Durham UK Conference - September 2003

The 23rd International Durham Conference on X-ray Analysis, organised by PANalytical Limited, was held at the University of Durham from 15th-18th September 2003. The conference was held at the Elvet Riverside complex, with accommodation provided in the impressive Durham Castle. There were 4 plenary lectures and over forty lectures concerning the methods and applications of XRD and XRF. These notes are intended to give a flavour of the breadth and depth of the quality of the XRD presentations over the two days of parallel sessions. The opening session dealing with a historical review of XRF and XRD and Recent Developments from PANalytical staff on Monday and the closing session on the Thursday morning on compliance with Environmental Legislation are not covered in these notes.

DETECTION LIMITS IN XRPD: A PRACTICAL APPROACH AND SOME PRACTICAL APPLICATIONS

By Stephen Hillier, Macauley Institute

Stephen explained that there is a general perception that 'routine' detection limits for crystalline phases by XRPD are of the order of a few weight percent. In contrast, exact statements regarding the lower limit of detection of specific phases 'by XRPD' can be found in some published industrial methods. Thus, generalisations can be misleading and exact statements for the general method are unsatisfactory. Stephen described how the internal standard form of the reference intensity ratio (RIR) method can be used to calculate the lower limits of detection of any phase – whether present in a sample or not. As a practical example, the calculation of detection limits for asbestos in cosmetic talcs was discussed.

WHAT ARE THEY AND WHAT ARE THEY FOR?

By Robin Aird, PANalytical

Robin reviewed the special stages, optical components, detector and upgrade options that are available from PANalytical. There is a range of positioning stages with movements in the psi, phi, x, y and z directions. The 'fast' X'Celerator detector was described. Sample alignment and positioning is now possible using a video camera. Several non-ambient stages are available from RT to 1600C with a choice of reducing, oxidising or inert atmospheres. These allow phase transitions and real time changes to be followed. A non-ambient capillary system is available from RT to 700C that reduces preferred orientation. Low temperature cryostat systems are also available. For those looking to upgrade instruments there are options to upgrade to Pre-Fix optics, to the new X'Celerator detector or to new anti-scatter slits for the X'Pert Pro. New software include, X'Pert Quantify and X'Pert Highscore Plus, the latter includes Rietveld analysis which can be used for standardless phase quantification.

USING A PORTABLE XRD TO MEASURE THE EFFECTS OF SERVICE LIFETIME & RESIDUAL STRESS ON RAILWAY RAILS

By Judith Shackleton (Joe Kelleher), Manchester Materials Science Centre

There is a need to evaluate the level of residual stress that accumulates in railway rails during there service lifetime. Judith described how a portable diffractometer and an AEA MAPS magnetic system are used to measure residual stress in large, awkward samples of up to 200lbs in weight. In service, the railway line sees high loads at relatively small contact points. The crystal structure starts to break down. The surface is in compression, underneath-tension. Thin slices of track are obtained and longitudinal stress calculated from Hook's Law [Young's Modulus – Stress/Strain] using the $\sin 2\psi$ method. In effect, the crystallographic planes act as an atomic scale strain gauge. A stress-free standard is not required and the method is easy to carry out, however, the method is only sensitive to the top few tens of microns of a surface. The AEA MAPS system can measure to depths of 500 microns and can produce stress distributions as maps. Results from the two approaches are compared and has led to a better understanding of residual stress in railway rails.

DATAINK™ AND THE X'CELERATOR - TOMORROW'S TECHNOLOGY TODAY

By David Gleeson, NanoMagnetics

Dataink is a novel approach to fabricating magnetic recording media with the potential for supporting Terabit/in^2 recording densities. David described how these protein-derived Co/Pt nanoparticles are prepared from acqueous reactants, with synthesis conditions controlling grain size, structure and composition. Thin films of these materials are then reduced at high temperatures without sintering of the alloy nanoparticles to produce the desired magnetic properties. Currently hard drives have a theoretical storage limit of 146Gbytes. With the Dataink process there is a potential to go 40x higher than this. David described the types of analyses obtained from these coatings using the X'Celerator X-ray detector, which has dramatically reduced XRD data acquisition times.

