram are shown in Figure 3.5.

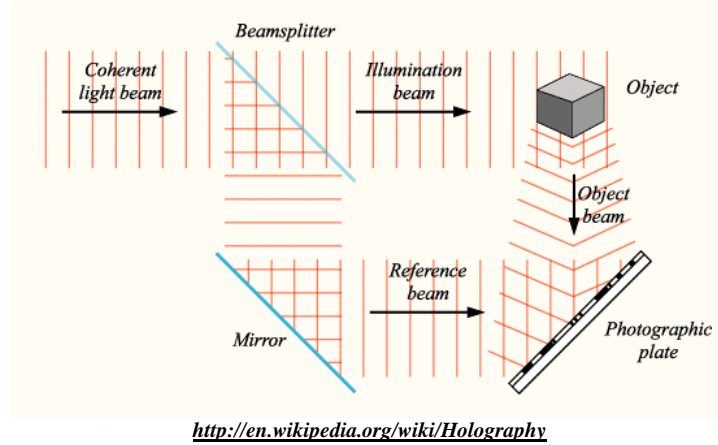


Figure 3.5: Typical arrangement used to record a hologram.

After the hologram has been recorded, if it is developed without moving it from the mount it is possible to interfere the holographic image with the object itself. If the object is deformed after the hologram was recorded, fringes will appear. These fringes can be counted in order to obtain a quantitative measure of the deformation experienced by the object. Frequently this form of holography is only used as a qualitative tool to highlight the positions of maximum deformation of the test object (see Figure 3.6).



Figure 3.6: Fringes show the deformation of the object compared to when the initial hologram was recorded.

The technique is not necessarily expensive, but does require the use of a dark room, a reasonably high power laser and the chemicals required to develop glass photographic plates. Stroboscopic holography can also be performed on fast moving objects like rotors and gears.

3.5 LASER SHEAROGRAPHY

This technique consists in illuminating the object to be tested with monochromatic coherent light (from a laser) and viewing the object through an image-shearing block, which can be phase stepped (a special variable beam splitter) – see Figure 3.7. The double images interfere with each other due to the coherence length of the light used and where the images overlap they produce fringes only where an object has small surface defects which give rise to changes in the axial distance (line of sight from the image shearing block and the object).

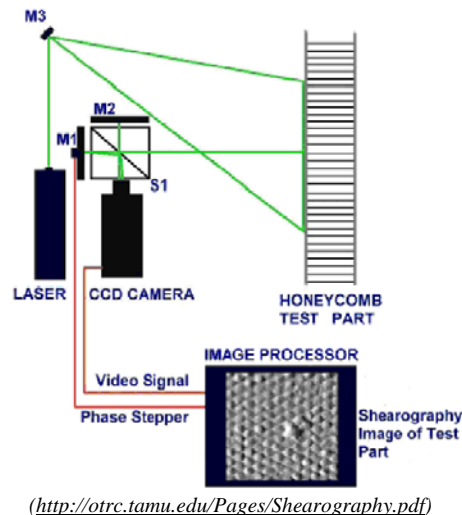


Figure 3.7: Schematic layout for laser shearography.

The sensitivity of the technique is such that very small defects that produce a raised or depressed area on the surface of just a few micrometres, will produce visible fringes, which can then be processed with image manipulation techniques to give a map of the surface defects.

Laser shearography enables the interrogation of the entire field of view without needing to resort to object or beam scanning, however it is totally insensitive to defects that do not give rise to axial displacements.

4 THERMAL TECHNIQUES

4.1 THERMOGRAPHY

This non-contact technique can be used for rapid inspection of large bonded structures capable of detection and discrimination of gross defects and discontinuities close to the surface. The technique requires the inspected component to be heated to produce a surface temperature distribution that can be correlated with structural integrity or defect distribution. In all cases the spatial and temporal temperature distribution is measured using infrared imaging CCTV cameras, and analysed either in real time or post processed to find hidden features. The cameras with best thermal resolution are cooled either with Peltier coolers or with liquid Nitrogen.

Where the heating is applied slowly the technique is referred to as DC Thermography and when flash heating is employed it is known as pulsed thermography. In DC and pulsed thermography the uptake and spread of thermal energy is measured. The heating of the objects under test can be achieved in a number of ways. Four of these are heating techniques are outlined below and the first two are shown in Figure 4.1.

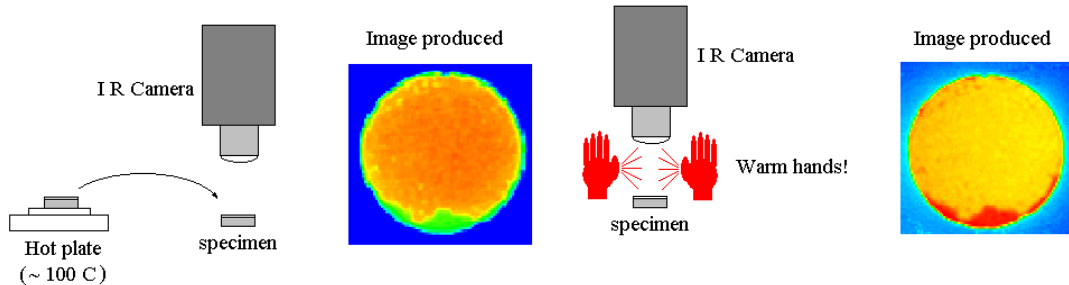


Figure 4.1: Thermograms of a failing coupon of thermal barrier coating obtained through conductive heating and radiative heating.

4.1.1 Conductive Heating

Thermally soaking the entire structure (known as soak) to a constant temperature (e.g. placing the object inside a furnace). This method is well suited to medium sized objects as it ensures uniform heating.

4.1.2 Radiative Heating

Where it is not practical to insert the object into a oven or furnace to warm it up, or where the response to incident heat may be of interest, radiating the object with a constant source of radiation (e.g. a bar heater) is a practical technique.

4.1.3 Pulsed Heating

By radiating with sources of heat that can be rapidly turned on and off it is possible to produce a thermal spike (e.g. large flash lamps). This technique is well suited to objects where transient thermal effects may reveal delaminations or damage, which are a small distance below the surface of the material.

4.1.4 Acoustic Heating (Vibro-thermography, Thermo-sonics)

When ultrasound is applied with a suitable transducer to an object ('vibro-thermography' or 'thermo-sonics'), some of the energy couples into heat. This frequently happens close to damaged zones of the object, and is caused by micro-fretting between the two surfaces of an open crack.

5 ULTRASONIC AND ACOUSTIC TECHNIQUES

Acoustic and ultrasonic techniques are frequently used to detect, measure and characterise a wide range of manufacturing and in-service defects in metallic and polymeric structures. The techniques are divided roughly in to two groups; those that make use of the sound naturally produced by the specimen as it deforms or fractures, and those, which inject sound waves into the material using a coupled transducer.

5.1 ACOUSTIC EMISSION

Acoustic emission monitoring (AE) involves detection of sound waves (usually inaudible to the human ear) made by a structure under load. The technique, which can be used for monitoring the "state of health" of a structure, involves attaching one or more ultrasonic microphones to the object and analysing the sounds using computer based instrumentation (see Figure 5.1). AE may arise from friction (including bearing wear), crack growth and material changes such as corrosion. Microscopic events can be detected if sufficient energy is released and source location is also possible using multiple sensors.

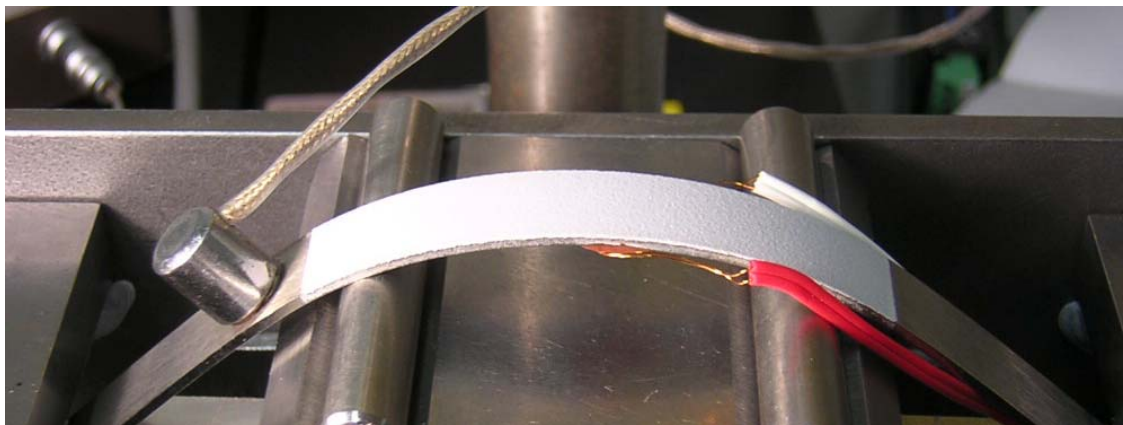


Figure 5.1: Acoustic transducer attached to a coated specimen undergoing a four-point bend test to detect the onset of fracture of the coating.

Large structures (e.g. pressure vessels) can be continuously monitored from a few locations, and proof and qualification tests for routine inspection purposes can be conducted whilst the structure is in service. Applications include testing pipelines and storage tanks (above and below the ground), fibreglass structures and weld monitoring. It can be used to monitor bonded joints for damage initiation and growth (e.g. debonds) during mechanical testing. The technique relies on the operator having sufficient experience to be able to identify particular defect types from the AE data. Figure 5.2 shows a typical AE spectrum obtained from a fractured coating.

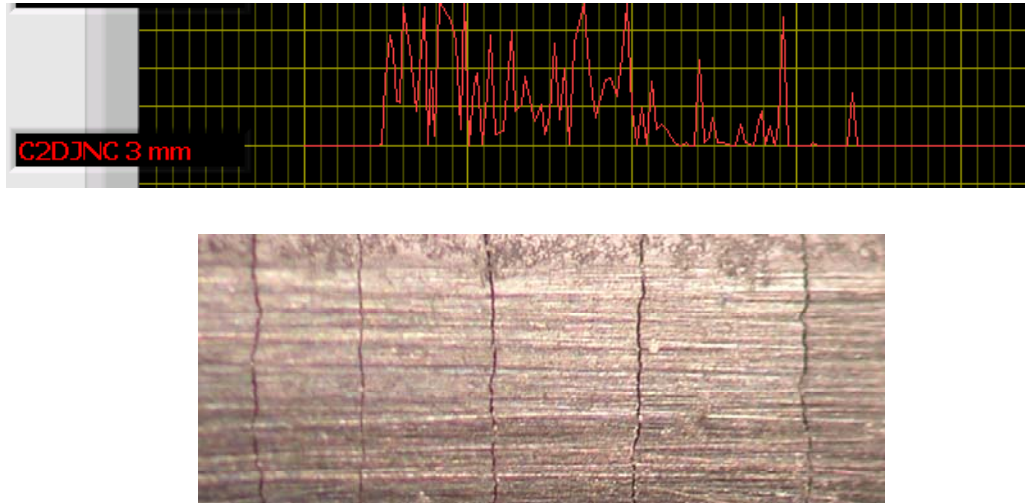


Figure 5.2: Acoustic emission recorded from the specimen, and fractures created in the coating as the substrate material was progressively bent.

5.2 ULTRASONIC INSPECTION

Ultrasonic inspection is routinely used within the aerospace/defence industry for quality assurance purposes and for in-service inspection of aircraft [2-6]. It uses high frequency sound energy to interrogate for surface and subsurface discontinuities or flaws. The sound energy is introduced and propagates through the material in the form of waves. The sound waves propagate through the material with attendant loss of energy (attenuation) and are reflected at interfaces. The reflected wave signal is transformed into an electrical signal, which is displayed and then analysed to determine the location, size and orientation of discontinuities or flaws (e.g. cracks or disbonds), and variations in material density. Ultrasonic signals are scattered or reflected from any interface that separates regions of differing acoustic impedance. Almost total reflection occurs at gas/solid interfaces, whereas partial reflection occurs at liquid/solid and solid/solid interfaces. The reflective signal at the interface becomes smaller as the differences in density between the two medium decreases. Discontinuities or flaws, such as cracks, shrinkage cavities, voids, inclusions and porosity are detectable using ultrasonic inspection. Thickness and elastic properties can also be measured using ultrasonic techniques.

The primary advantage of ultrasonic inspection is the ability to detect flaws deep within solid objects, whether the material is homogeneous or heterogeneous on either a micro- or macro-structural scale. For metal structures, ultrasonic inspection is carried out routinely on material ranging from a few millimetres to 6 metres thick (steel shafts and rotor forgings). The maximum inspection depth for fibre-reinforced laminates is typically 40-50 mm. Inhomogeneous materials, such as discontinuous reinforced polymers and rubber-toughened adhesives tend to be difficult to inspect due to attenuation of the ultrasonic signal as a result of dispersion due to the fillers. Visco-elastic effects in the polymer also contribute to attenuation along with porosity, and damage or defects within the material. A higher degree of signal amplification is required for filled polymeric systems compared with metals.

Ultrasonic inspection is particularly suited to the detection of planar type defects (e.g. disbonds and delaminations) normal to the incident beam. Planar defects as small as 0.3 mm in size can be detected and accurately located using ultrasonic techniques. Planar resolution is limited by the ultrasonic transducer diameter. Although a 0.3 mm spatial resolution is possible with many of the high resolution imaging systems, technical expertise is required to obtain this degree of accuracy. Discontinuities that are present immediately beneath the top surface are difficult to detect. This region is called the “dead zone” and is typically 0.1 to 0.25 mm thick. Hence, the technique is not suitable for detecting surface contaminants (e.g. oils and grease).

Ultrasound is non-hazardous to both operators and nearby personnel, and has no effect on equipment and materials in the vicinity of testing. Large-scale and small-scale (portable) inspection systems are commercially available. Considerable knowledge and experience is required to operate equipment and interpret data. Components that have rough surfaces, complex shape (i.e. curved surfaces), or are very small or thin are difficult to inspect. Couplants, such as water may be required for effective transfer of ultrasonic wave energy between transducers and the inspected part. Reference materials are also needed for calibration purposes [6].

A large range of ultrasonic transducers is available with operating frequencies between 0.5 to 75 MHz, and higher. Improved spatial resolution is achieved by using high frequency transducers. It is possible to ascertain fibre orientations for individual plies in laminated composite structures. Higher frequency signals, however, are more sensitive to surface anomalies and surface roughness and are subject to high signal attenuation (i.e. signal-to-noise ratio decreases with increasing frequency). Ultrasonic transducer beam diameters range from 6 to 25 mm, with the most commonly used being 10 mm. Increased spatial resolution can be achieved by the introduction of a small circular aperture (known as a collimator) in front of a parallel transducer (i.e. unfocused), although at the expense of a loss in beam power. The introduction of a collimator also improves near-surface resolution and increases penetration depth for use in inspecting thick honeycomb structures.

Ultrasonic inspection has been successfully used to detect flaws in cast and wrought metal parts, and in welded, brazed and bonded joints. Contact and immersion inspection are used to detect cracks, porosity, shrinkage, voids and inclusions in metal castings. Immersion inspection is preferred for castings with rough and irregular surfaces. Ultrasonic inspection is used for detecting flaws in forged, rolled or extruded metal billets. Transducers with frequencies of 1 to 5 MHz are used to inspect metal parts. Contact wheel transducers (or search units) are often employed to inspect flat rolled or extruded metal products. It is also possible to monitor slow crack growth in metallic parts (e.g. fatigue, stress-rupture, and stress corrosion cracks), and delaminations in flat or slightly curved composite panels under static and fatigue loading conditions.

