Department of Engineering Science,
University of Oxford,
Parks Road,
Oxford,
OX1 3PJ

UNIVERSITY OF OXFORD

Exploring natural and artificial materials design using micron-scale structure and strain mapping

Alexander M. Korsunsky

Professor of Engineering Science, Fellow of Trinity College Oxford
<< MBLEM >> Head, Multi-Beam Laboratory for Engineering Microscopy
Editor-in-Chief, Materials & Design (ELS)

www.korsunsky.org

November 1, 2015

Exploring natural and artificial materials design using micron-scale structure and strain mapping

The availability of sub-micron focused synchrotron X-ray beams has opened up exciting opportunities for understanding the internal architecture and deformation behaviour of intricately structured natural and artificial materials.

In recent years we have looked at a wide range of systems that range from human dental tissues to flax fibres to thermoplastic polyurethanes to carbon fibres and aerospace alloys and composites.

The unifying theme in our studies is the interest in strain:

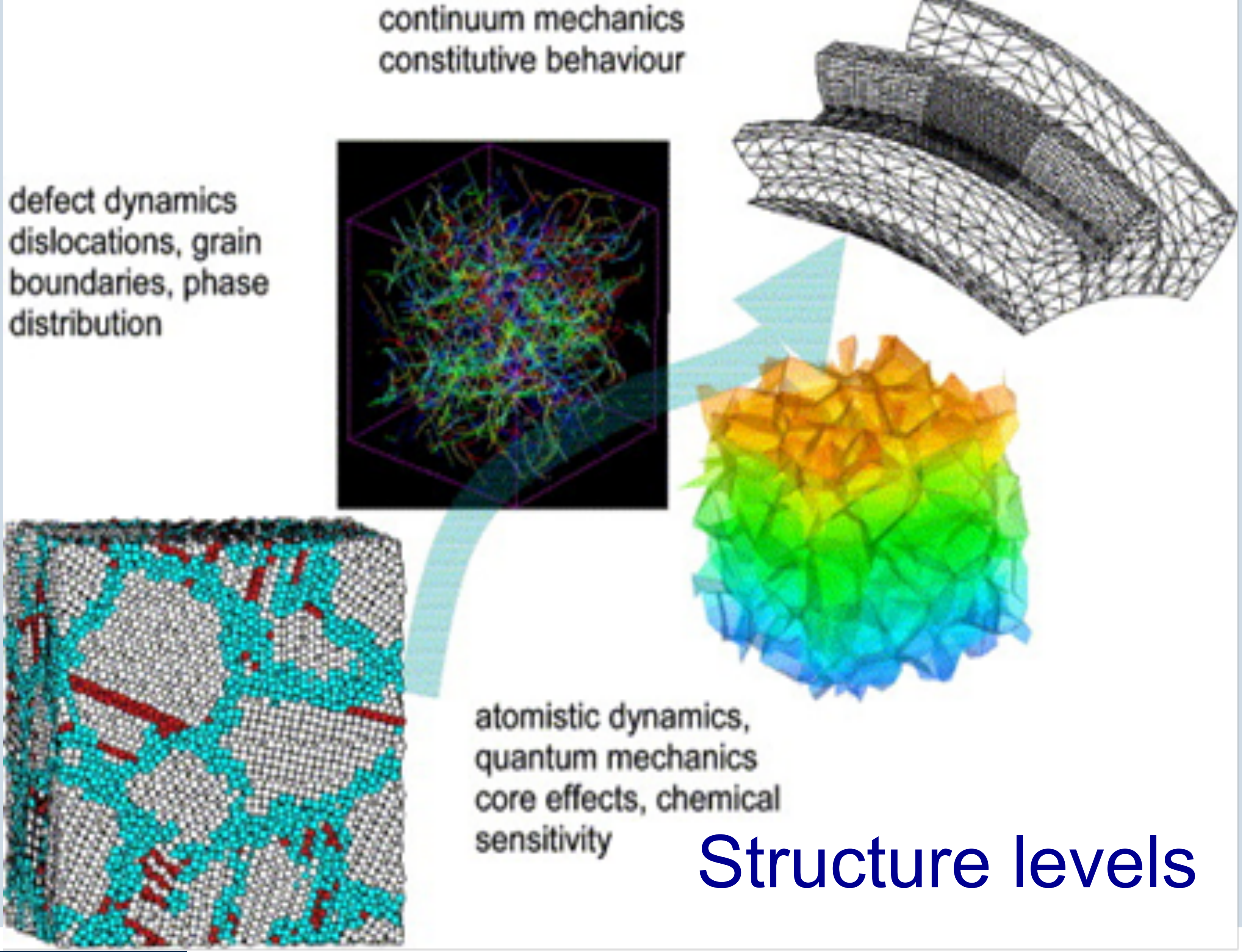
How does it manifest itself at different scales?
How can it be reconstructed in all its complexity of multiple components and spatial variation?
How do we overcome the decade-old $\boldsymbol{d_0}$ problem?

Answers will be provided using examples from recent research.