"ONE LUMP OR TWO" Small Angle X-ray Scattering (SAXS) Analysis of Sugar Based Structured Surfactant Systems

By Richard Morris, Huntsman Surface Sciences UK Ltd

Sugar based structured surfactant system is a novel aqueous delivery system that comprises surfactant, carbohydrate and water. This system is formed by the interaction of surfactants with water-soluble carbohydrates acting as a "structurant" pushing the dissolved surfactant out of solution as liquid crystals. Sugar induced 'Lamellar' sheets are formed with a spacing in excess of 500 angstroms. Richard explained how SAXS is used to measure the bi-layer spacing, to 'tune' formulations and to determine thermal stability. Richard showed that a 15% sugar solution produced a 315-angstrom bi-layer whereas a 45% sugar solution was not thermally stable. These systems have an internal yield stress which is high enough to suspend solid particles and low enough to allow the system to flow as a normal liquid. Richard demonstrated this in the clearest possible way by passing around several exhibits. He said that we could make similar solutions by mixing washing up liquid (the cheap stuff), sugar and Listerine mouth wash – give it a go!).

LINE PROFILE ANALYSIS OF MESSY SYSTEMS

By Steve Norval, ICI Measurement Science Group

Materials used in the chemical industry are frequently multiphased and produced broad, overlapping reflections. These 'messy' systems are difficult to analyse and generally require whole pattern fitting to extract microstructural information, provided the crystal structures are known. Steve described a Line Profile Analysis method, based on simulations of peaks broadened by crystallite size and other factors, and convoluted with a parameterised instrument function. Simulated peaks are fitted to measured data. A 'loss' method is used which simulates one set of profiles for each line in the region of interest. The method has been used to determine the Ni/NiO ratio in a Ni/alumina catalyst.

PREPARATION & ANALYSIS MESOPOROUS THIN FILMS VIA A SOL-GEL ROUTE

By Michael Morris, University College, Cork

A method has been found by which MTF's can be reproducably grown at silicon substrate surfaces. Perhaps their most important use might be in the area of thin-film, ultra-low, dielectric constant (K) materials, where the high porosity can lead to materials with K values less than 2. This is important in the future development of the microelectronics industry and the so-called inter-connect problem. SEM shows these films to be crack free to thicknesses around 1 micrometer. XRD shows the presence of reflections expected of pseudo-hexagonally ordered mesoporous systems. The PXRD data also shows that strain at the surface reduces the symmetry of the pore arrangement. Several properties of the MTF's need to be controlled; these include pore-structure, adhesion, film cracking and mechanical strength. There are about 1,000 million devices on a processor and this is expected to double every eighteen months (Moore's Law). Not every device on a chip is used; every other one is shorted to avoid capacitative 'talk' between adjacent devices.

"TWISTING THE VIEW POINT" - PRACTICAL APPLICATION OF POST MEASUREMENT TRANSFORMATIONS OF SINGLE CRYSTAL ORIENTATION DATA

By Kath Clay, Hexmat Materials Consultancy

Modified Back Reflection Laue methods are standard inspection operations within the production of single crystal turbine components. The single crystals are complex multiphased nickel super alloys with an aligned dendrite structure. However, inspection access can be limited as component size and complexity increase. Kath described the development and application of post measurement orientation data transformations. With three consecutive rotations, you can move from one point of view to another. Stereographic projections are used for the transformations that follow the standard rules for rotation.

METEORITES

By Martin Gill, Natural History Museum, London

Martin began by defining the word '*meteorite*'. This is material that has fallen to earth, in contrast to a meteor, which is an incandescent streak of light. Many meteorite types have been discovered, some of which are held at the Natural History Museum. Some are iron rich, others have silicate embedded in the surface, and others are iron-nickel alloys. Martin showed photographs of several impact sites. A meteor crater in Arizona was produced by a 150ft lump of rock that displaced 159 million tonnes of limestone and sandstone, ejected to form a crater 2km across. The Chicxulub Crater in Mexico is 10 - 15km across.