Ultrasonic techniques can also be used to determine differences in microstructure or for controlling microstructure in metals. This can be achieved through ultrasonic attenuation or bulk sound velocity measurements. It is possible to set attenuation levels for quality control on production lines.

There are four main formats for displaying ultrasonic data; A, B, C and D-scans.

A-Scan: This format provides quantitative information concerning signal amplitudes and time-of-flight data obtained at a single point on the surface of the specimen. The amplitude of the received signal, and its position relative to the signals corresponding to the upper and lower surfaces of the target, indicates the degree of severity and location of the damage or defect. The A-scan display is used to analyse the type, size and relative depth of discontinuities.

B-Scan: This format provides a quantitative display of time-of-flight data obtained along a line of the test specimen. The B-scan is essentially a linear collection of A-scans and can be considered as equivalent to taking a through-thickness slice of the specimen. B-scan displays show the relative depths of discontinuities and are used mainly to determine size (length in one direction), location (both planar position and depth) and, to a limited degree the geometry and orientation of damage or defects.

C-scan: This format provides a two-dimensional scanning pattern of ultrasonic attenuation, with threshold discrimination in the form of either a grey scale or a range of colours (Figure 5.3). For this type of presentation the transducer is scanned, in a plane that is essentially parallel to the specimen surface, in a rectilinear raster pattern. The C-scan format can also be used to display time-of-flight data.

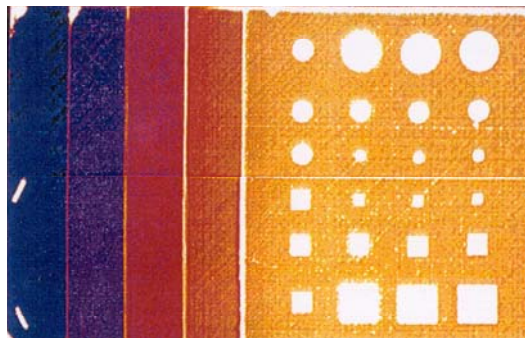


Figure 5.3: Reference panel with known defects.

D-scan, Time-of-Flight Scan or Depth Scan: This is essentially a C-scan format where a two-dimensional map of time-of-flight data is recorded rather than amplitude data.

Of the many ultrasonic methods that exist, the three that predominate in their use for inspection purposes [3] are: Pulse-echo, single through-transmission, double through-transmission.

5.2.1 Pulse-Echo Method

In this inspection mode, a single transmitter-receiver transducer scans along the material surface capturing signals that have been reflected from the back surface, or from discontinuities (interfaces or defects) in the material. Regions free of discontinuities return echoes from only the near and back surfaces. Additional echoes are produced due to the presence of discontinuities within the region being interrogated.

In the presence of a defect, the incident pulse is almost totally reflected at the interface with little or no ultrasonic signal transmitted to the material below the defect. The arrival time of these echoes provides information as to the through-thickness location of the associated defect.

The principle is to monitor a signal in a pre-set time window, or gate. The gate may be positioned between the front surface echo and before the back surface reflection, or actually on the back-wall echo. The amplitude of the signal in this gate indicates the level of acoustic impedance discontinuity in the material at that location. This method of operation can be carried out in an immersion tank with deionised water as the ultrasonic couplant or by using a contact transducer. For the contact mode, water is replaced by gel, oil or grease couplant (see Figure 5.4).

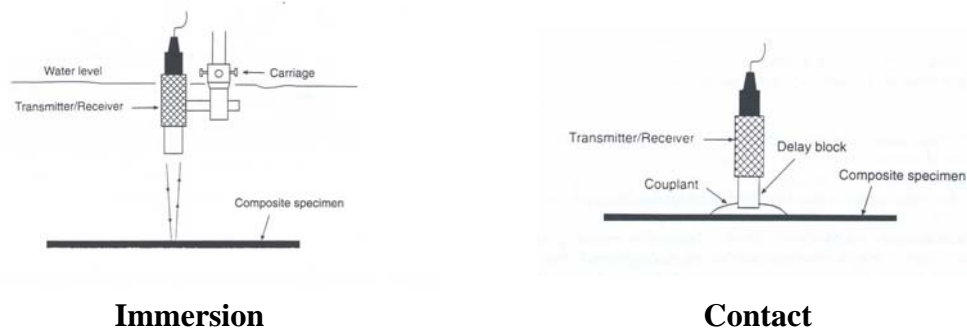


Figure 5.4: Methods of coupling the ultrasound into the object.

In some circumstances exposure to water may be detrimental to the product (e.g. water absorption in wood or paper based products or rust of ferrous metals). Water may also enter the structure (e.g. honeycomb structures) and act as a block to ultrasonic signals, thus inhibiting the detection of flaws. One solution is to employ a contact probe. This requires considerable pressure to maintain good coupling between the ultrasonic transducer and the specimen surface, which is not particularly suitable for the inspection of delicate structures.

Alternatively, air-coupling ultrasonic inspection could be used. For these systems, acoustic power output from the transmitter and sensitivity of the receiver have been maximised to partially overcome the inherent signal losses in air. Air-coupling systems, however, are less sensitive than immersion ultrasonic methods.

A strong reflection from the back surface means the specimen can be readily inspected from one side. This is particularly advantageous where access, as often the case, is limited to one side of a structure or component, hence the propensity of users to operate systems in the pulse-echo mode in preference to through-transmission. The pulse-echo mode is most sensitive to planar defects aligned normal to the interrogating beam. Pulse-echo is used for measuring amplitude attenuation and material thickness (time-of-flight). Measuring the amplitude of reflected signals by this method is preferred when inspecting thin or varying thickness structures.

5.2.2 Single Through-Transmission Method

This method of inspection involves two ultrasonic transducers (i.e. transmitter and receiver) facing directly opposite each other and separated by the specimen (see Figure 5.5). The principle of operation is the measurement of the transmission of ultrasound through the material. To avoid spurious multiple reflections a short pulse is generally used. The transmitted pulse is received, amplified and displayed on an oscilloscope as well as the amplitude being measured and recorded. Discontinuities are detected by comparing the ultrasonic signal transmitted through the test specimen with the intensity transmitted through a reference standard made of the same material. Water couplant is generally used to transmit ultrasound from the transmitter to the specimen and from the specimen to the receiver. This can be accomplished either by fully immersing the specimen and transducers in a water bath (i.e. immersion method), by water jets (squirters) or by a water film. Defects will either block or attenuate the transmitted ultrasonic signal, thus a reduction in the signal amplitude or a total loss of signal usually occurs in regions containing internal flaws.

This method is more suitable for large components (where water jets or squirters are used instead of a water bath), honeycomb structures and thick sections where multiple reflections occur due to the presence of numerous interfaces (composite laminates), often prevent the use of other methods. Single through-transmission is often superior to pulse-echo for detecting near-surface discontinuities, the reflections from which can often emerge from the front-surface signal. The main disadvantages are that access is required to both sides of the test material and that the method provides no information about through-thickness location of defects.

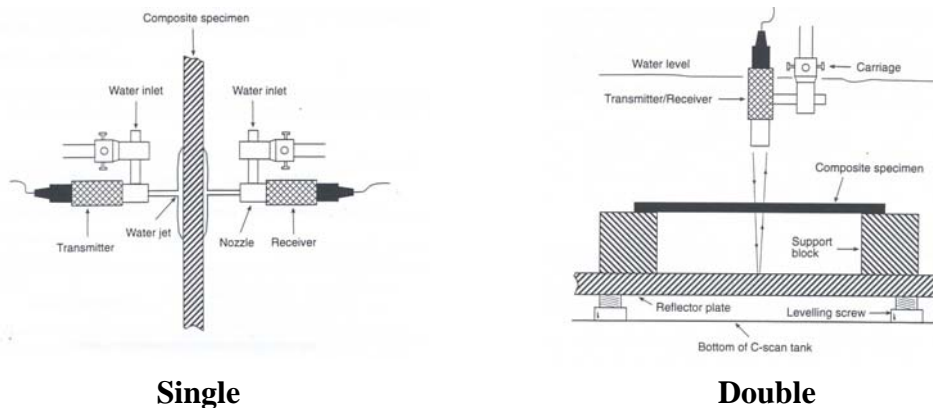


Figure 5.5: Through-transmission method.

5.2.3 Double Through-Transmission Method

In this inspection mode, a single transmitter-receiver transducer scans along the material surface capturing signals that have propagated through the specimen twice. The specimen is supported above a flat glass or metal reflector plate and the inspection area, transducer and reflector plate are fully immersed in water – see figure 5.5. A short ultrasonic pulse passes through the specimen, normal to the surface, is reflected by the reflector plate and travels back through the specimen again to the transducer. The reflected signal is captured, amplified and displayed on an oscilloscope and the amplitude is measured and recorded.

Using the double-through transmission approach enhances the detection of near-surface flaws by directly monitoring the amplitude of the back-surface reflection rather than monitoring intermediate signals between the front and back reflections. The presence of a near-surface discontinuity will result in a reflected signal, and thus a reduction in energy of the transmitted pulse that propagates to the reflector and back. This effectively reduces the amplitude of the reflection.

5.3 SCANNING ACOUSTIC MICROSCOPY (SAM)

This method of non-destructive imaging consists in immersing the test object in a liquid coupling medium, and then focussing ultrasonic waves on it and detecting either the transmitted or reflected pulses. The simplest case is reflected scanning acoustic microscopy, where the ultrasound source is also the detector (see Figure 5.6). When the detector is mounted on a 2 or 3 dimensional scanning head it can be moved around to map out areas of interest, and so form an image. The test object must always be amenable to being immersed in liquid (normally water) so that the ultrasound can be coupled into it. The maximum resolution depends on the Raleigh limit of the wavelength (frequency) used, but can be as good as some 20 μm . Higher frequencies provide better resolution, but lower frequencies achieve greater penetration into the material.

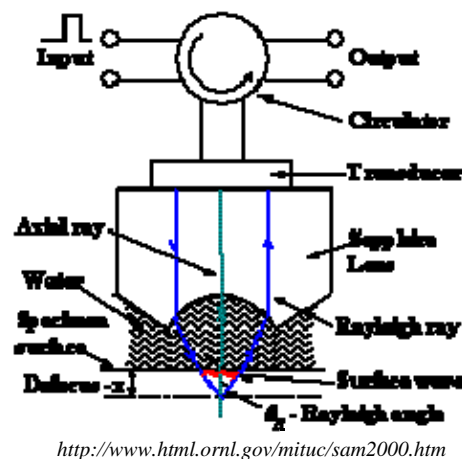


Figure 5.6: Schematic diagram of the focussing of ultrasound into the surface of a specimen.

The near-field acoustic microscope was developed to overcome the Raleigh resolution limit. The principle behind this kind of microscope consists of producing an acoustic wave in a tiny area just in the vicinity of the surface (near-field area) through different interaction mechanisms and by detecting this acoustic wave, the acoustic properties of materials are obtained at a high resolution, which is independent of wavelength.

SAM utilizes very high frequency (typically 5 to 75 MHz) ultrasound to view internal material integrity. Frequencies in this range are highly attenuated in air, and therefore the part is immersed in coupling medium, usually deionised water. SAM systems are generally operated in pulse-echo mode with a single ultrasonic transducer emitting and receiving the ultrasonic beam.

The ultrasonic beam is focused using lenses to a specific range of depth in the test sample. Since ultrasonic transducers have depth of field, the entire sample may be in focus on thinner parts. The ultrasonic signal is a short pulse that travels through the material being tested. It is reflected back to the transducer when it strikes interfaces within the material. The transmitted sound waves that are reflected back arrive back at the transducer at different times, which correspond to different depths in the material. High spatial (lateral) resolution of the order of 1-2 μm can be achieved through the use of high frequency transducers (i.e. 200 - 600 MHz), although signal-to-noise ratio decreases with increasing frequency. SAM has been used to detect surface cracks in soda lime glass and MgO single crystals with a depth as small as 25 μm , even though there is a dead zone of some 10-15 μm . The technique is suitable for studying biological samples, such as bone structures with the capability of lamellae thickness resolution.

Recent developments in acoustic microscopy have seen the emergence of scanning near-field acoustic microscopy (SNAM), a new method for imaging the topography of non-conducting surfaces with a potential lateral resolution in the sub-micron range. The basic element of this method is a distance sensor consisting of a sharply pointed vibrating tip, which is part of a high-Q (gain) quartz resonator driven at its resonance frequency. The decrease in resonance frequency or of the amplitude of vibration when an object comes into the proximity of the tip serves as the key signal. The dependence of this signal on pressure and composition of the coupling gas shows that the hydrodynamic forces in the gas are responsible for the coupling between samples and probe tip. The sensor is incorporated into a scanning device. Well-resolved line scans have been achieved for a grating of 8 μm periodicity with lateral resolution of 3 μm and a vertical resolution of 5 nm.

New developments include scanning probe systems that combine atomic force microscope (AFM) with scanning acoustic microscopy enabling simultaneous imaging of sample topography and monitoring of ultrasonic surface vibrations in the MHz range. For detection of the distribution of the ultrasonic vibration amplitude, a part of the position-sensing light beam reflected from the cantilever is directed to an external knife-edge detector (see AFM). Acoustic images with a lateral resolution of about 100 nm have been achieved at an ultrasonic frequency of 20 MHz.

5.4 ULTRASONIC RESONANCE SPECTROSCOPY

The basic principle of operation of ultrasonic resonance spectroscopy is similar to other ultrasonic techniques previously discussed. A continuous sine wave excitation of constant amplitude is used to drive an ultrasonic transducer in contact with the sample surface. The sample is forced into mechanical resonance. The response of the sample is detected using a receiver at a second location on the surface. Both the amplitude and the relative phase of the received signal are recorded over a range of discrete test frequencies so that spectra of amplitude and phase are recorded. Typical test frequencies ranging from 100 Hz to 10 MHz, and higher are employed. The technique can be used to inspect an entire component in a single test, thus enabling rapid inspection suitable for production environments. Ultrasonic resonance spectroscopy combined with spectra analysis and neural network techniques is an attractive tool for quality assessment purposes.

Volumetric flaws in the range 0.04% to 3% have been detected in tests on concrete paving slabs and using statistical analysis (i.e. neural networks) it has been possible to derive pass and fail criteria. Industrial applications include a wide range of industrially important components (e.g. forgings, pressings, brazings, bolts and composites).

Ultrasonic spectroscopy has been used to detect the damage caused to fibre-reinforced polymer materials due to hygrothermal ageing. Acoustic parameters, such as velocity and attenuation, are linked to the viscoelasticity and microstructure of the propagation medium. The acoustic parameters can be measured by means of pulsed ultrasonic spectroscopy. It is possible to relate changes in these properties to moisture content and the level of material degradation, and also identify damage mechanisms. Changes in frequency dependency of velocity and attenuation have been related to matrix cracking.

5.5 LONG RANGE ULTRASONIC TESTING



www.oceaneering.com/uploadedFiles/Inspection/OIS%20-%20LONG%20RANGE%20ULTRASONICS.pdf

Figure 5.7: Ring actuator and sensor for long range ultrasonic testing on pipelines.