STRAIN –

the ultimate frontier…

UNIVERSITY OF OXFORD



Structure levels

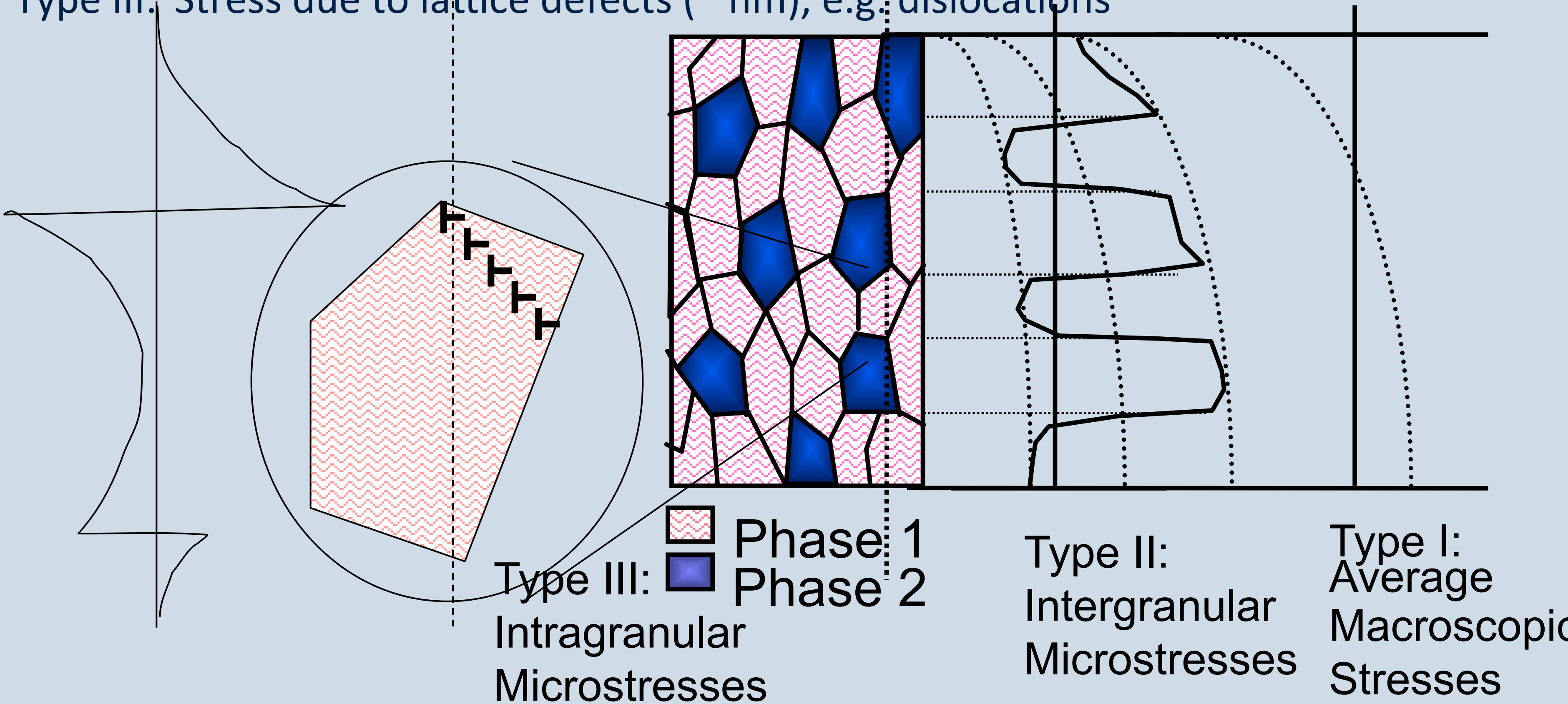
UNIVERSITY OF OXFORD

Stresses and strains in polycrystals

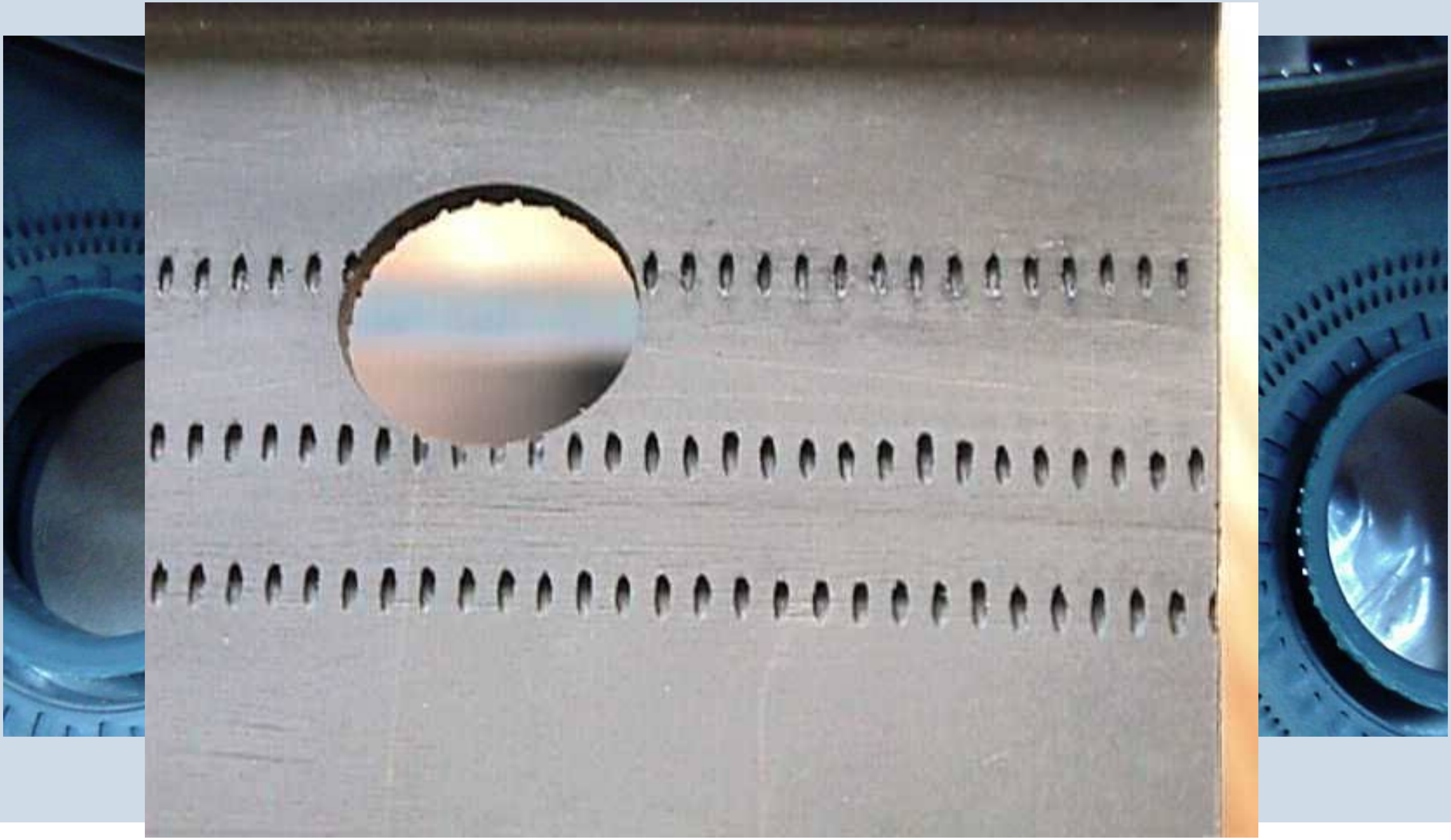
Type I: Stress varying on engineering scales (~ mm), macrostress