OBSERVING RAPID REACTIONS USING SYNCHROTRON ENERGY DISPERSIVE DIFFRACTION: CEMENT HYDRATION AS AN EXAMPLE

By Nicola Meller, Centre for Materials Science & Engineering, Edinburgh University

Cement hydrates rapidly, typically starting within the first minute of contact with water. Insitu XRD is not a particularly satisfactory technique for following these changes. Nicola showed that Synchotron X-Ray sources, with their high brilliance, allow count time to be reduced and the timing of mineral formation can be pinned down to within a minute. One system discussed was the hydration of aluminoferrite [Ca_2AlFeO_5] in the presence of gypsum [$CaSO_4.2H_2O$] at temperature. The examples showed that energy dispersive diffraction could be used to gain high quality time resolved data very rapidly.

HOW CAN WE MAKE STANDARDISATION OF XRD METHODS & ANALYSES A BENEFIT FOR SCIENTISTS & INDUSTRIAL USERS?

By Robert Delhez, Delft University of Technology, Delft, The Netherlands

Round Robin tests on XRD methods and analyses in recent years have shown that differences in the results obtained in different laboratories are larger than differences obtained in one laboratory, and that these differences are larger than expected for the diffractionists involved. These facts by themselves are a good reason for standardisation, because standardisation should imply verification, calibration, validation, and sometimes certification - procedures that can prevent such diverging results.

The benefits of standardisation include:

- assessment of non-removable systematic instrument errors
- quality improvement
- reference for development of new procedures
- incentive for improving instruments
- prevention of mistakes caused by inexperience
- consolidation and dissemination of expertise
- certified reference materials improving the reliability of results
- definition of terms to prevent misunderstanding

There are, however, sacrifices to be made if standardisation is to be addressed. These include:

- more/longer measurements
- more extensive reports
- rejecting the use of non-standard methods, even if they are 'better'
- rejecting the use of dedicated or in-house methods

The European XRPD standardisation project involves a few hundred people. There are three levels:

1. General standards - principles/procedures/instruments
2. XRPD applications, e.g. residual stress by XRPD and neutrons
3. Standard protocols and procedures (special products)

LARGE AREA DIFFRACTION SPACE MAPPING OF THIN FILM SAMPLES

By Tricia Kidd (Norman Andrew), PANalytical Research

In a large area map the diffraction pattern of the sample is explored over a wide angular range, many diffraction spots or rings are collected and the microstructure of the sample, be it single crystal, textured or random polycrystalline is readily revealed. The method involves carrying out 2theta-omega scans at either different omega offsets (rocking curves) or different psi offsets. Tricia uses a programmable divergence slit and the super fast X'Celerator detector. Data Collector software is used to obtain the data, which is then processed using PC Epitaxy. The 'probe' sizes (Δ omega) are approx. 0.5degrees. 2-theta-omega projections are produced by adding scans together. We were shown the results obtained from textured Nb-Al multilayer thin films on (001) silicon. Because the axial co-ordinates used to measure the intensity of any point on the map are digitally stored, any feature can be re-examined at a higher resolution, either as a smaller map, or a conventional scan. Large Area Diffraction Space Mapping offers an interesting perspective on the microstructures of materials under investigation and could be used as a starting point to tailor the choice of diffraction experiments to the analysis of new materials.

X-RAY STUDIES OF GaMnAs "SPINTRONIC" MATERIALS

By Chris Staddon, Nottingham University

Spintronic Materials are dilute ferromagnetic semi-conductors that utilise the magnetic state property of electrons – spin up/down. For Spintronic materials the ferromagnetic transition temperature has to be greater than room temperature. The magnetic properties of GaMnAs thin films make them suitable materials for Spintronic devices. Chris described how a series of 50nm and 1000nm GaAs thin films with different Mn compositions were grown and analysed with an X'Pert MRD, before and after annealing. He showed that Vegards's law holds for the Mn compositions in the range 0-8%.