This technique is also known as ‘guided wave ultrasonics’. It consists in applying pulse-echo methods to long structures (cables, pipelines) – see Figure 5.7. The pulse source also doubles up as the echo receiver, and this enables the method to obtain information on faults ranging up to 100 m away from the point of probing. Placing two actuators one quarter of a wavelength apart and firing them 90 degrees out of phase with each other makes it possible to steer the pulse either way along the pipe in order to interrogate the possible faults up or down the line from the probing point. Detection of faults giving rise to an effective reduction or increase in cross-sectional area of only 2 or 3 % can be detected. The effectiveness of the technique is reduced where the pipe or cable is lagged with heavily damping material, or buried in certain types of soil. Where geometries are complex, the pattern of echoes becomes more complicated and difficult to interpret, reducing the probability of detection of a fault.

5.6 ACOUSTO-OPTIC ULTRASONIC TESTING

This novel method uses the energy from ultrasonic waves to re-orientate liquid crystals directly inside an imaging screen. A thin screen comprising two layers of glass or polycarbonate has the gap filled with a proprietary liquid crystal. This screen is installed as a window of a tank in which the test object is to be studied. The liquid crystals inside the imaging screen are firstly polarised using a uniform electric field, this makes the screen appear dark. A transducer capable of producing a uniform ultrasonic wave is then placed at the other end of the tank, and the test object is placed between the two. The energy in the ultrasonic wave causes the liquid crystals to become depolarised and produce some optical contrast on the screen. Any faults in the object (porosity, inclusions, delaminations) capable of attenuating the ultrasonic wave will be revealed as dark patches on the screen.

The image obtained is comparable to that displayed on an X ray plate. It is an “acoustic shadow” of the test object. The type of defect that can be detected with this novel technique is restricted to those that attenuate ultrasound. If after immersion in the tank a hole becomes filled with the liquid, it will not show up as a defect on the screen because the ultrasonic wave can propagate without significant attenuation through the liquid. Although the technique is still in its infancy, and the full strengths and limitations of this method are yet to be determined, the ease of operation and the speed with which images are obtained make it an attractive technique in NDE.

5.7 LASER ULTRASONICS

Laser-ultrasonics (or laser-ultrasound) is a non-contact technique that uses lasers to generate and detect ultrasonic waves. It is used to measure material thickness, detect flaws and materials characterisation. Laser ultrasonics has been used for real-time sensing of grain size and grain growth, phase transformation and recrystallization of aluminium and steel alloys [7-8]. Prototype versions using remote sensors have been used in the hostile (high temperature) environment of steel production. The technique could potentially be used for on-line inspection of metal processing (i.e. monitoring microstructural changes).

A laser-ultrasonic system consists of a generation laser, detection laser and detector. Ultrasonic waves are generated using a pulsed laser (typically a few nanoseconds of duration with an energy less than one joule). Solid state Q-Switched Nd:YAG and gas lasers (CO₂ or Excimers) are used to generate the laser pulse. Detection lasers are continuous or long pulse (typically 10-20 microseconds) with a long coherence length. The detection laser light reflected (or scattered) by the material surface is perturbed (e.g. Doppler effect) by the arrival of ultrasonic waves. The perturbation is usually detected using interferometric techniques, such as confocal Fabry-Perot or photorefractive interferometers, which demodulate the detection light.

The physical principle behind the technique is based on thermal expansion or ablation. Ultrasound is generated by the sudden thermal expansion of material due to the heating of a tiny area on the surface by the laser pulse. If the laser power is sufficient to heat the surface above the material boiling point, some material is evaporated (typically some nanometers) and ultrasound is generated by the recoil effect of the expanding material evaporated.

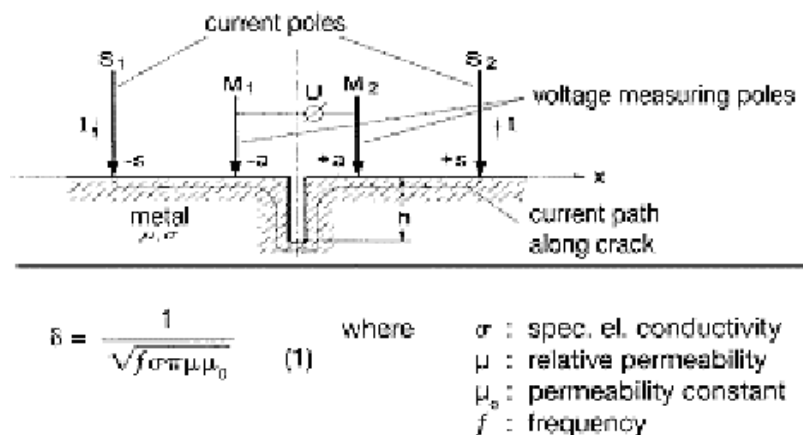
In the ablation regime, a plasma is often formed above the material surface and its expansion can make a substantial contribution to the ultrasonic generation. The technique allows for ultrasonic inspection of materials at high temperature at a convenient distance (typically tens of centimetres). In addition, there are few constraints with regard to material geometry (suitable for curved surfaces).

Ultrasonic signal attenuation can be used to determine the onset of phase transformations, whereas ultrasonic velocity can provide quantitative information relating to phase fractions during the transformation. The sensitivity of ultrasonic velocity to phase fraction is due to the different elastic constants and/or densities of the different phase components. In addition to classic allotropic phase transformation and second phase precipitation, ultrasound can also be sensitive to magnetic transitions. Longitudinal and shear wave velocities can provide important information on texture change. Although laser ultrasonics is potentially suitable for real-time, in-situ monitoring and/or control of metal processing, it is unable provide the detailed information possible using techniques such as metallography.

6 ELECTRICAL AND ELECTROMAGNETIC TECHNIQUES

6.1 POTENTIAL DROP MEASUREMENTS

This technique, also known as Electric Impedance Tomography, is similar to the Alternating Current Field Measurement described below, in that a large current is also made to flow through the length of the material, however in this case it is the surface potential that is being measured with a scanning probe. Wherever there is a crack, the effective cross sectional area for conduction is affected, and there will be a change in the potential gradient along the length of the object (see Figure 6.1). If high frequency AC currents are used, the skin effect will cause the current to be transported only through a thin layer immediately below the surface. Cracks that are perpendicular to the direction in which the current is flowing will present the greatest impedance to the flow of the current, and so the potential gradient will be highest in their vicinity.



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Figure 6.1: Schematic of the way additional electrical impedance is introduced when a surface crack is present.

Parallel cracks are not detectable with this technique, and surface cleanliness is extremely important in order to avoid false readings. The method is not very good for quantitative crack depth measurement. A variant of this technique being developed at Sussex University involves the use of capacitive contact to measure surface potential. This makes the technique applicable to insulating materials, such as glass and carbon reinforced plastics. The capacitive non-contact technique is still in its infancy and its full strengths and limitations are yet to be demonstrated.

6.2 SURFACE RESISTIVITY AND IMPEDANCE

Surface resistivity is defined as the electrical resistance of the surface of an insulator and is expressed in ohms (units ohms/m²) [9-10]. The technique involves placing two electrodes on the surface of the test sample, applying an electrical potential between the electrodes and measuring the resultant current. The surface resistivity σ is determined using the following relationship [9]:

$$\sigma = K_s \frac{V}{I} \quad (1)$$

where V is the applied voltage, I is the measured current and K_s is the test cell constant for surface resistivity based on cell geometry.

A configuration for measuring surface resistivity is shown in Figure 6.2. The current is only measured between the bottom two electrodes as shown in the diagram. The top electrode is guarded so that only current flowing between the two lower electrodes is measured by a picoammeter. The key test parameters are applied voltage, length of electrification time, humidity and temperature. The longer the voltage is applied, the higher the resistivity. This is because the sample charges exponentially with time. Also, surface resistivity measurements decrease with increasing humidity levels. The electrical and environmental conditions should be kept constant to ensure consistent data. Poor electrical contact between sample and electrodes will also have an adverse affect on the reliability of surface resistivity measurements. The electrode area must be equal to the contact area, and any discrepancies will contribute measurement errors.

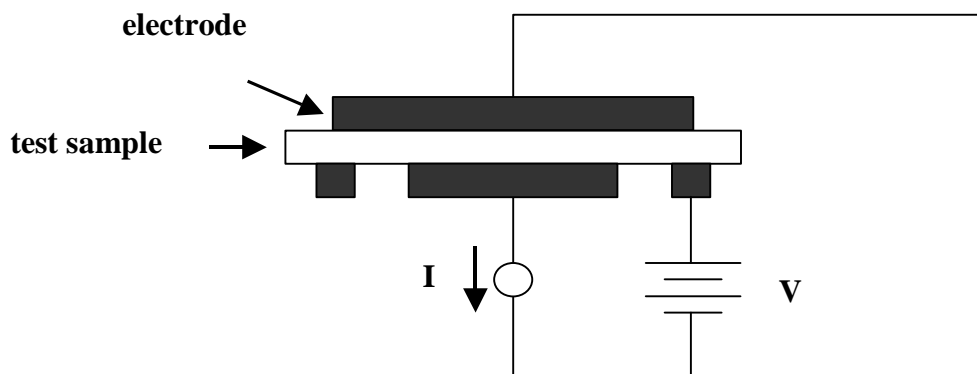


Figure 6.2: Schematic arrangement of the surface resistivity technique.

Problems can be encountered when measuring materials with high surface resistivity, background currents due to charging, static or triboelectric charge, or piezoelectric effects, may cause measurement errors. Background currents may be of the same order of magnitude as the stimulated surface currents. Background currents of opposing polarity to the stimulated current have a cancelling effect, and the measured (resultant) current will be lower than the true current. If the polarity of the background and stimulated currents are the same then the measured current will be higher than the true current.

An alternative approach is to employ the Alternative Current (AC) Method, which applies a bias polarity of positive polarity then the current is measured after a specified delay time. The polarity is then reversed and the current is then measured again using the same delay time. This process is repeated and the resistance is calculated on a weighted average of the most recent measurements. Both techniques are sensitive to surface contamination and affected by variations in composition and thickness of the surface layer and substrate. A note of caution, the resistance of an oxide layer, formed as a result of chemical treatment, may breakdown under prolonged exposure to applied voltage. The technique is easy to implement and could readily be adapted for on-line inspection.

Another approach that has proved successful for characterising oxide films and coatings is the AC impedance technique. This technique is an electrochemical method used for corrosion studies to measure oxide growth rates. In this method, the test surface is immersed in an electrolyte and an alternating voltage is applied. The resultant current is measured as a function of frequency (65 kHz to 10 MHz). The resistance, capacitance and inductance of the surface and the resistance of the electrolytic solution can be used to determine surface impedance. It is possible to relate film thickness, film composition and oxidation rate for anodised surface treatments from impedance measurements. The AC impedance technique is capable of differentiating between various surface treatments and levels of treatment for a given surface treatment. The technique is sensitive to variations in the composition and thickness of the oxide film and surface contamination. Although the technique is unsuitable for on-line inspection, there is considerable scope as a developmental tool and for modelling oxidation processes.

6.3 EDDY CURRENTS

Eddy current testing is routinely used in the aerospace industry (airframe inspection), and to a lesser degree in the automotive, marine and manufacturing industries for detecting cracks and subsurface damage, such as corrosion in bonded structures. The electromagnetic technique can only be used on conductive materials. Flaw size and material variations (e.g. thickness) can be determined using the eddy currents. The technique consists of an energising coil, through which AC current flows, for inducing currents into the metal component. The magnetic field of the coil when in close proximity of a conducting surface will induce circulating (eddy) currents in the surface.

The magnitude and phase of the eddy currents will affect the loading on the coil, and thus its impedance. The presence of defects or variations in material conductivity will either interrupt or reduce the eddy current flow, thus decreasing the loading on the coil and increasing its effective impedance.

The technique cannot detect cracks lying parallel to the current path. Changes in voltage are measured and displayed in a manner that indicates the type of flaw or material condition. The conductivity and permeability (ease of magnetisation) of a material will have a direct effect on the eddy current flow. Eddy current increases with increasing conductivity. Conductivity is often measured by an eddy current technique. The eddy current density, and thus the strength of the response from a flaw, is greatest on the surface of the metal being tested and decreases with depth. Probes can be designed to fit the geometry of the component to be inspected. Penetration depths of 10 mm are achievable on aluminium structures using low frequency eddy probe currents, thus enabling detection of subsurface cracking, which is invisible from the surface, or thinning of any of subsurface layers.

Since the eddy currents are detected as a change in the complex impedance of the energising coil, which is moved over the surface of the material, it is important that the probe-surface distance is maintained very nearly constant. Where surfaces are rough, the eddy current technique may give rise to the detection of false faults. Suitable material preparation through controlled grinding of the surface may be required prior to eddy current inspection

6.4 ELECTRO-MAGNETIC ACOUSTIC TRANSDUCERS

Generally, Electromagnetic Acoustic Transducers (EMATs) can use either the piezoelectric effect, the Lorenz force, or magnetostriction in order to convert electrically generated pulses into acoustic impulses to couple into the material.

6.4.1 Piezoelectricity

This is the name given to the ability of crystals to generate a voltage in response to applied mechanical stress. The piezoelectric effect is reversible in that piezoelectric crystals, when subjected to an externally applied voltage, can change shape by a small amount. The deformation is typically about 0.1% of the original dimension.

6.4.2 Lorentz Forces

The Lorentz force is the force exerted on a charged particle in an electromagnetic field. The particle will experience a force due to electric field of $q\mathbf{E}$, and due to the magnetic field $q\mathbf{v} \times \mathbf{B}$. Combined they give the Lorentz force equation (or law). Probes using this effect will normally make use of a permanent magnet and a small embedded coil to produce small eddy currents which will experience forces and so send an acoustic wave through the material.

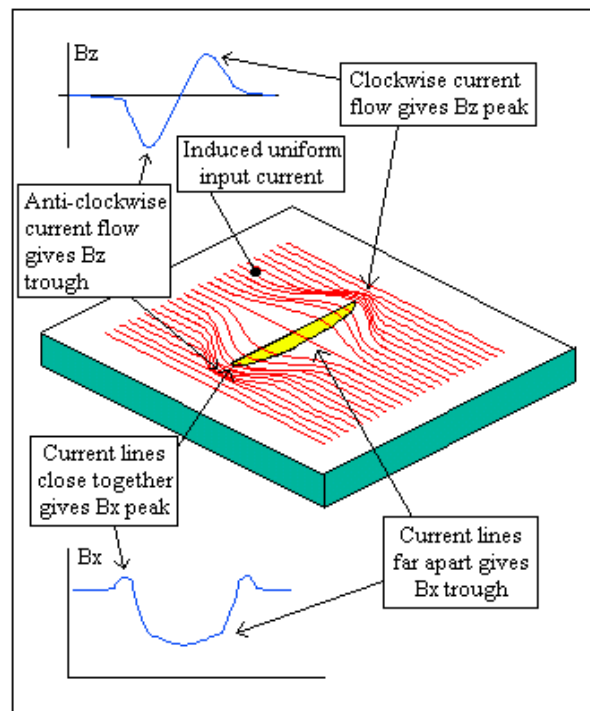
6.4.3 Magnetostriction

Internally, ferromagnetic materials have a crystal structure that is divided into domains, each of which is a region of uniform magnetic polarisation. When a magnetic field is applied, the boundaries between the domains shift and the domains rotate, both these effects causing a change in the material's dimensions. This effect is called magnetostriction. Some EMATs use this effect to produce a sharp acoustic signal.

Whatever principle is chosen for the EMAT, the device can be used both to emit and/or detect an acoustic wave into or from the material. Adequate coupling must always be ensured by operating through liquids or gels applied to the surfaces of the objects to be tested.