Type II: Stress varying on grain size scales (~ mm), e.g. interphase

Type III: Stress due to lattice defects (~ nm), e.g. dislocations

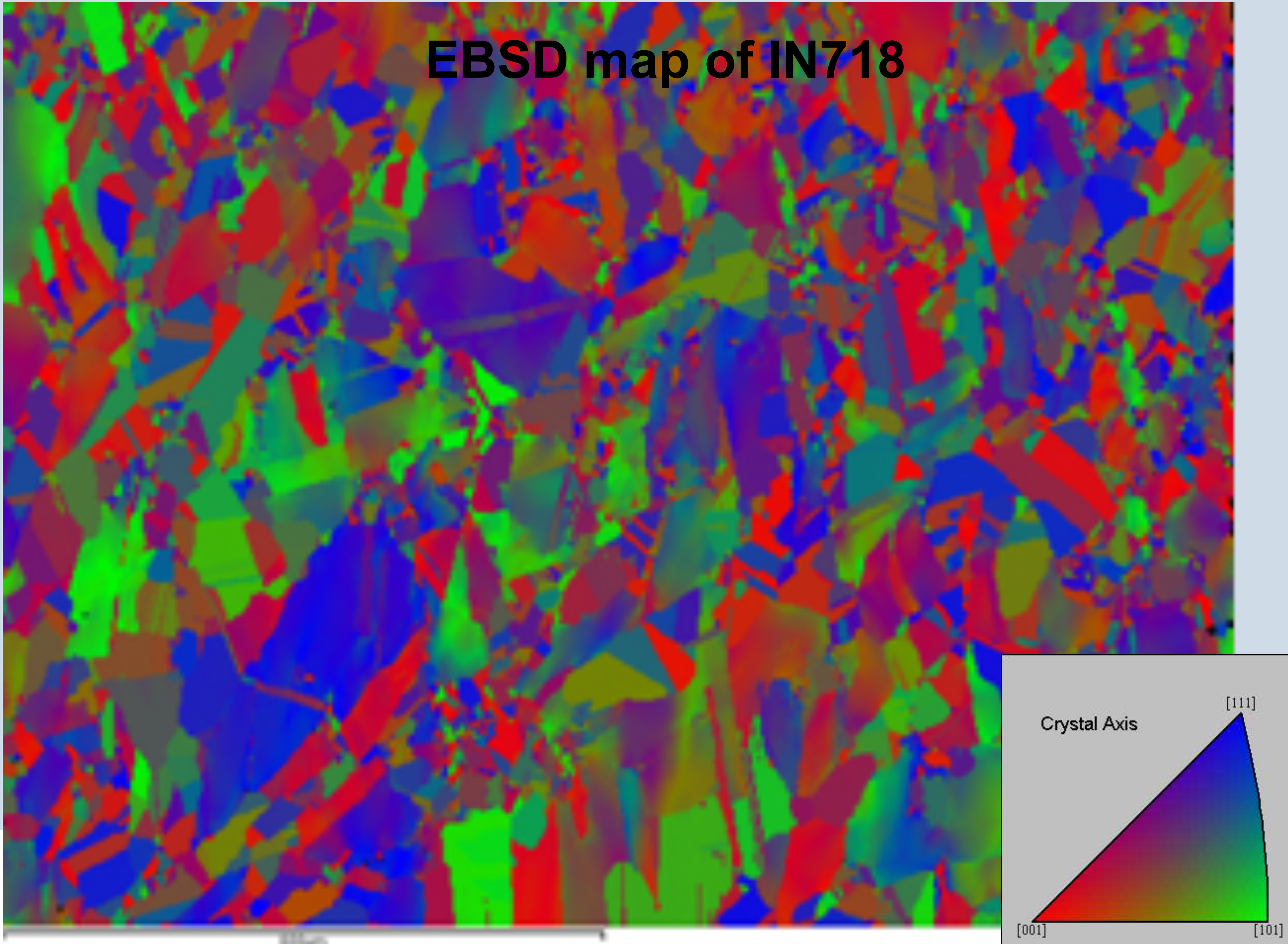


Combustion Liners

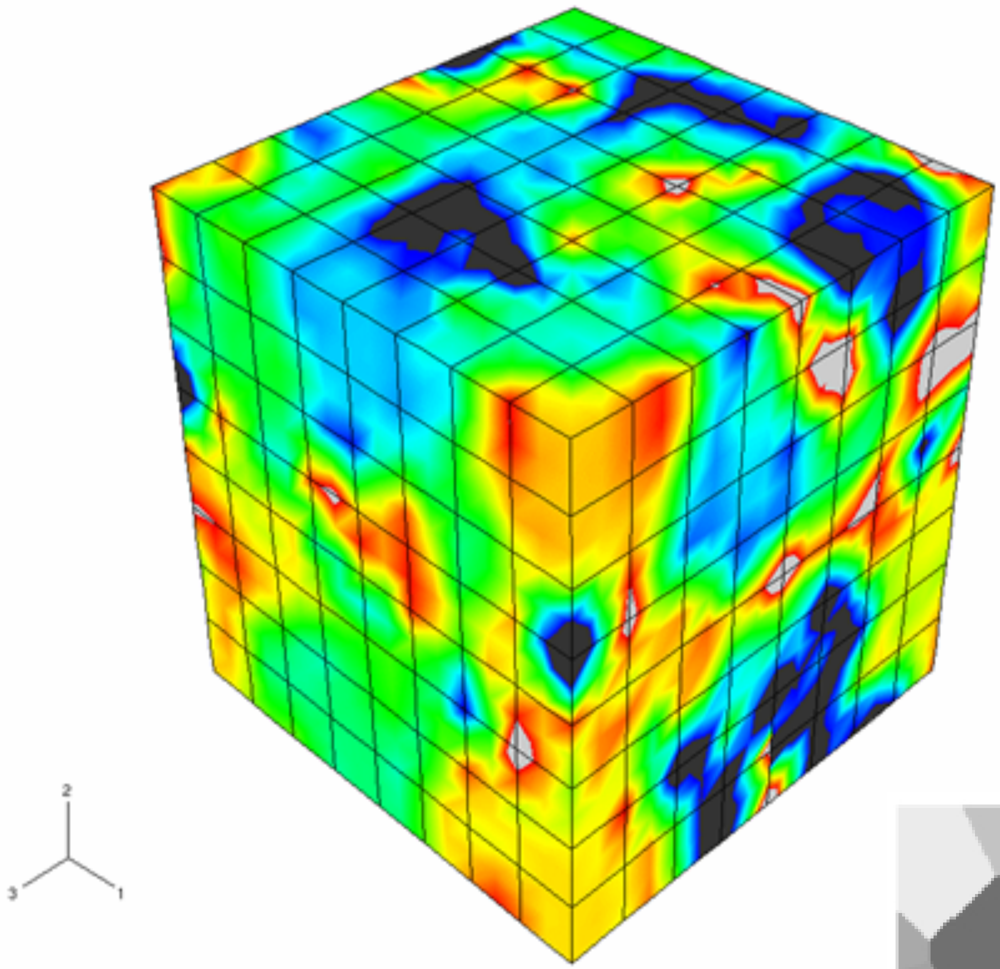


UNIVERSITY OF OXFORD

EBSD map of IN718

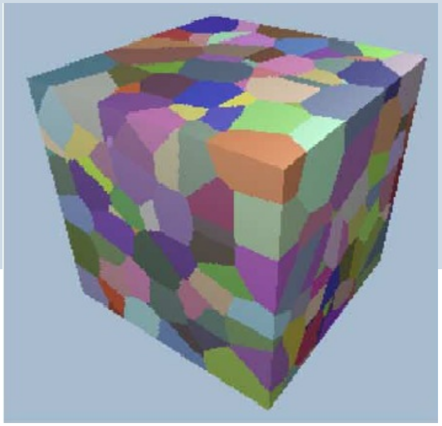


Anisotropic 3D polycrystalline plasticity



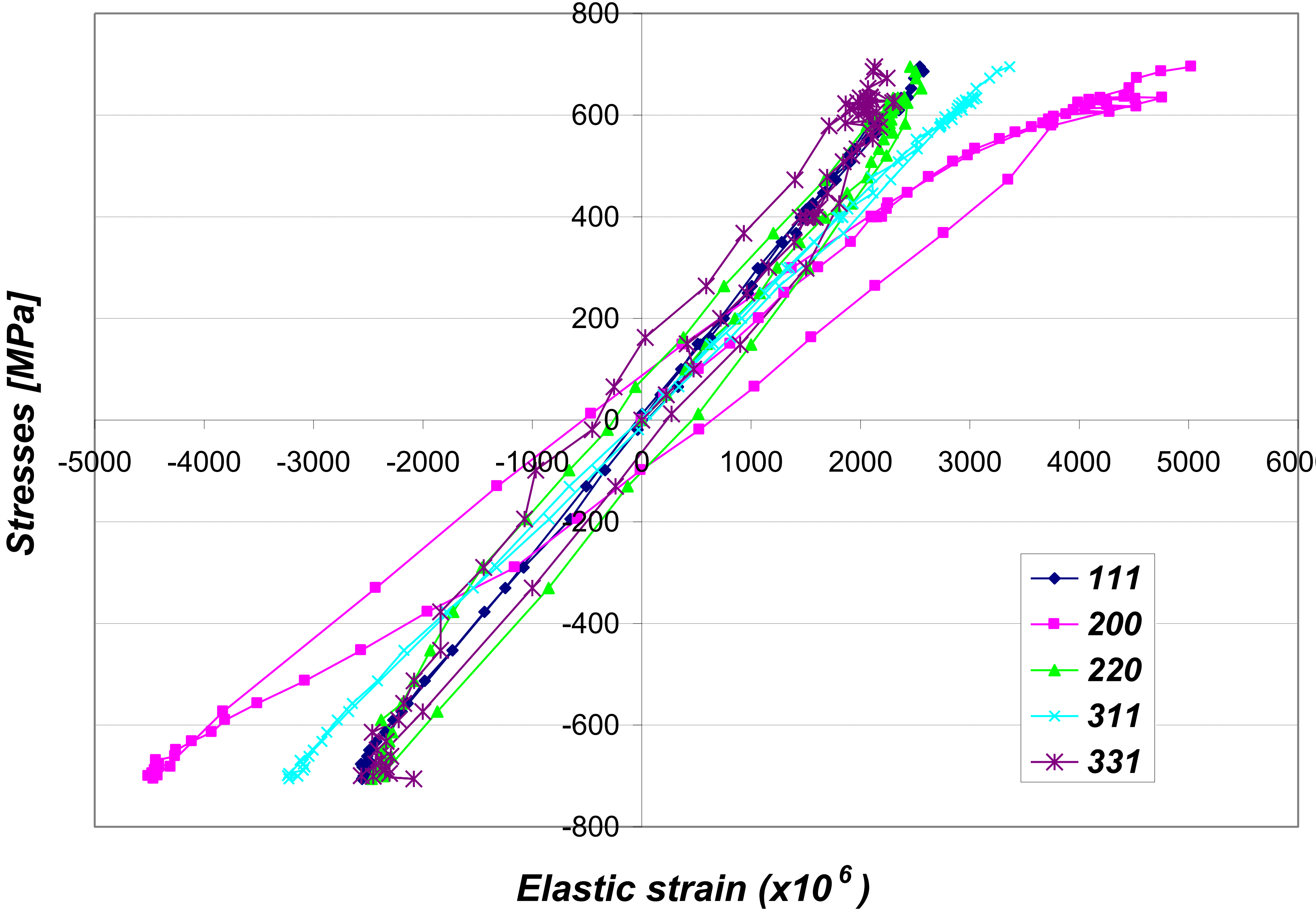
Microstructure is generated to match texture and grain size + assumed to be periodic.

Grain boundaries are smeared out (orientation set at Gauss points).