X-RAY REFLECTOMETRY OF THIN FILMS & MULTI LAYERS

By Tom Lyford, PANalytical Research

Patricia Kidd stood in for Tom to describe how the technique of X-ray Reflectrometry is used to obtain thickness, density and roughness data from single and multilayer coating stacks. The technique is sensitive to roughness and electron density, the latter feeds into the refractive index of the material. As roughness increases, the reflectivity decreases which decreases the intensity of high angle oscillations. This can be overcome, to some extent, by the use of high-resolution instruments that provide useful information at higher angles. X'Pert Reflectivity is used to fit the data and typical fits were shown to reveal the relative ease of fitting scans from different sample types.

HIGH RESOLUTION AND LOW ANGLE REFLECTIVITY STUDIES ON GAN AND GAINN/GAN MULTILAYERS

By Mary Vickers, University of Cambridge

Diffraction spots can be broadened in 3 dimensions by a variety of defects such as misorientation, limited coherence length and microstrain. Measuring reciprocal space maps for several different reflections, symmetric, asymmetric and in-plane allows us to attempt to

determine the major source of peak broadening in our samples and relate XRD results to those from microscopy. The cell parameters for GaN films are not constant but vary with growth conditions and hence number and type of defects. This does not influence chemical information from peak positions when TEM shows the dislocations going right though sample. For superlattices (multilayers or quantum well structures) the relative intensities from high or low angle data are used to give the thickness ratio before determining the chemical composition from peak positions.

INTRODUCTION TO QUANTIFICATION & THE RIETVELD METHOD

By Paul O'Meara, PANalytical

X-ray Diffraction is routinely used as a tool to accurately quantify mixtures of several phases. This has traditionally been achieved using ratios of individual peaks intensities but increasingly the Rietveld method is used to quantify mixtures from the whole diffraction pattern. A distinct advantage of the Rietveld method is that it does not require the preparation of standards but instead works by comparing experimental data with information about the crystal structures of the phases present.

The method was established by Hugo Rietveld in 1969. It was originally used for neutron diffraction but it was later found to be applicable to XRD. Since the whole pattern in used in the analysis, no crystallographic information is lost. A calculated pattern is compared against observed data and the difference between the two is minimised. The diffraction data is broken down into individual data points. There are two brands of Rietveld Analysis – crystal structure and standardless quantitative analysis. You need good quality data and structural information.

Data Collection:

Require high-resolution scans so as to minimise peak widths.
High intensity (>10^4 counts on the strongest peak)
Large 2-theta range – typically 5 to 100 degrees.
At least 5-10 steps across FWHM
Avoid preferred orientation
Particle size 1-10 microns

Refinement Parameters

Two types of parameter need to be refined – Global Parameters (background, zero shift) which affect every phase and Phase Related Parameters.

1. **Background**

   Manual: Set at beginning, straight line in drawn between points. Linear interpolation

   Automatic: A mathematical function is applied. These include

   - Polynomial
   - Chebyshev
   - Shifted Chebyshev
   - Amorphous sine function
   - Damped amorphous sine function

   The background function can be described by the following equation

   $$I = A + B\theta + C\theta^2 + D\theta^3$$

   If only parameter A was used, the background would be horizontal.

Manual background setting can be time consuming and weak reflections can be missed. However, it is good for difficult backgrounds. Automatic backgrounds are easy to apply and are adjustable throughout the refinement.

2 2-theta offset
Allow correction for sample displacement errors

3 Space Group
Determines the symmetry of the structure and is fixed at the start of the refinement. There are 230 space groups. For example, the space group for NaCl is Fm3m whereas for gypsum it is C2/C.