6.5 ALTERNATING CURRENT FIELD MEASUREMENT

The alternating current field measurement (ACFM), also known as the current perturbation technique, consists of injecting a large AC current through the material to be tested, and then scanning the surface with either a magneto-restrictive device, a small coil or a Hall probe to measure any variation in the magnetic field at the surface of the material. Where a surface crack is present, the alternating current must find a deeper path through the material, and this causes the magnetic field at the surface to decrease (see Figure 6.3). Scanning the selected probe over the entire surface of the material makes it possible to map out any vertical fractures, which lie in a plane perpendicular to the applied current.



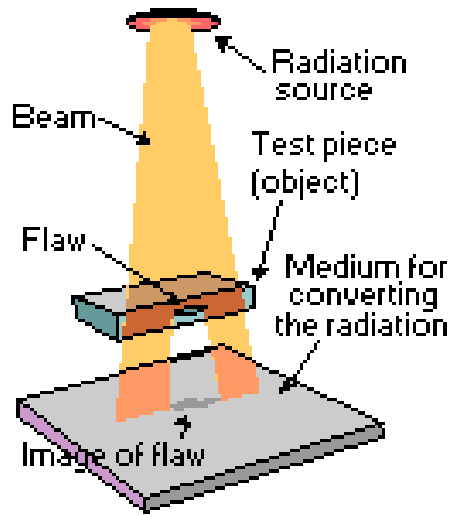
<http://www.tscinspectionssystems.co.uk/ACFMDetailPg1.htm>

Figure 6.3: Schematic illustrating the change in magnetic fields strength at the material surface when a fault is present.

Varying the frequency of the alternating current enables the system to probe different depths of the material; lower frequencies probe deeper into the material and higher frequencies are restricted to a thin layer at the surface of the material due to the 'skin effect'. If fractures are expected to lie in a single plane, the current can be applied in a single direction, but if the cracks may be present in any orientation it becomes necessary to rotate the direction in which the currents are applied. Where large surface areas need to be inspected, this can be a very time consuming technique.

7 X-RAY TECHNIQUES

7.1 X-RAY RADIOGRAPHY



<http://www.engineershandbook.com/MfgMethods/ndtrt.htm>

Figure 7.1: Schematic diagram showing the principle of X-Ray Radiography.

X-rays are a form of electromagnetic radiation with a wavelength in the range of 10 to 0.01 nm, corresponding to frequencies in the range 30 to 30 000 PHz (1 petahertz = 10^{15} hertz). X-rays are primarily used for diagnostic radiography and crystallography. X-rays are a form of ionizing radiation and as such can be dangerous.

This technique involves the use of penetrating gamma or X-radiation to examine parts and products for imperfections. An X-ray machine or radioactive isotope is used as a source of radiation. Radiation is directed through a part and onto film or other media. The resulting shadowgraph shows the internal soundness of the part (see Figure 7.1). Possible imperfections are indicated as density changes in the film in the same manner as an X-ray shows broken bones.

Radiographic applications fall into two distinct categories evaluation of material properties and evaluation of manufacturing and assembly properties. Material property evaluation includes the determination of composition, density, uniformity, and cell or particle size. Manufacturing and assembly property evaluation is normally concerned with dimensions, flaws (voids, inclusions, and cracks), bond integrity (welds, brazes, etc.), and verification of proper assembly of component pieces.

7.2 PHOTON INDUCED POSITRON ANNIHILATION (PIPA)

Photon Induced Positron Annihilation (PIPA) involves penetrating materials with a photon beam. This process creates positrons, which are attracted to nano-sized defects in the material. Eventually, the positrons collide with electrons in the material and are annihilated, releasing energy in the form of gamma rays. The gamma ray energy spectrum creates a distinct and readable signature of the size, quantity and type of defects present in the material.

Distributed Source Positron Annihilation (DSPA) uses a positron source emitter to deposit positrons into the subject material. The process is similar to PIPA after the positrons are deposited and attracted to nano-sized defects in the material. PIPA and DSPA technologies detect fatigue, embrittlement, and other forms of structural damage in materials at the atomic level, before cracks appear. PIPA and DSPA can also accurately determine the remaining life of various materials and are more precise than any other existing flaw detection technology on the market.

7.3 NEUTRON RADIOGRAPHY

Neutron Radiography is an imaging technique, which provides images similar to X-ray radiography. The difference between neutron and X-ray interaction mechanisms produce significantly different and often complementary information. While X-ray attenuation is directly dependent on atomic number, neutrons are efficiently attenuated by only a few specific elements. For example, organic materials or water are clearly visible in neutron radiographs because of their high hydrogen content, while many structural materials such as aluminium or steel are nearly transparent. At the present time, Neutron Radiography is one of the main NDE techniques able to satisfy the quality-control requirements of explosive devices used in aerospace/defence programs.

7.4 X-RAY DIFFRACTION (XRD)

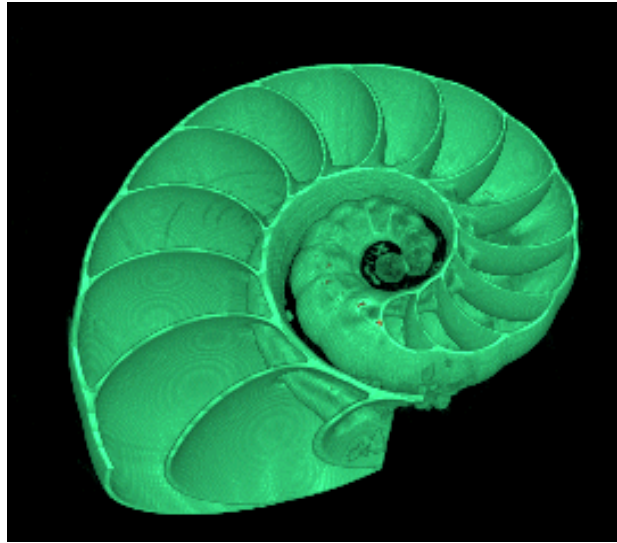
X-ray diffraction is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. A crystal lattice is a regular three-dimensional distribution (cubic, rhombic, etc.) of atoms in space. These are arranged so that they form a series of parallel planes separated from one another by a distance d , which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations - each with its own specified-spacing.

When a monochromatic X-ray beam with wavelength λ is projected onto a crystalline material at an angle θ , diffraction occurs only when the distance travelled by the rays reflected from successive planes differs by a complete number n of wavelengths. By varying the angle θ , the Bragg's Law conditions are satisfied by different d -spacings in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample. Where a mixture of different phases is present, the resultant diffractogram is formed by addition of the individual patterns. Based on the principle of X-ray diffraction, a wealth of structural, physical and chemical information about the material investigated can be obtained. A host of application techniques for various material classes is available, each revealing its own specific details of the sample studied.

7.5 X-RAY TOMOGRAPHY

X-ray Tomography is a branch of X-ray microscopy. A series of projection images are used to calculate a three dimensional reconstruction of an object (see Figure 7.2). The technique has found many applications in materials science and later in biology and biomedicine. Moreover the technology has been improved by implementing the microfocus X-ray sources in the computer tomography facilities.

In microfocus computer tomography (μ CT) the resolution of a system can be in the order of $10\ \mu\text{m} \times 10\ \mu\text{m} \times 10\ \mu\text{m}$ depending on the object size, which is much better compared to the typical $60\ \mu\text{m} \times 60\ \mu\text{m} \times 1\ \text{mm}$ resolution of the medical CT.



<http://ssf.ugent.be/linac/linac/Afbeeldingen/Tomo/snail.htm>

Figure 7.2: Typical optical sectioning made possible by X Ray tomography.

X-Ray tomography can be applied equally well to metals ceramics, polymers and composites. Current systems can accommodate objects as large as a typical engine block, and portable systems can image objects the size of a small apple. Computed Tomography (CT) is a powerful nondestructive evaluation (NDE) technique for producing 2-D and 3-D cross-sectional images of an object from flat X-ray images. Characteristics of the internal structure of an object such as dimensions, shape, internal defects, and density are readily available from CT images. Image manipulation after reconstruction enables the user to view any surface or cross-section to locate defects or features of interest. Although the technique is perhaps the most powerful and versatile, its main drawback at present is its high investment cost.

7.6 X RAY TOPOGRAPHY

X-ray topography is characterized by the spatially resolved detection of scattering of a sample – see Figure 7.3. It combines both the advantages of radiographic imaging and the analytical information of X-ray scattering like wide and small angle diffraction, refraction and total reflection. Scanning techniques under Small and Wide Angle scattering conditions permit the topographic characterisation of any crystalline or amorphous solid or liquid. Wide Angle X-ray Scattering (WAXS) (diffraction) is elastic scattering (no energy shift) and is sensitive to the atomic and molecular structure below the scale of nanometers. Small Angle X-ray Scattering (SAXS) is suitable for studying colloids, polymers and biological materials. Particle dimensions smaller than $50\ \text{nm}$ can be determined. In combination, the two techniques can be used to provide information on molecular orientation. The high quantum efficiency of scintillation counters permits the intensity measurement at reasonable speed.

X: X-ray source
C_s: Collimator
P: Primary beam
S: Sample (limited rotation)
S_c: Sample scanner
F_s: Scattering Foil
D_A: Absorption Detector,
D_R: Refraction Detector
S_c: Sample Scanner

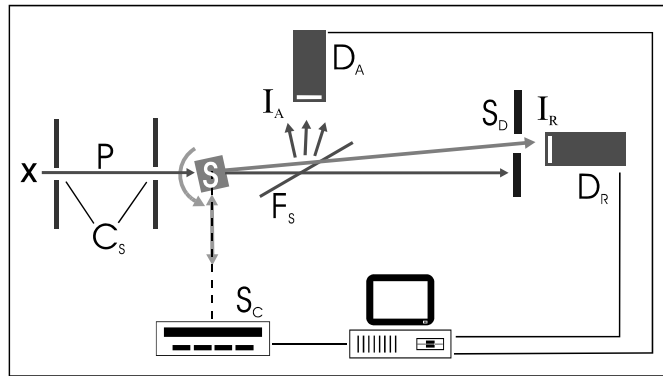


Figure 7.3: X-ray diffraction topography (courtesy of BAM).

X-Ray Refraction-Topography developed at BAM utilises the optical effect of refraction at interfaces, which for X-rays happens at small scattering angles of a few minutes of arc (Figure 7.3). Using a Kratky camera, a very narrow X-ray beam traverses a sample, which is scanned in the surface plane and scattering intensities are taken at all positions. The technique provides nearly linear contrast by inner surfaces and interfaces. 2-D images are generated with a possible spatial resolution of about $10\ \mu\text{m} \times 300\ \mu\text{m}$. Usually the strong intensity of the X-ray refraction signal enables scanning of samples within relatively short time. Between 0.1 and 5 seconds per sample position are required for 2 % signal to noise ratio depending on the sample absorption and the inner surface concentration.

It is possible using X-Ray Refraction to generate inclination topography projections of bonded joints manufactured from non-metallic materials (e.g. fibre-reinforced polymer composites) to identify regions of poor bonding. The technique can also be used to determine crack density in polymers after chemical ageing (i.e. crazing) and for studying fibre debonding in fibre-reinforced laminates. For some practical applications, like evaluating the flow pattern of injection moulding parts, it is often sufficient, to image solely the changes in orientation by texture topography. The rotation slit is fixed at an inclination angle of maximum slope of the rotation profile. While the sample is scanned any changes in texture and preferred orientation result in intensity changes.

A limitation of Refraction-Topography is the averaging of the interface signals over the thickness of a sample. But a transversal section image can be achieved by a combination of Refraction line scans and computer tomography techniques. At zero scattering-angle, multiple linear scans of the sample are repeated at different inclination angles about an axis perpendicular to the incident beam. The absorption signals can be reconstructed according to the rules for "parallel beam filtered back projection".

8 SCANNING TECHNIQUES

8.1 SCANNING OPTICAL TECHNIQUES

8.1.1 Scanning Photoemission Electron Microscopy (SPM or SPEM)

SPM is a relatively simple and inexpensive technique that can be used to provide in-situ spatial and chemical information on chemical processes (e.g. oxidation and catalytic reactions) [11]. It is possible using SPM to accurately measure the local work function for surfaces and has been used for measuring the work function for different oriented grains in polycrystalline materials. SPM uses a small focused photon probe to illuminate the sample surface. A deuterium discharge lamp (typically 30 watts) is used to generate ultraviolet (UV) light, which is monochromated by a high density grating monochromator with a blaze of 200 nm. A reduced image of the exit slit is projected via a lens and Schwarzschild (reflection) objective onto the sample. For high resolution, the exit slit can be replaced with a small diameter aperture (typically 20 μm) resulting in a spot size of approximately 0.5 μm . A lateral resolution of the order of 150 nm with an overall energy resolution of 200 meV is now possible using Fresnel zone plates. Energy range is typically between 100 to 800 eV.

SPM systems can operate in two modes (imaging and spectroscopy). In imaging mode, the sample surface is mapped by synchronised scanning the sample with respect to the focused photon beam and photoelectrons of known kinetic energy collected. Photoelectrons emitted from the surface are collected using a channel electron multiplier (CEM or Channeltron), a high gain device ($\times 10^8$) for amplifying electronic signals under a vacuum environment (i.e. ultrahigh vacuum or UHV). These devices can amplify very weak signal sources and can be used to detect a wide range of particles (i.e. electrons, protons, UV photons and very low energy X-rays).

The second mode of operation consists of photoelectron spectroscopy from a micro-spot. Samples can be heated and cooled during the measurements. SPM systems are equipped with a preparation chamber to allow in-situ heating and cooling, sputtering and atomic gas plasma deposition, and a chamber for gaseous exposure (e.g. oxidation studies). SPM systems will often form part of a larger UHV surface analysis facility (e.g. LEED (Low Energy Electron Diffraction), AES (Auger Electron Spectroscopy) and PEEM (Photoemission Electron Microscopy)).

8.2 SCANNING ELECTRON MICROSCOPY TECHNIQUES

8.2.1 Scanning Electron Microscopy (SEM)

This is the most widely used of the surface analytical techniques. High resolution SEM has proved an invaluable tool for studying surface topography, oxide growth and failure analysis. The technique enables qualitative three-dimensional (3-D) imaging of surface features, however, it does not easily lend itself to quantitative surface roughness characterisation. This can be overcome by complementing SEM investigations with atomic force microscopy (AFM). In SEM, a highly focused high-energy (typically 10 keV) electron beam is scanned across the sample surface. The incident electron beam causes a large numbers of secondary electrons to be generated of which a number escape from the surface into the surrounding vacuum.

Detection is achieved by attracting the secondary electrons onto a phosphor screen, which emits light (i.e. glows) when struck by the electrons. The intensity of the emitted light from the phosphor screen is measured with a photomultiplier. In the process of interaction with atoms, some of the incident electrons may strike the atomic nucleus and reflect back into the vacuum. These electrons are known as backscattered primaries and can be detected using a backscattered electron detector. Backscattered electrons can provide information on the surface topography and on the average atomic number of the area under the electron beam.

SEM is suitable for all materials, but non-conducting materials must be given a thin conductive coating (e.g. gold and carbon sputtered), which can alter or mask the true surface morphology. The conductive film prevents charging. The resolution of topographical features achievable using SEM is approximately 5 nanometres. SEM is often used to survey a surface before more specialised techniques are employed. Applications include surface structure analysis, an increased depth of field, backscatter imaging and morphology. Figure 8.1: shows typical SEM images of 6Al-4V-titanium alloy that have been subjected to different surface treatments for adhesive bonding.