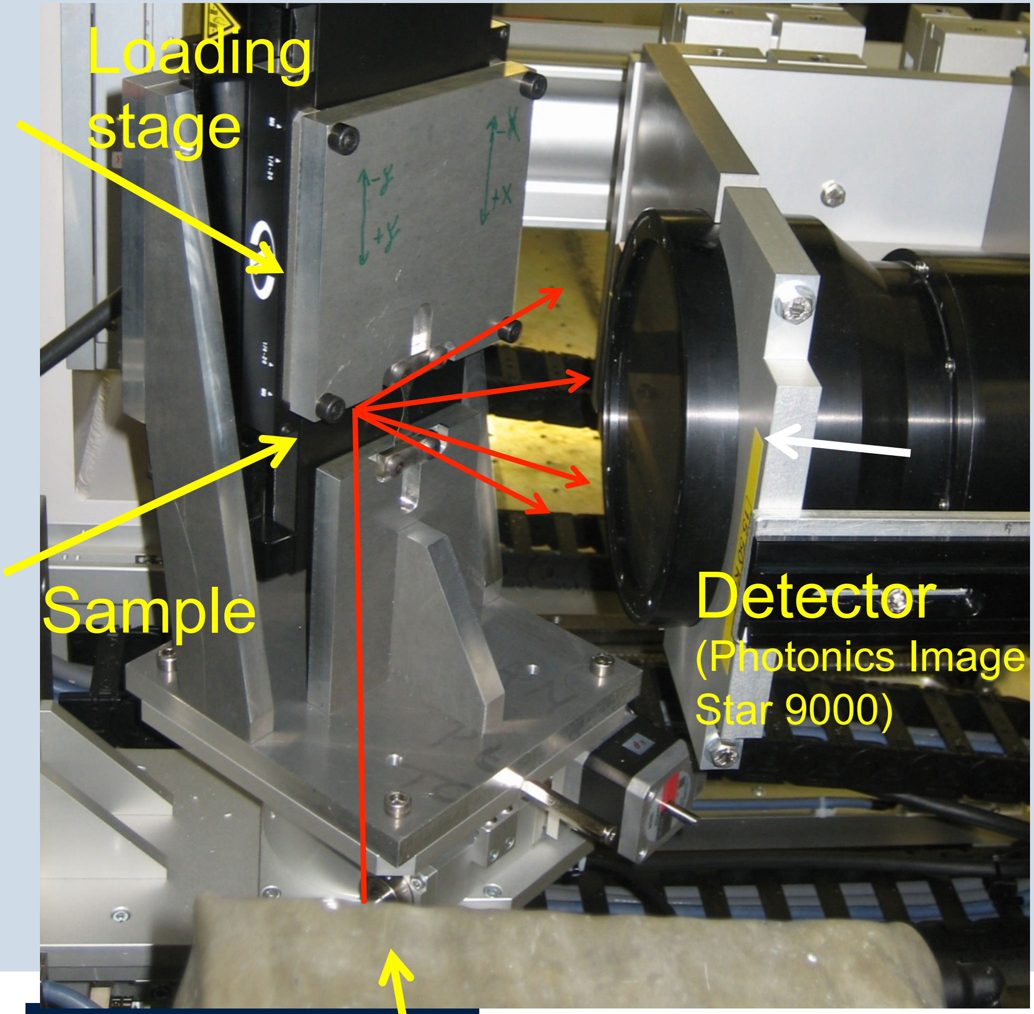


UNIVERSITY OF OXFORD

Cyclic stress-strain behaviour of grain sub-ensembles



B16: micro-beam Laue

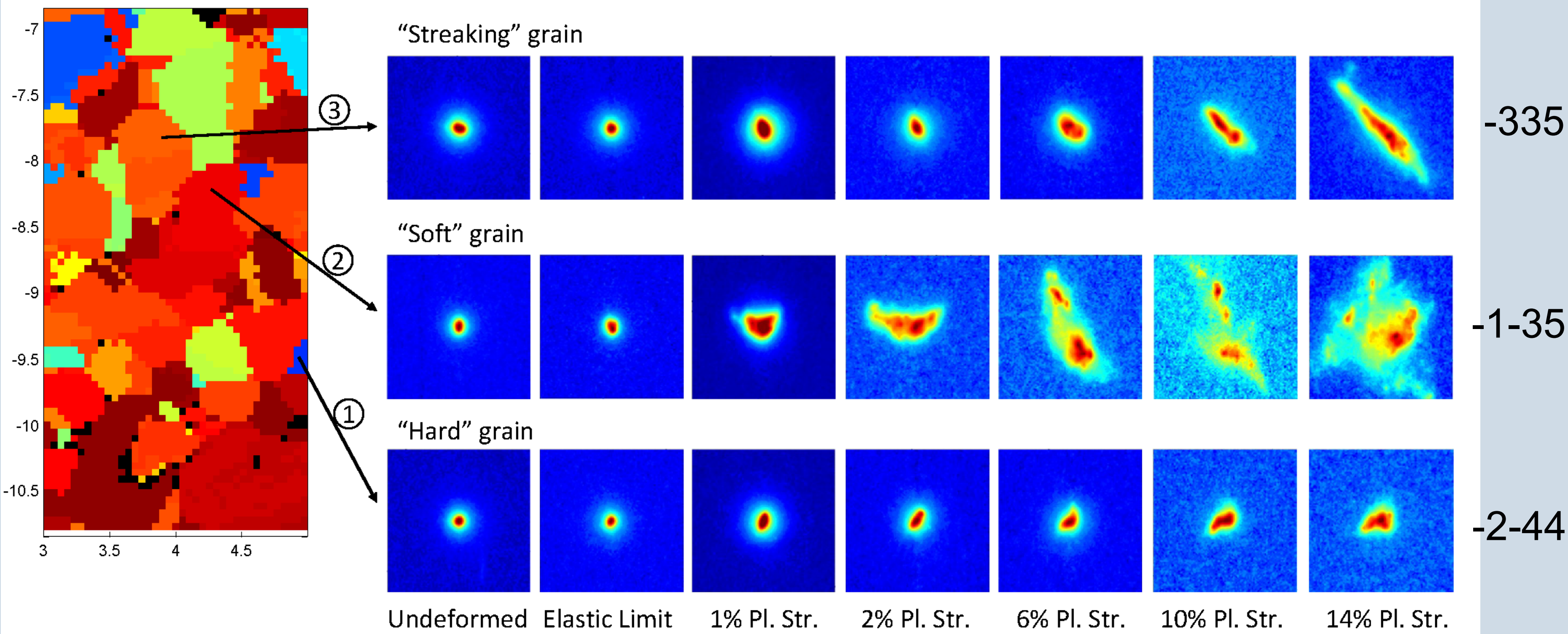


- White beam (5-25keV) focused or collimated to spotsize < grainsize
- Illuminate gauge volume within single grain
- Lattice planes with H_{hkl} in the permissible q range diffract and give rise to diffraction spots on the detector
- Collect large number of spots in one shot

UNIVERSITY OF OXFORD

Hofmann F, Korsunsky AM et al (2009) Procedia Engineering, v.1

Laue Spot evolution

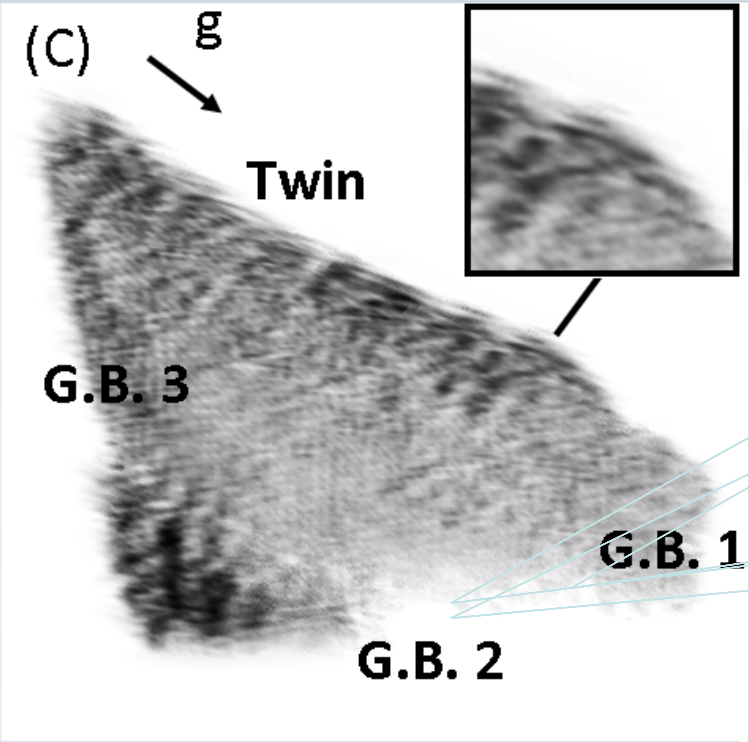


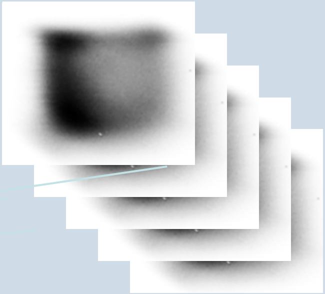
- Laue Spot evolution in different grains confirms the Schmid factor prediction
- Breaking up of Laue spots with deformation makes indexation difficult
- For streaked spots fitting with a more appropriate function than a 2D Gaussian might help