4 **Cell Parameters**
These are due to the size of the unit cell and they determine the positions of diffraction peaks. Only refine cell parameters allowed by symmetry. Indexing routines can be used to get the unit cell values.

5 Atomic Positions
Each atom must have its atomic co-ordinate recorded. Atoms at 'special' positions (defined by symmetry) cannot be refined. The positions of other atoms can be refined.

6 Preferred orientation (PO)
A refinable parameter. PO is due to crystallites lining up with each other due to crystal growth mechanism or special cleavage planes. Use back loading and spin samples to minimise PO.

7 Peak Shape functions
These can be Gaussian, Lorentzian or a mixture of the two (Pseudo-Voight).

8 Scale Factor
A simple scalar variable that leads to the quantification of mixed phases.

9 Peak Widths
Determine FWHM. A Cagliotti function is used.: $-H^2 = U\tan^2\theta + V\tan\theta + W$
It is often sufficient just to refine W.

10 Site Occupancy Factors
Ensues that all sites in the unit cell are 'fitted'.

11 Peak Asymmetry
Takes account of peaks that are not symmetrical either side of their max intensity.

12 Temperature Factors
Take account of how atoms vibrate. The vibration may be uniform in all directions (isotropic) or it may be in one particular direction (anisotropic).

Refinement Strategy
Start with a few parameters to refine

- Background plus scale factors
- Cell Parameters plus zero shift
- Peak Width, W
- Preferred Orientation
- Site Occupancy Factors
- Temperature Factors

R-factors are parameters that indicate how well the model fits the observed diffractogram. R_{wp} a weighted profile R-factor is commonly used.

Rietveld Refinement can be used when preferred orientation is unavoidable, when standards are not available, when site occupancies vary and when peaks overlap. The refinement process is difficult to automate since although a refinement can look good it can actually be incorrect and numerically unstable.

QUANTITATIVE ANALYSIS OF ZIRCONIUM OXIDES - DEGREE OF STABILISATION

By Steve Unsworth, MEL Chemicals

Steve described how Rietveld Refinement is used to quantify the phases within stabilised and non-stabilised zirconium oxides that are used in the chemical catalysis, automotive catalysis and ceramic industries. Three common zirconium oxide phases are monoclinic, cubic and tetragonal, the phase type being dependent on composition, crystallite size and conditions of manufacture. The X'Pert Plus software (now Highscore Plus) is used for the Rietveld Refinements.

HOW PURE IS MY GYPSUM?

By Alison Burke, Huntsman Tioxide

The purity of gypsum, CaSO4, is a critical parameter for its end use. Currently, a time consuming gravimetric method is used, where Ba is substituted for Ca, which drops out of solution as BaSO4. This is then weighed. Alison described how Rietveld Analysis is used as a fast alternative method for purity determination. Gypsum samples are scanned from 10 to 100 degrees 2-theta at a rate of 1sec/step (0.05°/step). Highscore Plus is used for the Rietveld Analysis. Comparisons of results from Rietveld and Chemical analysis show a 7% discrepancy. Since this is a systematic bias, a correction factor is applied and customers are asked to accept the corrected Rietveld purity values.

An Overview on Structure Solution from X-ray Powder Data

By Christian W. Lehmann, Max-Planck-Institut fuer Kohlenforschung

Direct space algorithms play a key role in the solution of crystal structures from powder data. Based on the combination of prior knowledge of the molecular constitution and configuration with effective global optimisation strategies, even complex problems can be solved. However, this process is by no means a push-button method. The successful application requires sound crystallographic knowledge and critical review of the proposed solution.
During the tutorial a step-by-step procedure was introduced and potential difficulties were illustrated. A comparison of the different structure solution methods highlighted their individual strengths and weaknesses.

Overall, the meeting, as ever, gave a comprehensive coverage of the XRD and XRF techniques. This, combined with good food and a picturesque location, made the meeting a huge success. To those who were unable to attend, you missed a real opportunity to participate in something special.