Figure 8.1: SEM images of different surface treatments of 6Al-4V-titanium alloy for adhesive bonding (magnification x 900).

A large number of spectroscopic techniques can be adapted and fitted directly on to many SEMs. Most of these techniques are described in the chapter dealing with Spectroscopy and Chromatography Techniques.

8.2.2 Photoemission electron microscopy (PEEM)

PEEM is a powerful analytical tool for investigating surfaces and interfaces, enabling fast parallel image acquisition and providing fields of view from almost 1 mm down to 1-2 μm . The technique can be used to study chemical reactions (e.g. catalytic oxidation), surface defects and magnetic structures. Combined with a high resolution of the order of 20 nm, PEEM enables access to many aspects in surface and thin-film magnetism on the mesoscopic length scale with sensitivity in the sub-monolayer range. PEEM systems are capable of imaging the signal of subsurface layers within 5 nm of the surface. As with SPM, image formation is based on the lateral photoelectron intensity distribution from a solid sample surface using a well-focused electron beam, which is scanned across the sample surface or employing parallel imaging through the use of electrostatic lenses.

8.3 SCANNING PROBE TECHNIQUES

Scanning probe microscopy (SPM) describes any technique (e.g. AFM and STM (Scanning Tunnelling Microscopy)) where the surface is imaged at high (or atomic scale) resolution by rastering (or scanning) an atomically sharp tip in close, but not in direct contact, with the surface in a back and forward pattern across the surface (see Figure 8.2) [11]. The measurement of the interaction between the probe tip and surface is combined with the measurement of the relative position of the probe tip to produce an image of the interaction strength as a function of position in the x-y plane and providing information on surface topography, lateral force, conductance, magnetic attraction or electrochemical response. Alternatively the probe can be stationary and the sample rastered.

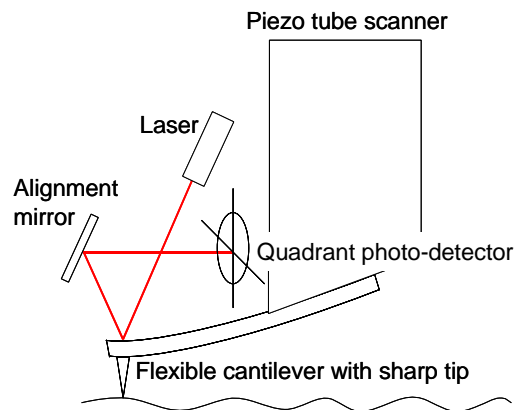


Figure 8.2: Schematic of scanning probe microscope.

8.3.1 Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a subset of SPM and measures surface characteristics, such as topography on the atomic scale [12-16]. A small tip mounted on a flexible cantilever attached to a measuring device is used to analyse the small vertical movements of the probe as it travels over the contours of the surface of the sample (similar principle of operation to the stylus profilometer). The cantilever is typically silicon or silicon nitride (typically 100 – 200 μm in length) with a tip radius of curvature of the order of 5 - 10 nm. The surface deflection of the cantilever, caused by changes in topography, is usually measured using a laser spot reflected from the top of the cantilever into an array of photodiodes. The deflection of the cantilever behaves according to Hooke's law.

Optical interferometry, capacitive sensing and piezoresistive AFM probes are also used for measuring deflection. These probes are fabricated with piezoresistive elements that act as a strain gage. A Wheatstone bridge is used to monitor strain in the AFM probe due to deflection, but this method is not as sensitive as laser deflection or interferometry. A feedback mechanism is generally employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample, and also to prevent the tip colliding with the sample and damaging the tip. High-resolution scans can take some time, and effects from thermal drift and probe shape de-convolution must be considered. A typical AFM image is shown in Figure 8.3.

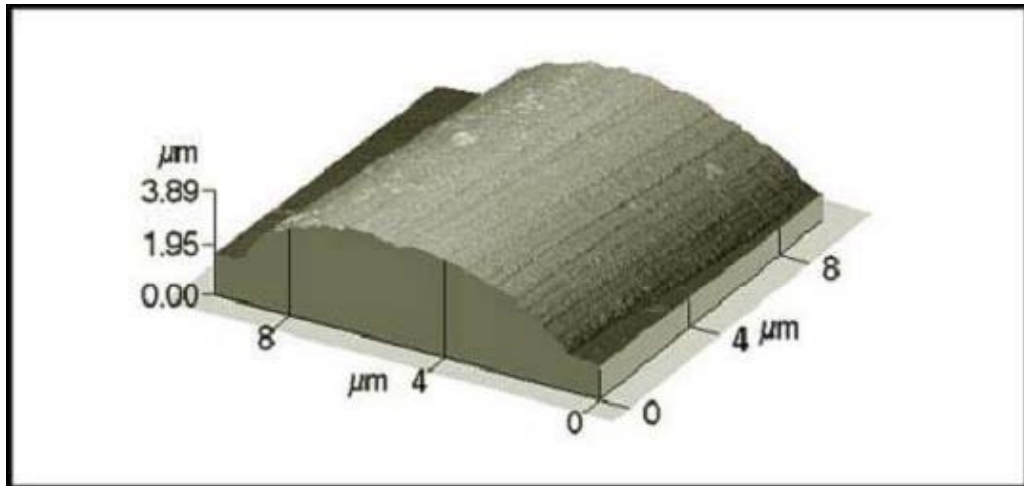


Figure 8.3: AFM surface map of a treated carbon fibre.

AFM has a spatial and depth resolution in the order of a few nanometres. Maximum scan range is typically 100 μm in the x- and y-directions, and 7 μm in the z-direction. Forces of the order of a few pico-newtons can now be routinely. AFM can be used to monitor interaction forces, such as van der Waals, magnetic, electrostatic, capillary and chemical bonding forces as a function of the separation distance between the probe tip and the sample surface.

AFM has several advantages over scanning electron microscopy. Unlike the electron microscope, which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM provides a true 3-D surface profile. Additionally, samples viewed by AFM do not require any special treatments (such as metal/carbon coatings) that would irreversibly change or damage the sample. While an electron microscope needs an expensive vacuum environment for proper operation, most AFM modes can work perfectly well in ambient air or even a liquid environment. This makes it possible to study biological macromolecules and even living organisms. Almost all materials can be studied without the need for sample preparation.

There are two main modes of operation: static (contact) and dynamic (non-contact), which maintains a constant force or separation to the sample surface, respectively. In contact mode, the probe is brought into contact with the surface with a low force (nN to μN) and rastered across the surface; the force between the tip and the surface is kept constant during scanning by maintaining a constant deflection (i.e. static tip deflection is used as a feedback signal). Measurement of static signals is prone to noise and drift, hence low stiffness cantilevers are used to boost the deflection signal. However, close to the surface of the sample, attractive forces (i.e. lateral (shear) and normal forces) can be quite strong, causing the cantilever tip to “snap-in” to the surface. The combination of lateral and normal forces can result in reduced spatial resolution and may cause damage to soft materials, such as biological and polymer samples, due to scraping between the tip and sample. Consequently, contact mode AFM is almost always done in contact where the overall force is repulsive. Atomic resolution images can only be achieved using contact mode AFM.

In dynamic mode (i.e. tapping mode and non-contact mode imaging), the cantilever is externally oscillated, at or close to its resonance frequency with oscillation amplitude ranging typically from 20 nm to 100 nm. In tapping mode AFM, the cantilever tip “lightly” taps on the sample surface during scanning, contacting the surface at the bottom of its swing. Tip-sample interaction forces modify the amplitude, phase and resonance frequency of the oscillating signal with changes in oscillation with respect to the external reference oscillation providing information about the sample's characteristics. By maintaining constant oscillation amplitude, via a feedback loop, a constant tip-sample interaction is maintained during imaging. The vertical position of the scanner at each position in the x-y plane is recorded to form the topographical map of the sample surface. Samples are less prone to being damaged, as lateral forces are virtually eliminated. Scanning speeds are slightly reduced in comparison with contact mode AFM.

In non-contact mode, the tip does not contact the sample surface, but oscillates above the surface at a frequency slightly higher than the resonance frequency of the cantilever. Amplitude of oscillation is less than 10 nm. Van der Waals forces, which extend approximately 1 nm to 10 nm above the surface, interact with the cantilever tip causing the resonant frequency of the cantilever to decrease. The decrease in resonant frequency is accompanied by a decrease in amplitude of oscillation. The feedback loop is used to either maintain constant oscillation amplitude or frequency and the distance the scanner moves vertically recorded to form a topographic image of the sample surface. The advantage of non-contact mode AFM is that no force is exerted on the sample surface. Limits on the tip-sample separation results in lower lateral resolution. In order to avoid surface contact, scan speeds need to be reduced, and hence scan speeds are lower than contact and tapping modes.

Schemes for dynamic mode operation include frequency modulation and the more common amplitude modulation [17-18]. In frequency modulation, changes in the oscillation frequency provide information about tip-sample interactions. Frequency can be measured with very high sensitivity and is used for atomic resolution imaging in ultra-high vacuum (UHV) conditions. In amplitude modulation, changes in the phase of oscillation can be used to discriminate between different types of materials on the surface. Amplitude modulation can be operated either in the non-contact or in the intermittent contact regime.

AFM nanoindentation has been used to measure and map nanohardness and elastic modulus [12]. Problems with the technique include no direct measurement of the tip-sample separation and the common need for low stiffness cantilevers, which tend to “snap-in” to the surface. The “snap-in” can be reduced by measuring in liquids or by using stiffer cantilevers, but in the latter case a more sensitive deflection sensor is needed. By applying a small dither to the tip, the stiffness (force gradient) of the bond can also be measured. The radius of curvature of the probe tip limits the quality of an image, and an incorrect choice of tip for the required resolution can lead to image artefacts. Surface contamination and dust can also adversely affect test results.

As previously mentioned, there are also shear forces acting on the AFM tip, which lead to torsion of the cantilever. These forces can be used to measure the friction between the tip and sample. Lateral forces can be measured using regular AFM instrumentation.

The term Friction Force Microscopy (FFM) or Lateral Force Microscopy (LFM) is frequently used to describe this form of measurement. A quadruple photodiode is used to simultaneously detect deflection and torsion of the cantilever, thus enabling both topographic and lateral force imaging.

8.3.2 Scanning Tunnelling Microscopy (STM)

STM has revolutionised surface science enabling real space atomic resolution images of surfaces. The technique consists of rastering a conductive sample with a fine metallic tipped probe with the probe in close proximity to the sample surface. A voltage is placed between the probe tip and the sample surface. As the probe tip approaches to within 1-2 Å of the surface, a tunnelling current (0.01-50 nA) can be induced in either direction between the tip and the surface with current flow being sensitive to the distance between the tip and the surface, and conductivity of the sample.

The exponential dependence of the tunnelling current on the probe tip to surface distance results in a high vertical resolution. The current between the probe tip and sample surface is continuously monitored and the vertical position of the tip with the surface can be adjusted either towards or away from the surface in order to maintain a constant current flow. By maintaining a constant current (constant current mode) it is possible to generate a topographic image of the surface. As the current is proportional to the local density of atomic states, the probe tip follows a contour of constant density of atomic states during scanning.

In constant current mode, image generation is slow. A single image may require seconds to a few minutes to generate, whereas images can be generated within 10^{-4} seconds using constant height mode. In this mode, the vertical position of the probe tip remains constant with the current as a function of lateral position representing the surface image. This mode of operation is only suitable for atomically flat surfaces otherwise the tip would inevitably collide with the surface damaging the probe tip and sample. A conductive sample is needed to generate a current flow between probe tip and sample surface. The STM needs to be operated under UHV conditions in order to produce atomic resolution images.

8.3.3 Scanning Thermal AFM

Micro-scale thermal properties of materials, such as FRPs, can be investigated using Scanning Thermal AFM [19]. The technique may be used with either a passive or active thermocouple probe. Although passive thermal probes have been used in a number of applications, particularly for evaluating heat generation in small-scale electronic devices, the passive nature of the probe limits the capability of the technique. Passive probes are unable to detect property-based variations at the micro-scale. In contrast, active thermocouple probes when coupled with an AFM are able to resolve material differences based on thermal properties instead of mechanical force. Tillman et al [12] produced a device (5 µm diameter platinum wire surrounded by a 75 µm diameter silver sheath) that acts simultaneously as a miniature thermocouple and a resistive heating element.

As with traditional AFM, the probe is held in contact with the sample using a feedback control loop to maintain a constant load on the surface. Using a separate feedback loop to maintain the probe at a fixed temperature, it is possible to raster the probe over the surface generating a thermal map of the sample surface. This provides information on localised thermal conductivity of the surface, and enables visualisation of the micro-scale heterogeneity in composite materials. By comparing the response of the active probe with a reference probe, differential thermal analysis can be performed. Samples as small as several cubic microns can be examined.

Modulated local thermal analysis AFM (LTA-AFM) has been used to measure transitions in thermoplastics and in-situ glass transition temperature, T_g , of glass and carbon fibre-reinforced epoxy laminates [11]. The transition temperature measurements have correlated well with results obtained using differential scanning calorimetry (DSC).

8.3.4 Atomic Force Acoustic Microscopy (AFAM)

Atomic Force Acoustic Microscopy (AFAM) is a hybrid acoustic/AFM technique that involves vibrating the cantilever at ultrasonic frequencies (10 kHz – 10 MHz) to excite its mechanical resonances [20-26]. The resonant frequencies of the AFM cantilever shift when the cantilever tip is in contact with the sample surface. The cantilever can be considered a miniaturised elastic beam that can vibrate in different types of modes (i.e. flexural, torsional and extensional). A piezoelectric ultrasonic transducer is used to excite either longitudinal or shear acoustic waves in the sample under examination. Longitudinal waves and shear waves cause out-of-plane surface vibrations and in-plane surface vibrations in the sample, respectively. Surface vibrations are coupled to the AFM cantilever beam through the tip when it is in contact with the sample. The AFM photodiode sensor using a lock-in amplifier detects changes in the amplitude of the cantilever vibration.

As the excitation frequency approaches the resonance frequency of the cantilever, the detected amplitude of the cantilever vibrations increases, enabling its resonance frequency to be determined. The amplitude and phase of the cantilever vibration, as well as the shift of the cantilever resonance frequencies contain information about local tip-sample contact stiffness. Quantitative elastic property data can be extracted by measuring the resonant frequencies under both free-space and surface-coupled conditions. Elastic forces dominate tip-sample interactions. AFAM systems are fitted with small diameter tips capable of lateral resolutions of 5-10 nm. Frequency-tracking electronics have been developed to enable rapid imaging of the contact resonance frequency in a given area on the sample surface, thus enabling maps of the contact stiffness and the indentation modulus to be obtained. The technique is capable of measuring the elastic properties of ultra-thin films (i.e. 50 nm). In order to generate reliable quantitative data, requires further work to understand and control tip wear and tip-contact sample behaviour. Silicon tips have been known to experience considerable wear during testing, which can cause large uncertainties in elastic property measurements. Using diamond-coated tips, however, the wear can be avoided (or at least minimised). The effects of tip abrasion/erosion and deformation are key to measurement accuracy. Concerns also exist in relation to the effects of viscoelastic damping and need for finite element analysis to account for geometric effects on resonant frequency for cantilever beams with non-rectangular geometries.