Hofmann F, Korsunsky AM et al (2009) Procedia Engineering, v.1

Scanning X-ray micro-beam topography

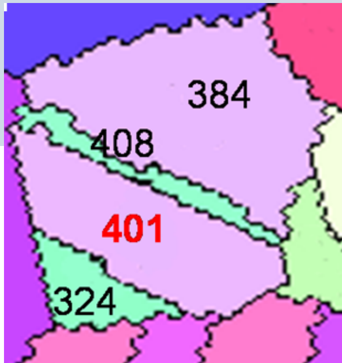
Full grain white beam topograph





Scanning micro-beam diffraction topography

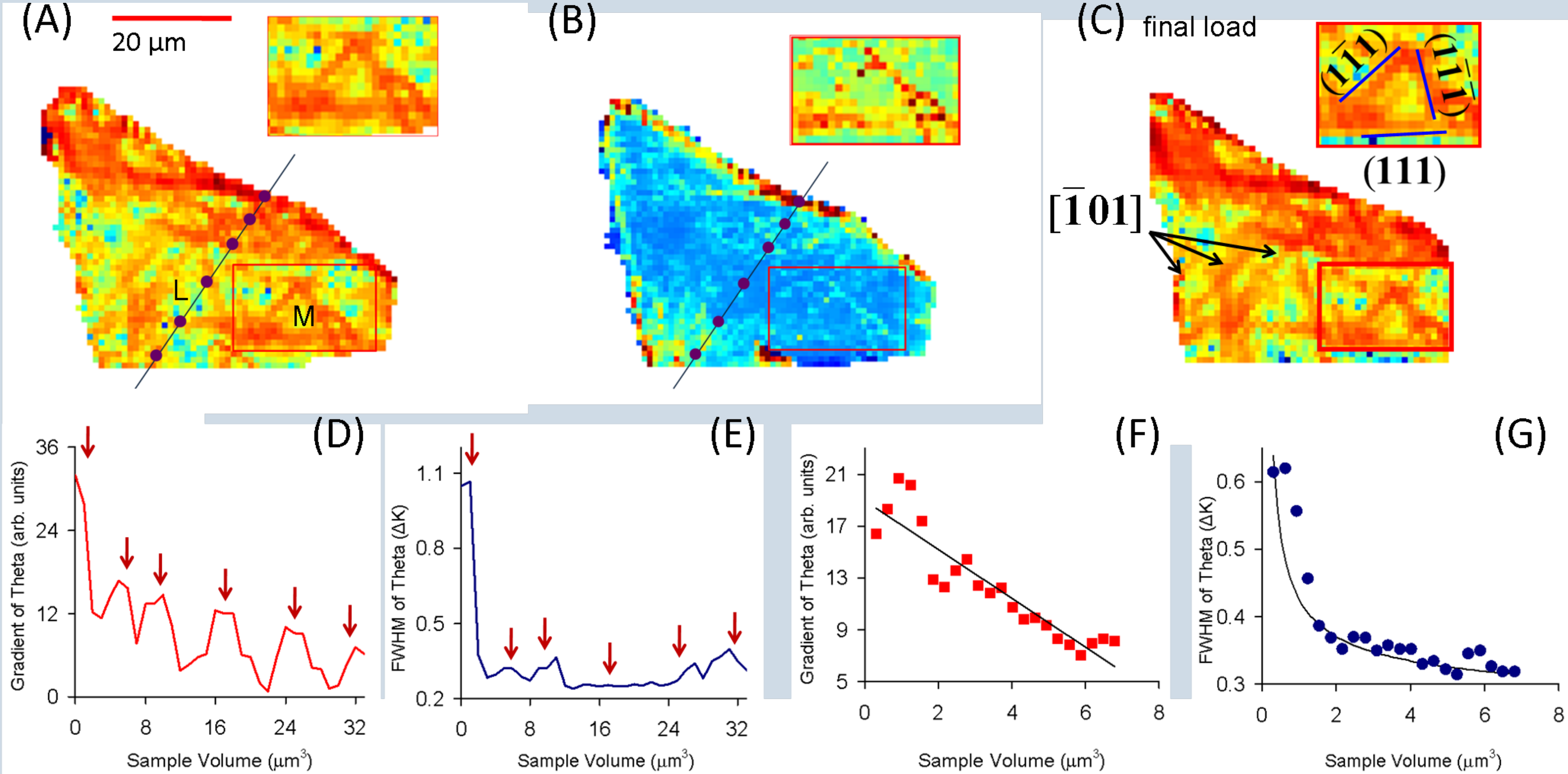
- Composed of individual micro topographs, positioned with CoG according to motor position
- Reveals sub-pixel lattice mis-orientation



UNIVERSITY OF OXFORD

Abbey B, Korsunsky AM et al (2011) Scripta Mater.

Scanning X-ray micro-beam topography

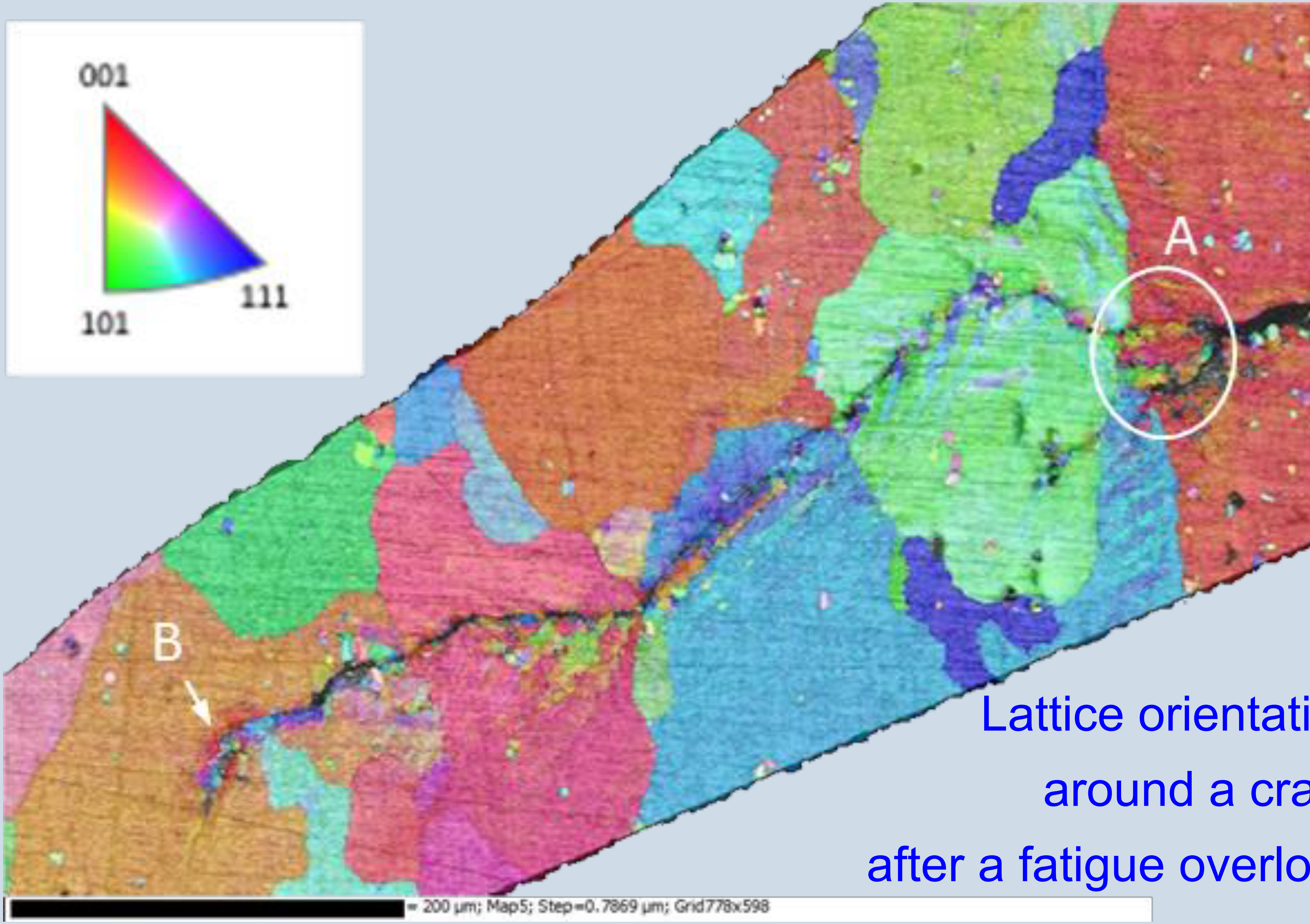


- Clearly visible regions of high and low rotation gradient – agree with slip systems
- Rotation gradient agrees well with FWHM
- FWHM shows power-law variation with sample dimension – similar to Hall-Petch
- Suggests that dislocations become trapped and pile up at boundary

UNIVERSITY OF OXFORD

Abbey et al., 2012

Abbey B, Korsunsky AM et al (2011) Scripta Mater.



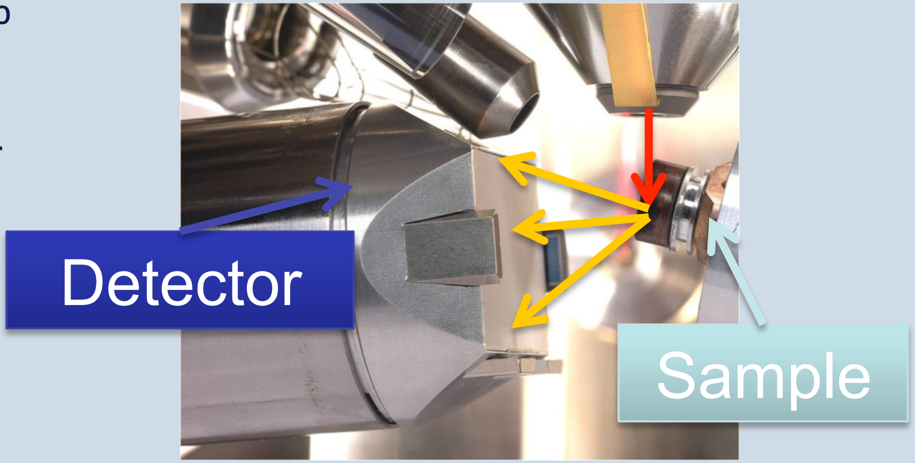
Lattice orientation around a crack after a fatigue overload

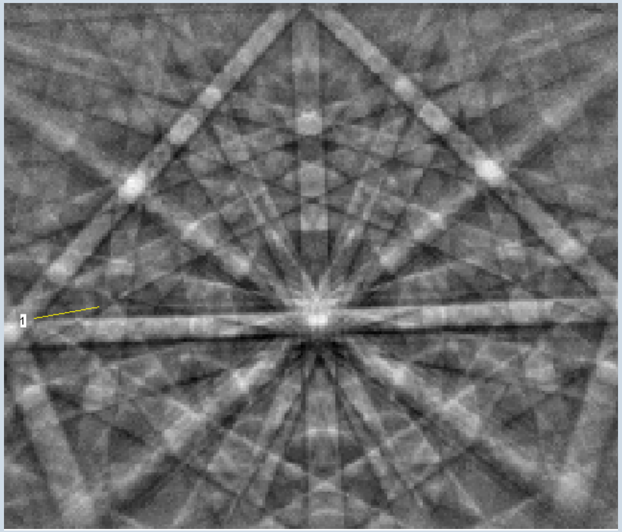
Salvati E., Korsunsky AM et al (2015) Crack Paths conference (Ferrara)