8.3.5 Scanning Electrochemical Microscopy (SECM)

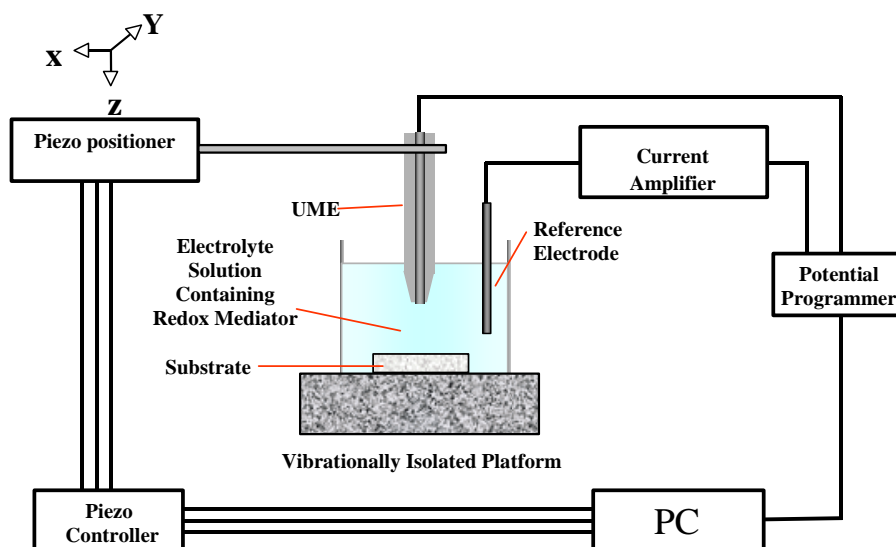


Figure 8.4: Schematic diagram of a scanning electrochemical microscope.

Scanning Electrochemical Microscopy (SECM) is a scanning probe technique that is based on Faradaic current changes as an ultramicroelectrode (UME) is scanned in an electrolyte solution a few microns above a sample's surface (Figure 8.4) [27-28]. The electrochemical response of the UME is recorded as it approaches or scans over a surface. The images obtained depend on the sample topography and surface reactivity. The response of the scanning electrochemical microscope is sensitive to the presence of conducting and electro-active species, which makes SECM useful for imaging heterogeneous surfaces and studying dynamic electrochemistry processes.

The SECM uses piezoelectric based controllers to position the tip in any of the three axes at scan speeds from 0.05 to 1000 $\mu\text{m/s}$, although 1 to 20 $\mu\text{m/s}$ is a more typical scan rate. In addition, the position controllers allow movements of less than 0.1 to 300 μm during imaging. The tip and substrate potential will often be simultaneously controlled and the Faradaic current flow monitored during imaging. This is aided by use of a bi-potentiostat. Hardware on the personal computer supplies control signals to the piezo-position controller and collects data from the tip and substrate. A video microscope is useful to observe the tip electrode as it approaches the substrate.

A commonly used tip is based on an embedded disk-shaped geometry (see Figure 8.5). Disk-shaped UMEs are made by heat sealing microscopic wires (platinum, gold, silver or carbon fibres) in an insulating sheath of borosilicate glass (or a polymeric resin). The end is then polished to expose an embedded disk. The tip is then ground so that the glass insulator forms a truncated cone, thus enabling the tip to approach the sample surface more closely. A typical disk electrode would have a radius of 1 to 25 μm . An insulator radius of 3 to 10 times larger than the electrode radius (known as the RG ratio) surrounds the electrode. Spatial resolution of SECM is limited by the size of the SECM tip and the minimum current that can be accurately measured. SECM spatial resolution is comparable to the size of the UME probe (typically 0.1 – 25 μm in diameter). For high-resolution SECM measurements, laser-pulled platinum nanoelectrodes and electrochemically etched carbon fibre UMEs with a tip diameter of 1 μm are routinely being used.

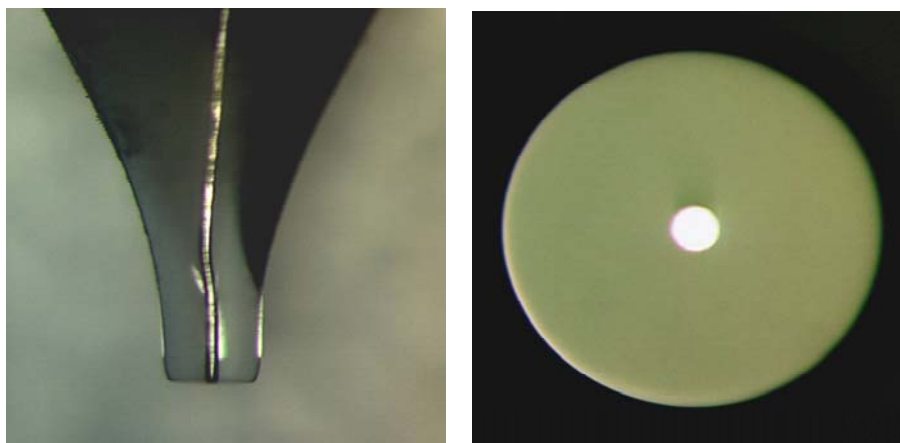


Figure 8.5: SECM disk-shaped UME viewed side on (left) and end on (right).

SECM has excellent chemical selectivity, and therefore is an excellent tool for examining local interfacial electrochemical properties and reactions. The technique could potentially be used to determine absolute rates of diffusion and for monitoring chemical degradation at the fibre/matrix interface in composite materials. Strong electric fields need to be avoided as these may affect physical conditions at the sample surface. A Faraday cage is recommended to shield the equipment.

8.3.6 Scanning Kelvin Probe (SKP)

Scanning Kelvin Probe (SKP) is an electrochemical technique similar to SECM, which is used to measure the electrode potential at metal/polymer interfaces [29]. The probe tip and sample surface form essentially a parallel plate capacitor plate with height regulation achieved through the application of a small modulation voltage (300 mV) across the tip-sample gap and then monitoring the modulated current, which is proportional to the average tip-sample separation. The modulated current is measured at the desired distance and then kept constant by a piezo-position controller (see reference [22] for a full description of the basic principles of operation). The technique enables both topography and voltage potential to be measured simultaneously. SKP can detect changes in sub-surface metal oxide structures (50 μm in depth) and variations in the interfacial ionic conductivity, hence it is possible to study the kinetics of interfacial reactions and de-adhesion processes that cause interfacial degradation. For moisture degradation studies, it is recommended that tests be conducted under normal atmospheric pressure and high humidity. The spatial resolution is typically 50 μm .

9 SPECTROSCOPY AND CHROMATOGRAPHY TECHNIQUES

Chemical characterisation can be achieved using either spectroscopic or chromatographic techniques. Spectroscopic analysis provides detailed information about molecular structure, conformation, and physical-chemical characteristics, and chromatographic techniques enable quantitative compositional characterisation. This section provides a brief summary of surface and chemical analysis techniques that can be used to analyse and evaluate chemical, physical and mechanical changes due to processing and service conditions.

These techniques can provide important information on (see also Appendix 1):

- Failure modes and mechanisms;
- Chemical composition and morphology (e.g. surface roughness) of surface layers;
- Effects of surface preparation on surface chemistry;
- Stability of surfaces and interfaces;
- Surface contaminants; and
- Chemical and physical degradation of both the adhesive and oxide layers.

9.1 ELECTRON DISPERSIVE X-RAY SPECTROSCOPY (EDX OR EDS)

EDX involves analysis of the elemental composition of a surface from X-rays emitted upon exposure to a primary beam of electrons. The X-rays emitted are characteristic of the atom from which they originated. Detection and analysis of characteristic X-ray lines of various elements can be obtained using an EDX system attached to an SEM. The maximum operational depth of EDX is typically 2 to 10 μm , and therefore is not a surface science technique. The volume analysed can be as large as several cubic microns. The actual penetration depth depends on the type of material being analysed and the acceleration potential used in the SEM. The technique can be used generate elemental distribution maps of the area of interest, enabling both qualitative (boron to uranium) and quantitative (sodium to uranium) elemental analysis.

Element mapping is generally a slow process due to the low X-ray intensity. Images may take a few hours to generate. Recent developments have seen the emergence X-ray microcalorimeter detectors that are capable of an X-ray energy resolution of approximately 3 eV, at least 10 times better than conventional detectors. EDX cannot provide information on chemical bonds, although it can provide information on element depletion and migration as a result of environmental exposure. Non-conductive EDX specimens are generally sputtered coated with a thin conductive layer of carbon in preference to gold, as the latter tends to attenuate X-ray signals. EDX applications; include qualitative X-ray mapping, line scans and spot analysis.

9.2 X-RAY PHOTOEMISSION ELECTRON MICROSCOPY (X-PEEM)

X-PEEM is an analytical tool combining PEEM (using UV light) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy that can be used to investigate simultaneously topological, elemental, chemical state, and magnetic properties of surfaces, thin films, and multilayers.

NEXAFS spectroscopy is an established technique for studying elemental composition, chemical bonding, and molecular orientation. PEEM enables high spatial resolution (typically 20 nm) for NEXAFS. Potential applications include the study of different phases in ceramics (e.g. boron nitride) and metal alloys, and the analysis of small particles. The technique can be used to perform element selective magnetic domain imaging on heterogeneous samples with different magnetic layers, like spin valves and tunnel junctions. Nanosecond time resolution measurements are possible using X-PEEM, thus enabling the study of processes, such as the nucleation and subsequent growth of reversed domains in permalloys, and catalytic reactions at surfaces.

9.3 X-RAY FLUORESCENCE SPECTROSCOPY (XRF)

In XRF, the target material is irradiated with X-rays, which results in the release of a photon of characteristic energy. Each element has its own set of characteristic emissions and can be used for qualitative and semi-quantitative elemental analysis in a wide range of materials, above aluminium in the periodic table. Minimal sample preparation is required. A variant, total reflection X-ray fluorescence uses X-rays impinging on the surface of a sample at glancing incidence such that total reflection occurs. This excites photon emission from atoms in only the topmost layers of the material. Whilst this technique is very sensitive it does require very flat samples. Museum curators often use XRF to study ancient objects because the measurements are non-destructive and usually the whole object can be analyzed without the need to take samples from the object.

9.4 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

XPS (or Electron Spectroscopy for Chemical Analysis (ESCA)) is an analytical technique that measures the energies of photoelectrons emitted from atoms of a sample when it is irradiated with soft (or low energy) X-ray photons. Electrons are emitted from the sample if the photons are of sufficient energy. The analyser measures both the kinetic energy of the emitted photoelectrons and the binding energy of the photoelectron (i.e. energy required to remove the electron from the atom) is calculated. A work function is required for photoemission from the solid, as extra energy is needed to transfer the electron from the surface to the vacuum. The value of the work function is a predetermined for each spectrometer. The binding energy of an electron is characteristic of the element, orbital and chemical environment.

XPS is capable of detecting all elements with the exceptions of hydrogen and helium, and can provide information on chemical structure (e.g. bonding and oxidation states) and element distribution present on the surface of any solid material. Chemical analysis is achieved through the identification of the characteristic peaks for each element present and analysis of the peak areas. The technique is surface-sensitive with a maximum operational depth of less than 10 nanometres with a spatial resolution of less than 10 μm . It is now possible to obtain spatially resolved chemical maps of surfaces for very small features (known as imaging or iXPS).

XPS can be used to determine the effect of elevated temperature and surface preparation on surface chemistry and is used to examine the cause of adhesion problems. The technique can be used in conjunction with inert gas ion sputtering to determine the variation in chemical composition with depth. It is worth noting that many polymeric material samples are sensitive to ion beam damage. XPS is frequently used for quantitative elemental analysis of fracture surfaces, to determine the effect of surface preparation on surface chemistry and for monitoring chemical changes for adhesive bonding. Surface contamination can affect adhesion, optical properties, and even flammability of materials. Common contaminants like hydrocarbons, silicones, or salts can be detected with XPS and AES. These techniques have been used to identify and quantify contaminants responsible for adhesion failures in plating and bonding processes. Identification of contaminants is a first step in eliminating these types of problems.

9.5 AUGER ELECTRON SPECTROSCOPY (AES)

AES is a surface sensitive, non-destructive technique for identifying the elements in the first few atomic layers (~1 to 5 nanometres) on a specimen surface and is able to provide quantitative data on the detected elements. High-energy electron beam bombardment of the surface results in the emission of Auger electrons at characteristic discrete energies. Combined with inert gas ion sputtering, AES can be used to obtain depth composition profiles. The technique can be used to map the distribution of elements present on a specimen surface (spatial resolution of 0.5 μm). The technique is capable of detecting all elements with the exception of hydrogen and helium. Spectrometers can be fitted with a facility for in-situ testing of bonded joints and other specimen configurations, which are rapidly analysed under high vacuum conditions. Ultra-high vacuum (UHV) conditions (1×10^{-10} Pa) are required to prevent contamination and oxidation of the fracture surfaces.

The technique is not particularly suited to examination of polymers (i.e. insulating materials) due to the possibility of beam damage and electrical charging of the sample, which can complicate data interpretation. The technique provides limited information on oxidation states. AES is a useful and complementary technique to XPS as it has better spatial resolution (smaller spot size is possible), but exhibits more sample damage and is less suited to determining chemical bonding or oxidation state.

9.6 ELECTRON ENERGY LOSS SPECTROSCOPY (EELS)

This technique uses the inelastic scattering of low energy electrons in order to measure the vibrational spectra of surface species (electron-analogue of Raman spectroscopy). Since the technique employs low energy electrons, it is necessarily restricted to use in ultra-high vacuum environments. However, the use of low energy electrons ensures that it is a surface specific technique. The energy loss of a beam of electrons of fixed incident energy is analysed. This method has high sensitivity but requires flat, preferably conducting samples and has lower resolution than IRS techniques.

9.7 SECONDARY ION MASS SPECTROMETRY (SIMS)

In SIMS, the surface is bombarded with a beam of high-energy ions resulting in the ejection of molecular fragments, atoms and ions from the surface, which are subsequently analysed (traditionally only the positive ions). It is capable of providing surface elemental analysis and depth concentration profiles on areas from several mm to sub micron. SIMS can detect all elements and isotopes including hydrogen and hydrogenated compounds with very high sensitivity (parts per billion). It is, however, not readily amenable to quantitative analysis (complex and requires reference standards). The depth resolution is under 200 nanometres and areas of up to 500 μm can be studied. Whilst SIMS is suitable for all materials, flat sample surfaces are required to give the best spatial and depth resolution. There are a number of different variants of the technique including static SIMS (sub-mono-layer elemental analysis), dynamic SIMS (depth composition profiles) and imaging SIMS (elemental mapping) analysis.

9.8 RUTHERFORD BACKSCATTERING SPECTROMETRY (RBS)

RBS is one of a number of ion scattering techniques, which provide different information on an elemental level, depending on the primary ion energy (typically 1-3 MeV) and the scattered ion that is detected. A beam of positive helium ions (He^+) is directed at the target surface and the ions, which are scattered by the sample nuclei, are measured and analysed. RBS is a non-destructive technique since the erosion and the radiation degradation of the sample material by the particle impact is negligible. As a result RBS is used for the quantitative, non-destructive compositional depth profiling and thickness measurements on thin films. The depth distribution of constituents can be reconstructed with a depth resolution of 10 to 20 nm. This method can probe several thousand atomic layers and is ideal for surface analysis up to 2 μm depth.

9.9 INFRARED SPECTROSCOPY (IRS)

IRS provides information on molecular structure based on specific frequencies associated with internal vibrations of groups of atoms in molecules using a laser in the infrared region to excite the target material and analyse the frequencies absorbed. It makes use of the fact that for polymeric materials the chemical bonds between the atoms in the polymer molecules can vibrate at frequencies in the IR range of the electromagnetic spectrum (i.e. at wave numbers from 100-4000 cm^{-1}).

By directing IR light at a polymeric material and measuring the absorption (or transmission) of the various frequencies, it is possible to characterise, or “finger-print”, the polymeric material since it will have specific frequencies at which it is seen to absorb strongly. This “finger-print” of the various frequencies at which the material absorbs is referred to as the IR spectrum. By monitoring the IR spectrum (i.e. absorption intensities) of a polymer during cure it is possible to determine the formation/transformation of chemical species. Change in intensities, the basis of cure monitoring techniques, gives direct information about the timescale within which the chemicals involved in the cure reaction have been used and the reaction is complete. The technique can be used to analyse gases, liquids and solids. Both qualitative and quantitative chemical analysis data can be obtained. A very powerful automatic IRS system with a scanning stage suitable for imaging is shown in Figure 9.1.



Figure 9.1: Imaging IRS system from Perkin-Elmer.

IRS is often used in conjunction with Raman spectroscopy as a complementary identification technique. Some quantitative analysis is possible by analysing the magnitude of the characteristic absorption peaks. It requires minimal sample preparation, but samples need to be transparent to infrared, the method is less useful for inorganic materials. Water is problematic as it obscures the spectrum. IRS is not inherently surface-specific (analysis is possible to within 0.5 to 3 μm of the sample surface), but variants improve this aspect. One variant, attenuated total reflectance uses a prism in optical contact with the sample resulting in total internal reflection after penetrating a small way into the sample surface and is particularly useful for investigating adhesion problems and surface treatment for strong IR absorbers provided the surface is flat. There are various ways of performing IR spectroscopy on a material, and probably the most widely used is known as Fourier transform infra-red or FTIR. Computerised databases of spectra for common polymeric materials are available to enable characterisation of molecular structure by observing spectral differences between known materials and the test sample.

9.10 RAMAN SPECTROSCOPY

Raman is based on the inelastic scattering of monochromatic light. A laser (e.g. Ar+ or He-Ne) excites the material, which is usually in the visible region of the spectrum (Figure 9.2). The frequency of scattered light is analysed compared with incident values. The technique is similar to infrared spectroscopy (IRS) in determining the nature of molecular structures and is a complementary technique to IRS when characteristic frequencies are weak or for highly absorbing materials. Raman spectroscopy is sensitive to a material's composition and structure and can distinguish between different structural arrangements of similar atoms. The vibrational spectrum of a material is a function not only of its constituent atoms, but also the spatial arrangement and the strength of bonding between atoms. Samples require minimal preparation, but need to be stable to high intensity light and contain no species that fluoresce when excited by visible radiation.

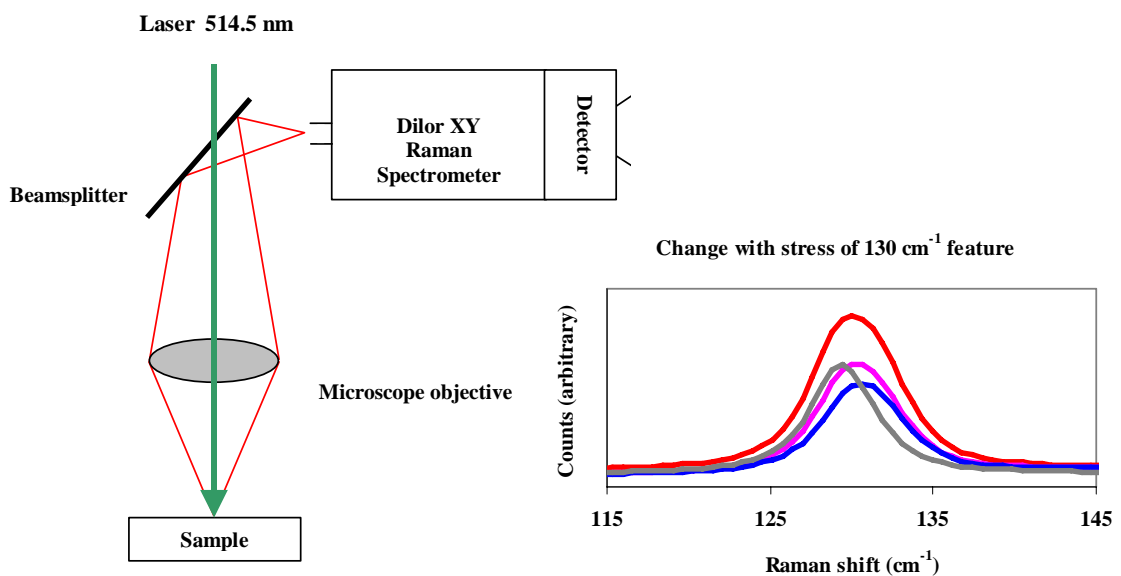


Figure 9.2: Schematic of scattering from α -quartz (SiO_2) (Dilor XY Raman spectrometer)

Raman spectroscopy can be used to determine near surface strain distribution. The use of the technique for determining strain relies on detecting frequency shifts in Raman spectra. The frequency and intensity (peak height) of the scattered peak will change with stress. Frequency is dependent on the strain state of the material (i.e. residual strains will cause the peak to shift). In general, compressive stresses result in an increase in Raman frequency and conversely tensile stresses cause a reduction. The relation between strain or stress and the Raman frequency tends to be linear under uniaxial and biaxial loads. By monitoring the Raman scattering frequency at different positions on the sample, a strain map can be produced with a spatial resolution of $0.5\ \mu\text{m}$ (or better). Raman spectroscopy systems are capable of measuring frequency changes of $\sim 0.02\ \text{cm}^{-1}$.

Using the well-defined relationship between the peak frequency position of a strain sensitive Raman band and the applied strain, the true axial strain distribution in an embedded fibre can be determined at the microscopic level (limited to non-amorphous reinforcement with strong Raman signals and transparent matrices). Residual strains and thermal effects will also cause the Raman peak to shift. Figure 9.3 shows a linear shift in the Raman peak at $464\ \text{cm}^{-1}$ with applied torque for a quartz surface acoustic wave strain sensor subjected to torsion loads. This shift can be directly related to shear strain.

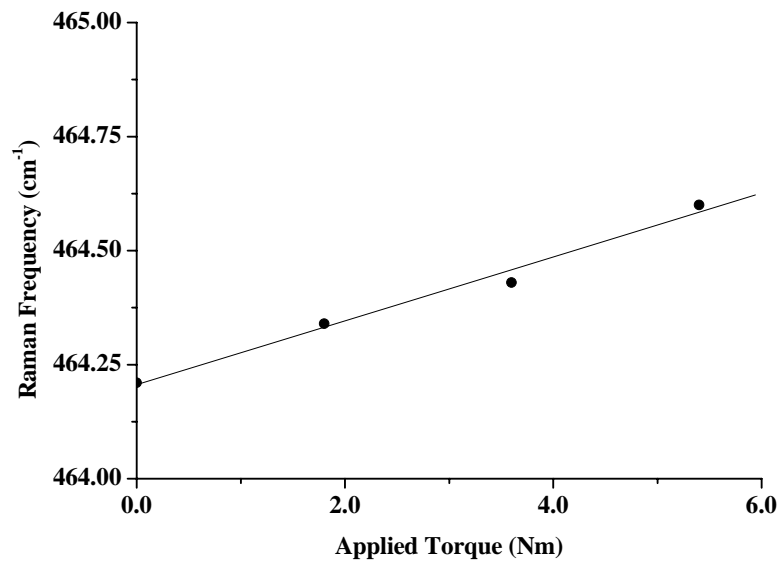


Figure 9.3: Raman frequency shift ($464\ \text{cm}^{-1}$) with applied.

It should be noted that the intensity or peak height is dependent not only on the strain state of the inspected area, but also on the separation distance between the optical microscope objective lens and the inspected surface. In order to use the peak height, the beam needs to be focused identically at each location on the sample surface; a difficult task on structures that have undergone out-of-plane deformation as a result of twisting. Hence, it is recommended that the Raman frequency shift, which is independent of focal path, be used in preference to the peak height.

9.11 OPTICALLY STIMULATED ELECTRON EMISSION (OSEE)

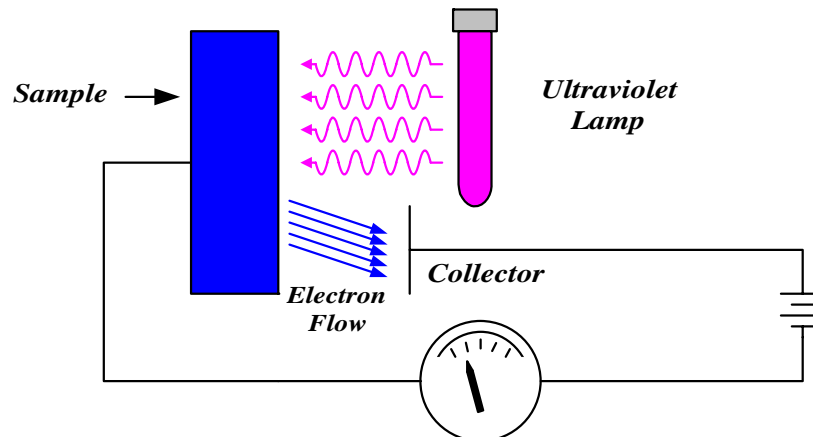


Figure 9.4: Principle of Optically Stimulated Electron Emission (OSEE).
(courtesy of Alcan International Ltd)

Optically stimulated electron emission (OSEE) has proved a useful tool for monitoring surface contamination and optimisation of surface treatments for metallic substrates. It is highly sensitive to very low levels of contamination, and has been successfully used for determining surface characteristics in multi-stage processing. OSEE operates by illuminating the area of inspection with ultraviolet (UV) radiation in the presence of a direct current (DC) electric field (see Figure 9.4). The UV radiation liberates electrons in the area of inspection by the photoelectric effect. The free electrons are collected on the positively charged anode with the magnitude of the resultant current being strongly related to the level of surface contamination.

Contaminants absorb the UV radiation, thereby reducing the number of electrons emitted from the substrate, thus the greater the current the cleaner the surface. OSEE is particularly suited to studying contamination build-up following surface treatment, and could be used to determine maximum time allowable between treatment and application of an adhesive (i.e. open time).

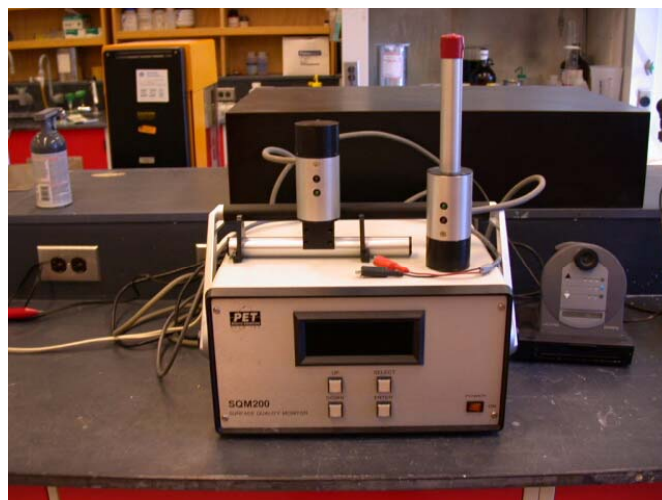


Figure 9.5: Portable optically stimulated electron emission (OSEE) unit
(courtesy of Alcan International Ltd)

In summary, OSEE is best suited for on-line inspection to determine the level of cleanliness or degree of treatment. OSEE is unable to provide absolute measurements of surface activity for different treatments or ageing times. The technique is only able to detect barrier layers/cleaning levels through changes relative to initial substrate surface measurements. Hence, calibration is required for each surface to be assessed. Efficacy is compromised when contaminants fluoresce. OSEE is a non-contact, non-destructive technique that provides quantitative data. It is fast and relatively inexpensive, and straightforward to operate. A portable system is shown in Figure 9.5. The technique can be used to assess different methods of cleaning or the effectiveness of different cleaning agents.

10 CONCLUSIONS AND RECOMMENDATIONS

The array of techniques available is truly diverse and wide ranging. In many cases the advantages of the different methods described in this document are limited to a fairly narrow range of applications, and in selecting the techniques that are being recommended by the authors of this report, consideration is given to the competitive advantage, potential use, range of applications and level of investment required to enable the strength of the technique to be exploited to their full extent.

10.1 DAMAGE ASSESMENT

Although there are a number of attractive potential techniques for the assessment of microstructure (see section 10.2), there is only one clear leader when in the case of damage assessment. The considerations leading to this conclusion are presented below. Pulsed and transient thermography techniques were seen to be the best method to meet the selection criteria for assessing damage initiation and growth. As well as being a non-destructive technique it is also non-contact, making it more amenable to operate the technique in-situ. Another strong advantage of this technique is that can be applied to a broad range of materials: metals, polymers, ceramics and composites. Pulsed, or and transient thermography is also normally a very rapid technique (often real-time) and this extends the possible applications to include process control and on-line inspection.

One of the limitations of the DC thermography technique presently in use at NPL is the large effect of surface emissivity. Surface discoloration of components used in industrial environments completely dominates the apparent temperature distribution of the image obtained with DC Thermography. This dominance persists whether the object under observation is soak heated or radiated because darker surfaces both absorb and re-emit heat at higher rates than light coloured surfaces. Surface emissivity has restricted the application of thermography to test coupons of thermal barrier coatings, as these are of uniform colour because they have not been subjected to the products of combustion. Real turbine blades that have been in service have a large range of discolouration due to carbon and other deposits on the surface.

One of the advantages of pulsed thermography is that it enables transient effects (both in heating as well as cooling to be studied. Heating and cooling rates can be calculated by differentiating the heat intensity levels with respect to time. It is also possible to double differentiate the thermograms to obtain the thermal equivalent of acceleration.

Some work carried out at Bath University suggests that when these single or double differentials are then normalised (dividing them by the instantaneous intensity) it may be possible to obtain thermal information that is far less sensitive to the surface emissivity.

To begin, it is envisaged that NPL may be able to use its present thermal imaging camera and write software to control the image acquisition and post processing, however it will be necessary to purchase the high power flash lamps and interface them to the computer to enable a synchronous start to the data acquisition. This is likely to cost some £3k. Once the technique is tried on a suitable case study, it is expected that this will highlight the need for faster frame rates and faster data processing requiring a new camera and computer. Should this be necessary the cost for further development is likely to be of the order of £30k.

10.2 MICROSTRUCTURE ASSESSMENT

It was clearly evident from the review that only a few non-invasive techniques are sufficiently developed for monitoring microstructural changes in engineering materials for production and service inspection purposes. These techniques were generally restricted to providing surface or bulk properties, topographical or chemical information, and limited by material type and scale. The equipment costs associated with many of the techniques was generally high, especially those techniques requiring UHV conditions. In many of the categories, there were one or more techniques that with further development could prove invaluable to current and future research work.

This section summarises the findings from the review in relation to selection of a suitable non-invasive method for quantitative microstructure measurements warranting further investigation.

Optical Microscopy: The number of optical microscopy techniques available is considerable. These techniques are generally used for imaging purposes providing information on surface topography (e.g. roughness), although techniques such as near field microscopy can be used to provide quantitative information on the size, shape, distribution and location of grains, particulates and defects, and phase changes (e.g. metallic alloys). Suitable surface treatments (e.g. etching) are often used to enhance (or highlight) surface textures. Standardised procedures (including measurement uncertainty) exist for most optical microscopy techniques. Work is still required to produce traceable calibration standards for 3D optical microscopy to enable verification of measurements of surface features (including surface roughness) obtained using 3D microscopes, such as the Alicona infinite focus microscope, over the range of scales these microscopes operate.