Electron Back Scatter Diffraction (EBSD)

- Sample positioned at an angle of 70º

1. Focused electrons interact with regular atomic structure (lattice)
2. Kikuchi diffraction patterns produced
3. Patterns detected and recorded
4. Angle and shape of patterns used to gain information on material\





- Inter- & intra-granular analysis of
  - Orientation
  - Size
  - Phase
  - Dislocation density + type
  - Stress ? ***…needs reference!***

UNIVERSITY OF OXFORD

The FIB ring-core and DIC Technique

- In-plane residual stress determination

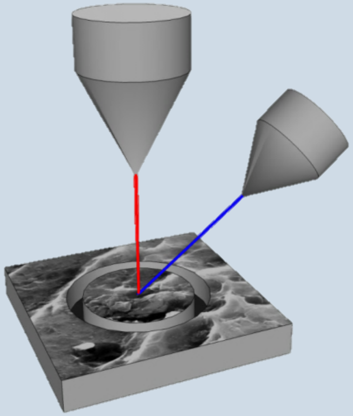
1. Region of interest is located on FIB and Scanning Electron Microscope (SEM)

2. Micrograph captured using SEM

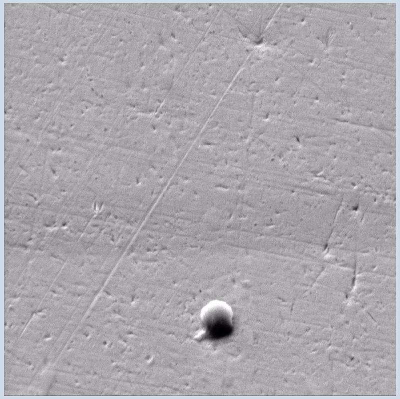
3. Small increment of a ring-core milled into surface
   - Careful balance of material dependent parameters to produce effective milling shape

4. Second SEM image captured

5. Process repeated until large depth (approx. equal to core diameter) is reached



FIB and SEM directed at same position on sample surface



Video of resulting SEM images

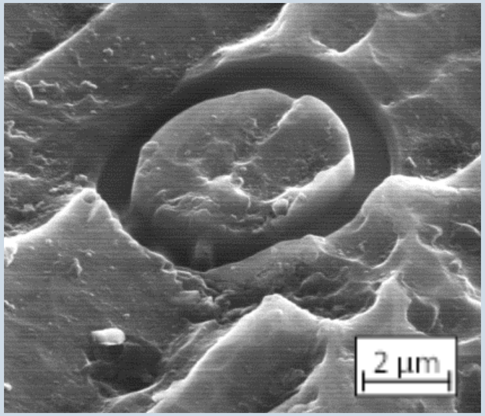
UNIVERSITY OF OXFORD

Lunt A, Korsunsky AM (2015) J Strain Analysis

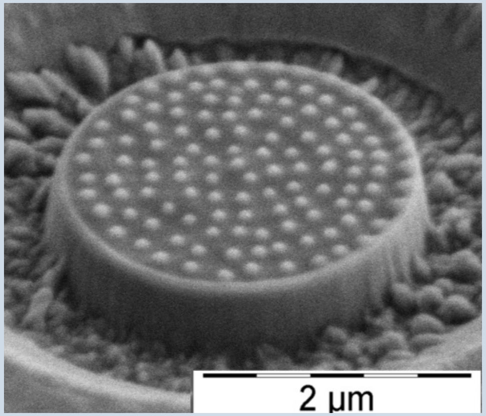
Lunt A, Korsunsky AM (2015) Surface & Coatings Technology

Strain Relief of micro pillar

- Core approaches fully stress-relieved state
  - Core-size defines resolution of the analysis technique – typically in the range 0.5-20μm
- SEM images provide a record of the surface relaxation as a function of milling depth
- Digital Image Correlation (DIC) provides evaluation of displacement and strain relief
- Surface quality and contrast is key to effective DIC:
  - High resolution imaging required
  - Re-deposition of material must be minimised
  - Intrinsic surface roughness may be used for contrast
  - e-CVD marker deposition helps improve contrast



Rough surfaces can be provide sufficient contrast for DIC

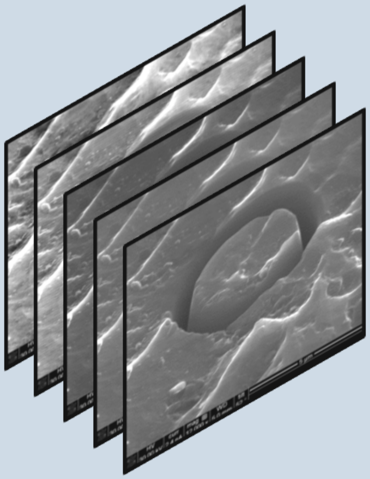


Electron deposition patterning is necessary on untextured surfaces

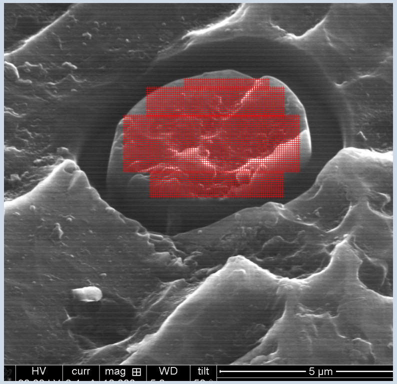
Lunt A, Korsunsky AM (2015) J Strain Analysis

Lunt A, Korsunsky AM (2015) Surface & Coatings Technology

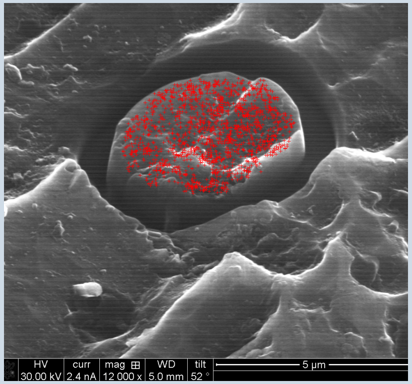
Digital Image Correlation (DIC)



1. Collection of SEM images



2. Place markers onto core surface and run automated DIC scripts



3. Outlier removal of poorly tracked markers

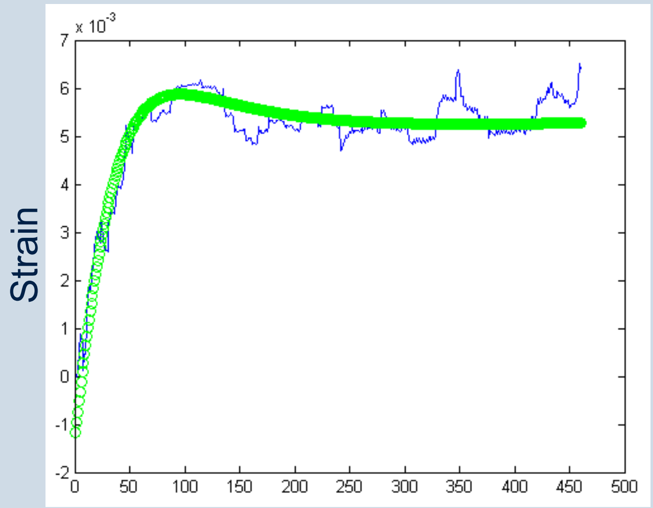
UNIVERSITY OF OXFORD

Lunt A, Korsunsky AM (2015) J Strain Analysis

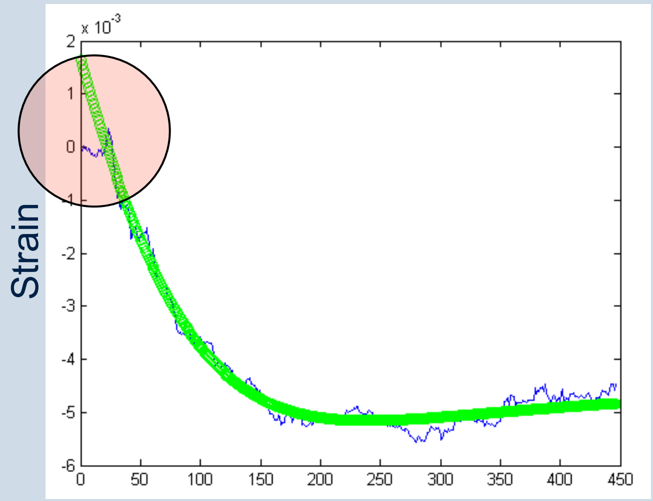
Lunt A, Korsunsky AM (2015) Surface & Coatings Technology

Complete strain relief estimation

- Least squares fitting, allowing for variation in the material removal rate and start depth (influenced by surface roughness)
- Signal to noise ratio dependent upon specific implementation



Compressive strain profile showing fit



Tensile strain profile showing fit

UNIVERSITY OF OXFORD

Lunt A, Korsunsky AM (2015) J Strain Analysis

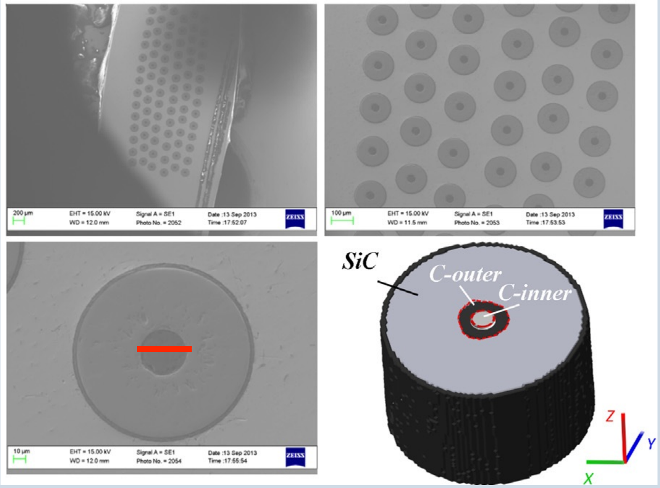
Lunt A, Korsunsky AM (2015) Surface & Coatings Technology

Nano-scale mapping of lattice strain and orientation inside carbon core SiC fibres by synchrotron X-ray diffraction

- Cross validation with high resolution XRD

- Aerospace composite
  - Titanium alloy (Ti-6Al-4V) matrix
  - Unidirectional SiC fibres
  - Carbon monofilament core
    - C-inner and C-outer layers

- Built-in elastic strain - structural integrity
  - C core + SiC shell
  - Manufacturing amd processing optimisation

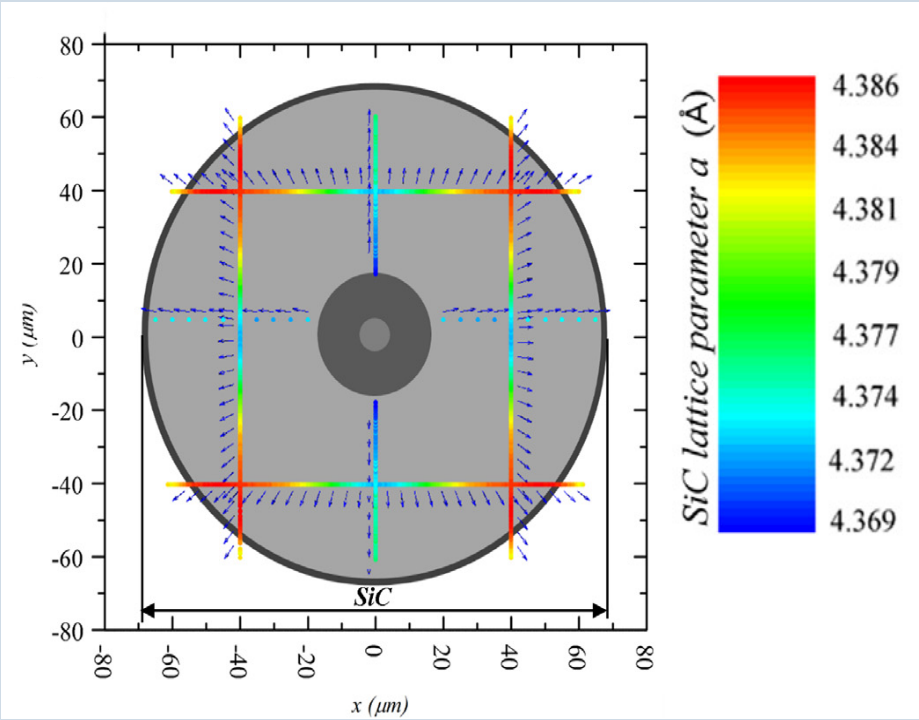


SiC fibres with carbon monofilament core

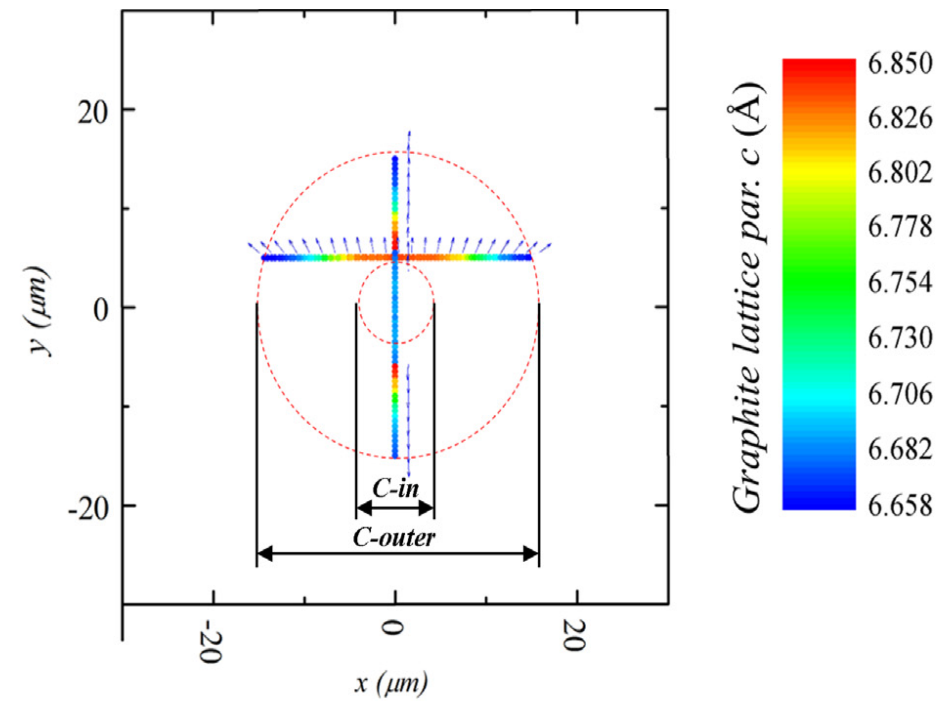
N. Baimpas, A.M. Korsunsky et al., Carbon, 2014