Ultrasonics and Acoustics: A versatile group of techniques capable of providing information on microstructural features (including damage) within the bulk of the material and elastic property data [30]. Ultrasonic parameters, such as velocity, attenuation, scattering amplitude, scattering spectrum and frequency dependence are being used to provide information on a wide range of material properties. For example, ultrasonic velocities provide information relating to material composition, phase fraction and phase transformations, and can be used to determine elastic properties. Scattering amplitude can be used to determine grain structure and re-crystallisation.

It is possible to differentiate between grain effects and dislocations based on frequency or time dependence measurements. Laser ultrasonics has potential for real-time, in-situ microstructural measurements for monitoring/controlling metal processing. Although a number of proto-type systems have been developed to investigate the capability of this technique for monitoring steel and aluminium production, there are no commercial systems available. In order to develop a working system, considerable capital outlay would be required. Data analysis and interpretation is also considerably complex.

A number of ultrasonic techniques could be investigated including scanning acoustic microscopy (SAM). The SAM system at NPL currently operates from 0 to 75 MHz. A frequency range of 200 MHz to 600 MHz would enable information to be obtained on micro-scale features down to approximately 2 microns suitable for use in studying material and biological microstructures. The layer thickness and mechanical properties of layered solids could be studied by examining the dispersion properties of surface acoustic waves. The development of a high frequency bandwidth (GHz) ultrasonic system capable of measuring 3D elastic properties and investigating internal structures (including damage) warrants further consideration. It would require capital investment in equipment in order to produce a system with a suitable bandwidth to enable determination of elastic properties and microstructural differences.

Electrical and Electromagnetic Techniques: Although this group of techniques are used for NDE purposes, particularly for maintenance and service inspection there is concern that each method is limited to a narrow range of applications. A study was conducted at NPL [31] using surface resistivity measurements to determine the effect of chromic acid etching (CAE) on oxide film formation on aluminium samples. The technique proved insensitive to the different levels of CAE treatment. Surface contamination and the state of the surface/substrate prior to treatment were key factors that affected adherence and growth of the oxide layer. The resistance of the oxide layer, formed as a result of chemical treatment, tends to breakdown under prolonged exposure to applied voltage. Eddy current techniques are commonly used to inspect metallic structures for corrosion products that can result in debonding. As previously mentioned, eddy current increases with increasing conductivity, and therefore these techniques are not particularly suited to non-metallic substrates, thus limiting their applications. Considerable amount of information provided by eddy currents can be obtained using thermography.

X-Ray Techniques: A powerful collection of techniques capable of providing detailed information relating to microstructure, composition and residual stress state. As shown in Section 7, the potential for these techniques is immense. The two techniques that stand out are XRD and X-ray tomography. XRD systems are now capable of residual stress measurements and strain mapping (e.g. strain distribution in piezoelectric devices), micro-chemical composition analysis (20 μm square inspection area), phase identification between grains, measurement of surface texture, crystal size and layer thickness of thin films (nanofilms), and inspection of micro-circuitry. Further work is required to establish a relationship between the XRD measurements and engineering strain measurements. The latter would require accurate calibration specimens that could be subjected to known loading conditions. Engineering strains would need to be independently verified using either contact or non-contact techniques.

X-ray tomography can provide 3D microstructural information (i.e. internal cracking, corrosion pitting and void content). Internal micro-damage due to cavitation and shrinkage not evident on the surface can be detected using this technique. It would be possible to determine the volume fractions of constituents in composite materials and foams.

Scanning Probe Microscopy (SPM): SPM consists of a powerful set of techniques, which could potentially provide in-situ quantitative mechanical and chemical measurements for characterising surface and interfacial properties. Combined with atomic force, acoustic, thermal and electrochemical probes, SPM could provide a comprehensive set of data sufficient to fully characterise these properties for a wide range of materials. This is in addition to information relating surface topography. SPM techniques are not restricted by material type or format, or limited to ambient conditions, and thus could be used for sub-zero and elevated temperature studies. The review identified a number of issues still to be resolved with SPM techniques in order to provide the necessary confidence in the use of these techniques in providing accurate and reliable engineering data. There is a high degree of uncertainty in the measured data, which can be attributed to a number of factors, such as load frame compliance correction, calibration errors, difficulty in establishing true zero for load and displacement, variability in probe tip geometry, wear and deformation of indenter tip, surface roughness effects, thermal drift and vibration effects.

All these issues need to be addressed in rigorous and controlled manner in order to formalise methods based on these surface techniques for characterising mechanical and chemical properties. Increasing the multi-functionality of AFM systems to include one or more of the following facilities: Atomic Force Acoustic Microscopy (AFAM), Scanning Thermal AFM and Scanning Kelvin Probe (SKP) would add substantially to NPL's capability. Further developmental work investigating the different modes of AFM operation (i.e. tapping mode for elastic property and glass transition measurements and frequency modulation providing increased sensitivity) could also prove beneficial.

Spectroscopy and Chromatography Techniques: These techniques can provide important information on surface and bulk physical-chemical characteristics of materials both at the surface and within the bulk (see Appendix 1). Techniques covered in Section 9 were only the tip of the iceberg, as a quick perusal of Wikipedia on the internet will confirm. Major concerns with most of these techniques relate to the need for UHV conditions and the high capital equipment outlay required and high maintenance costs. IRS and Raman Spectroscopy are two techniques that are not restricted by the need for UHV conditions. IRS can provide chemical composition information on polymers, metallic oxides and ceramics. It is possible to determine the formation/transformation of chemical species in polymeric materials during cure, providing direct information about the timescale within which the chemicals involved in the cure reaction have been used and the reaction is complete. The technique can be used to analyse gases, liquids and solids. Combined with dielectrics and other techniques it could be used to assess the degree and rate of cure, and efficacy of catalysts and curing agents. IRS can also be used to evaluate changes in surface chemistry due to environmental effects (e.g. weathering).

As previously mentioned, Raman spectroscopy is a complementary technique to IRS. It is sensitive to a material's composition and structure and can distinguish between different structural arrangements of similar atoms. The technique is widely used to measure surface strains, although there is little work been carried out to produce test procedures and traceable calibration standards. Stain mapping facility for Raman spectroscopy would compliment existing Digital Image Correlation (DIC) and Electronic Speckle Pattern Interferometry (ESPI) facilities at NPL. The use of an accurate calibration specimen also applies to Raman spectroscopy. The technique would need further investigation in order to establish a relationship between Raman frequency shift and engineering strain measurements.

Selection Criteria: A decision analysis technique was applied to quantitatively evaluate those non-invasive techniques that were considered the most promising candidates for monitoring changes in microstructure. The objective was to identify the technique with the most potential for further investigation in “**SM07: Assessment of Damage and Microstructural Condition of Materials Using Non-Invasive Techniques**”. Each of the selected methods (see Appendices 2 and 3) was evaluated in terms of 12 criteria, encompassing a number of key issues (see below). There was no attempt made to assign weightings to the different criteria to indicate relative importance. Each criterion was numerically rated, as shown below, depending on the range of possibilities available.

- Surface/sub-surface capability (0 = surface only, 1 = sub-surface only, 2 = both)
- Depth resolution (0 = surface only, 1 = low-medium, 2 = high)
- Spatial resolution (1 = low, 2 = medium, 3 = high)
- Inspection area (1 = small, 2 = medium, 3 = large)
- Information provided (1 = molecular and/or thermo-elastic properties/stress and strain, 2 = limited microstructure information, 3 = comprehensive microstructure information, 4 = comprehensive microstructure information + additional material data (inc. chemical/elemental, stress and strain))
- Quantitative/type of data (1 = qualitative, 2 = semi-quantitative, 3 = quantitative)
- Chemical/elemental distribution (0 = unavailable, 1 = possible)
- Depth profiling (0 = unavailable, 1 = available)
- Material applicability (1 = restricted, 2 = moderate, 3 = all materials)
- Specimen preparation requirements (1 = low, 2 = medium, 3 = high)
- Existing equipment (0 = unavailable on-site, 1 = existing equipment)
- Capital requirement /cost (1 = new equipment required, 2 = upgrade required or limited access, 3 = no additional equipment required)

Allowing for a degree of subjectivity, which was unavoidable considering the nature of some of the criterion, the overall evaluation (see Appendix 3) from the decision analysis technique indicates that XRD is by far the strongest candidate. As indicated in Appendix 2, XRD is capable of providing a wide range of material properties (see also previous comments in this section). Portable systems for in-situ strain measurements are available, and it is envisaged in the foreseeable future that XRD systems will be capable of in-situ microstructure measurements for production and service inspection.

It is recommended that XRD be pursued further in-depth. In order to facilitate this exercise, it is recommended that the existing XRD facility at NPL should be upgraded to include improved optics. This would expand the facilities and enable a far wider range of technical problems to be addressed. Additional capabilities would include residual stress measurements and strain mapping, micro-chemical composition analysis, phase identification between grains, measurement of surface texture, crystal size and distribution, and layer thickness of thin films. Case studies would need to be defined and tests conducted on materials with known microstructure to assess the sensitivity and resolution of the technique to be followed by further assessment on materials whose detailed microstructure is unknown. The actual microstructure of the material would be determined subsequently using conventional metallographic techniques.

Although ultrasonic techniques (e.g. laser-ultrasound) are potentially suitable for in-situ microstructure measurements, it would require a significant capital outlay in addition to considerable time and effort to design and assemble an ultrasonic system, and produce reliable data. Data interpretation is difficult requiring an expert knowledge of both ultrasonics and materials.

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APPENDIX 1: SURFACE ANALYTICAL TECHNIQUES

Parameter	AES	XPS	EELS	EDX	XRF	IRS	Raman	XRD	SIMS	RBS
Excitation/Probe Beam	Electron	Photon (X-ray)	Electron	Electron	Photon (X-ray)	Photon (Infra-red)	Photon (Visible)	Photon (X-ray)	Ion (Ar ⁺ , O ₂ ⁺)	Ion (He ⁺⁺)
Emission/Analysed Beam	Electron	Electron	Electron	Photon (X-ray)	Photon (X-ray)	Photon (Infra-red)	Photon (Visible)	Photon (X-ray)	Molecular fragments	Ion
Analysis method	Energy of Auger electrons	Energy of photoelectrons	Energy loss of scattered electrons	Energy or wavelength of X-ray	Energy of X- ray	Absorbed frequencies	Frequency changes	Diffracted angle	Mass of fragments	Energy loss of scattered ions
Depth resolution	1 - 5nm	1 - 5nm	1 μm	0.1 - 1 μm	1 nm	100nm – 5μm	100nm – 5μm	10 μm	1 – 200 nm	1 nm - 1 μm
Spatial resolution	1 nm – 10 μm	5 μm - 10mm	1 nm - 1μm	1 μm	5 μm–10 mm	1 μm	1 μm	20 μm	50 nm-10 mm	1 mm
Information provided	Elemental, chemical state	Elemental, chemical state	Elemental and chemical	Elemental	Elemental, chemical state	Molecular	Molecular Strain mapping	Microstructure Chemical/elemental Stress and strain	Elemental, chemical state, isotopes	Elemental, isotopes
Quantitative	Semi with standards	Semi with standards	Yes	Yes (Na to U)	Semi	Semi	Semi	Yes	Semi with standards	Yes
Destructive technique	For some materials	No	No	No	No	No	No	No	Yes	No
Chemical/elemental distribution	Yes	Yes limited	Yes	yes	Yes limited	No	Yes	No	Yes	No
Depth profiling	By ion sputtering	By ion sputtering	No	By ion sputtering	Yes	No	No	Yes	By ion sputtering	Yes
Material applicability	All non- insulators	All materials	Li to U	All non- insulators	All solids	Organics and metal oxides	Most materials	Crystalline only Organics/Inorganics	All solids	All solids
Sensitivity	Not H , He	Not H , He	N/A	B to U	Al to U	N/A	N/A	All elements	All elements	Not H, He

APPENDIX 2: SURFACE/SUBSURFACE NON-INVASIVE TECHNIQUES

Parameter	3-D Microscopy	Ultrasonics	SAM	IRS	Raman	XRD	X-Ray Tomography	SPM
Analysis Method	Optical image	Time of Flight Attenuation/frequency	Time of Flight Attenuation/frequency	Absorbed frequencies	Frequency changes	Diffracted angle	Energy of X-ray	Mechanical Electrostatic
Surface/Sub-surface	Surface	Sub-surface PMCs - 40 mm Metals - 6 m	Sub-surface PMCs - 40 mm Metals - 6 m	Surface	Surface	Both	Sub-surface	Surface
Depth Resolution	Topography only 20 nm	1 - 2 μm	1 - 2 μm	100 nm - 5 μm	100 nm - 5 μm	10 μm	5 μm	Topography 5 - 10 nm
Spatial Resolution	0.1 μm	2-3 mm	> 1 μm	1 μm	1 μm	20 μm	10 μm	1 μm
Inspection Area	0.2 - 50 mm ²	25 mm ² or greater	100 - 150 mm ²	8 mm diameter		200 μm^2 - 150 mm ²	Volume 10 μm^3	100 μm^2
Information Provided	Microstructure Grain size/phase	Elastic properties Damage/defects Grain size/phase	Elastic properties Damage/defects Grain size/phase	Molecular	Molecular Strain mapping	Microstructure Chemical/elemental Stress and strain	Microstructure Damage/defects	Thermo-elastic properties
Quantitative	Semi with standards	Semi with standards	Semi	Semi	Semi	Yes	Semi	Yes
Destructive Technique	No	No	No	No	No	No	No	No
Chemical/Elemental Distribution	Yes - surface treatments	Inferred through phase information	Inferred through phase information	No	No	Yes	No	No
Depth Profiling	No	Yes	Yes	No	No	Yes	Yes	No
Material Applicability	All materials	All solids	All solids	Organics and metal oxides	Most materials	Crystalline only Organics/Inorganics	All solids	All materials
Specimen Preparation	Sometimes	No	No	No	No	No	No	Yes
Existing Equipment	Yes	No	Yes - limited	Yes	Yes	Yes	No	Yes
Capital Requirement /Cost	No	New system required (£100-200k)	Yes - High frequency replacement (£100- 150k)	Yes - Biotechnology Group	Yes - Upgrade or purchase high resolution system	Contribution to replacement (£60k)	No - purchase of CT tomography system (>£200k)	No - Increase Multi-functionality

APPENDIX 3: NON-INVASIVE TECHNIQUE CRITERIA RATING

Parameter	3-D Microscopy	Ultrasonics	SAM	IRS	Raman	XRD	X-Ray Tomography	SPM
Surface/Sub-surface	0	1	1	0	0	2	1	0
Depth Resolution	0	1	1	0	0	1	2	0
Spatial Resolution	3	1	3	3	2	2	2	3
Inspection Area	2	3	3	1	1	2	1	1
Information Provided	2	2	2	1	1	4	3	1
Quantitative	1	1	2	2	2	3	2	3
Chemical/Elemental Distribution	1	1	1	0	0	1	0	0
Depth Profiling	0	1	1	0	0	1	1	0
Material Applicability	3	3	2	1	1	2	3	3
Specimen Preparation	2	3	2	3	3	3	3	1
Existing Equipment	3	1	2	3	3	3	1	3
Capital Requirement /Cost	3	1	1	2	2	2	1	2
Total	20	19	21	16	15	26	20	17