SXM

- High resolution (~200nm step) line scans in SiC shell and carbon core



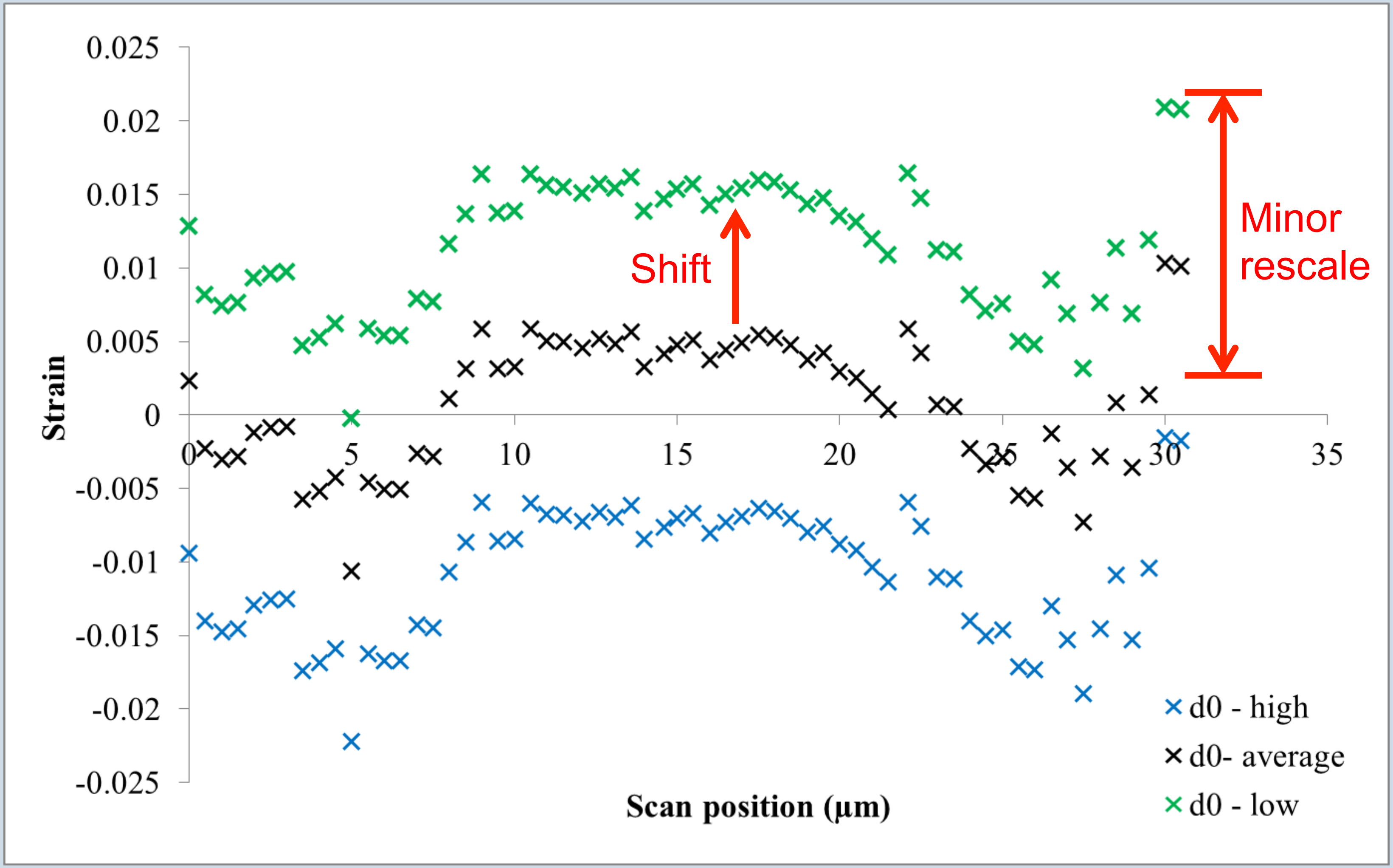
SiC coating



Carbon monofilament

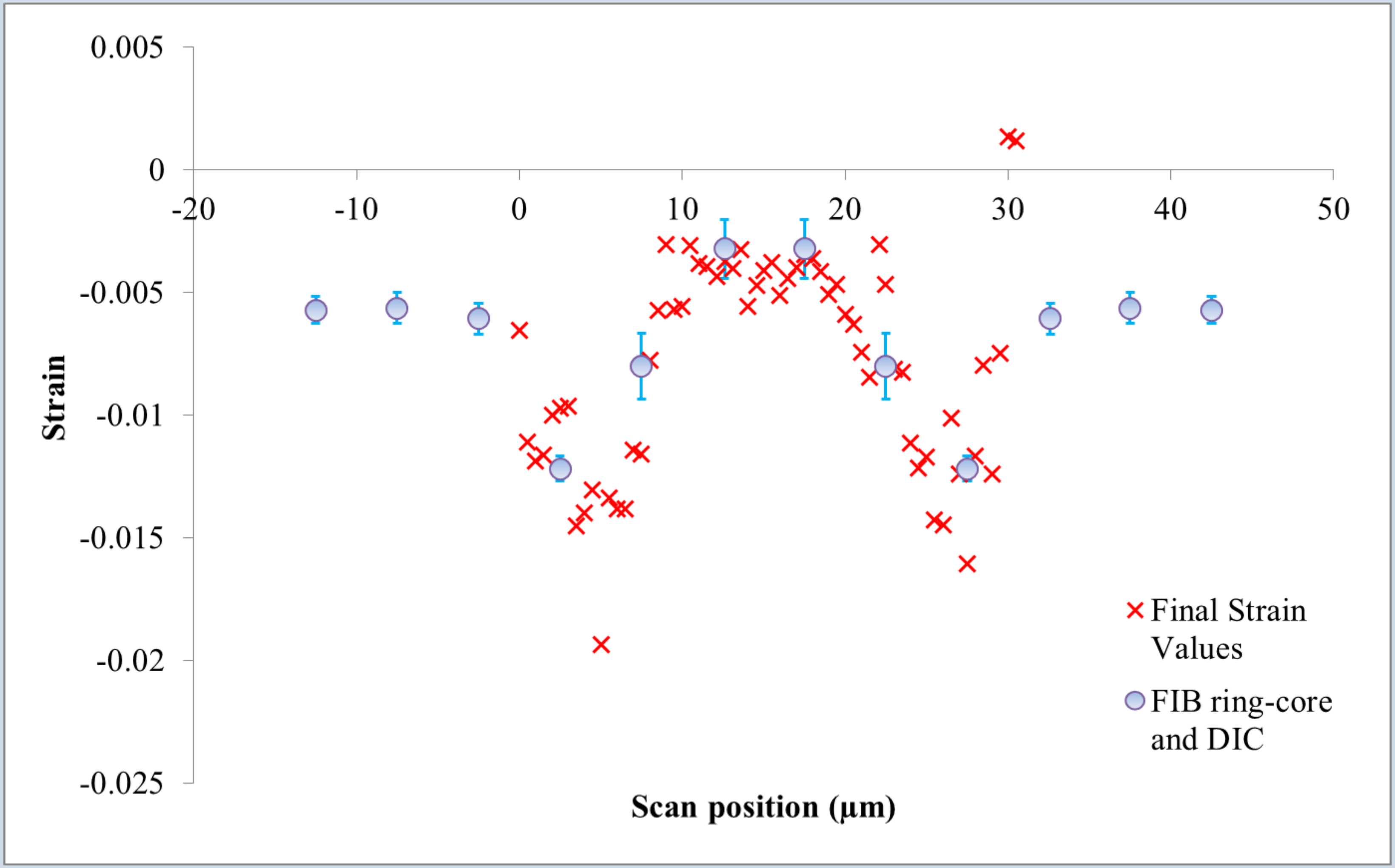
N. Baimpas, A.M. Korsunsky et al., Carbon, 2014

Strain profiles



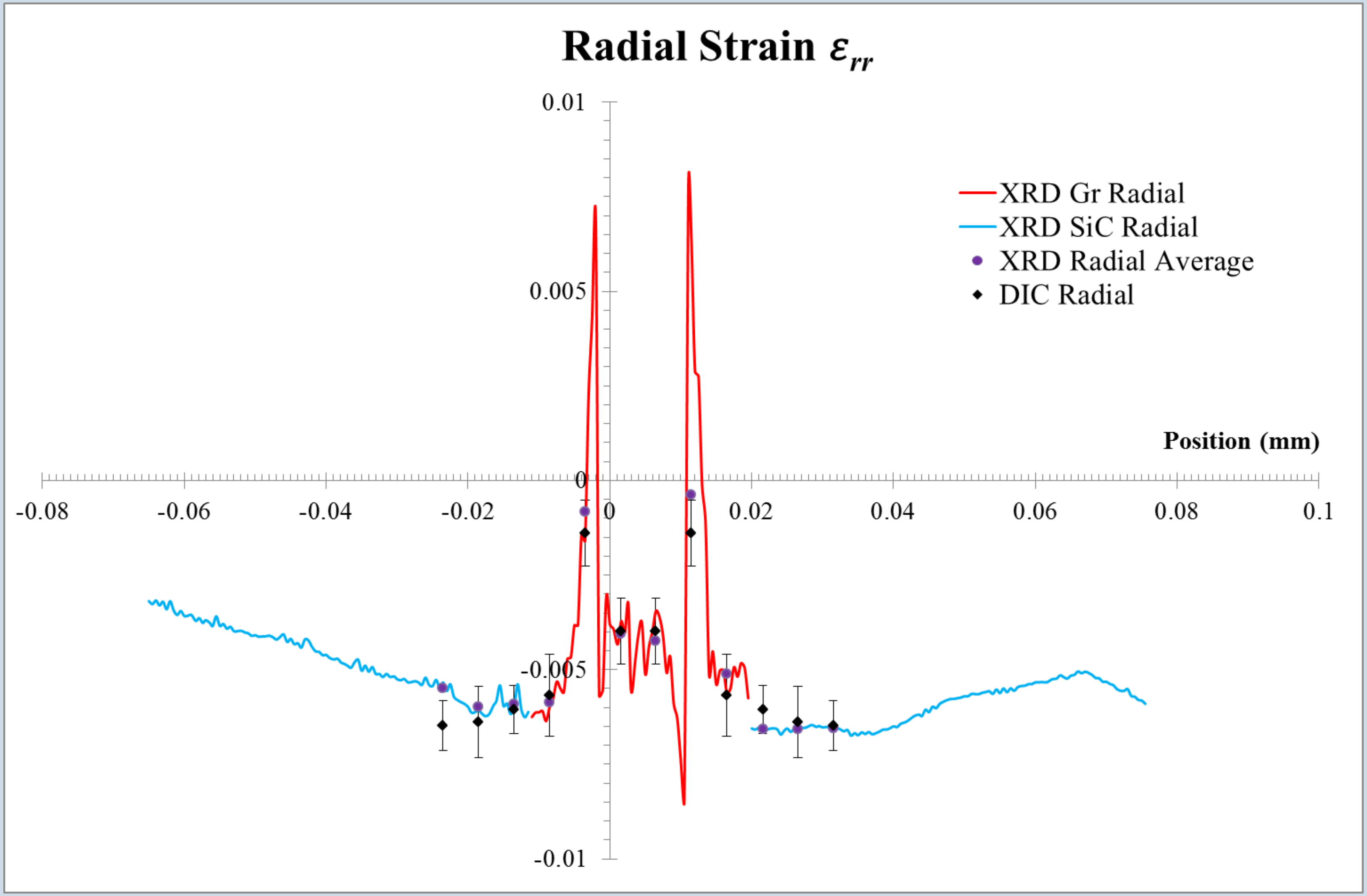
N. Baimpas, A.M. Korsunsky et al., Carbon, 2014

Absolute stress evaluation



N. Baimpas, A.M. Korsunsky et al., Carbon, 2014

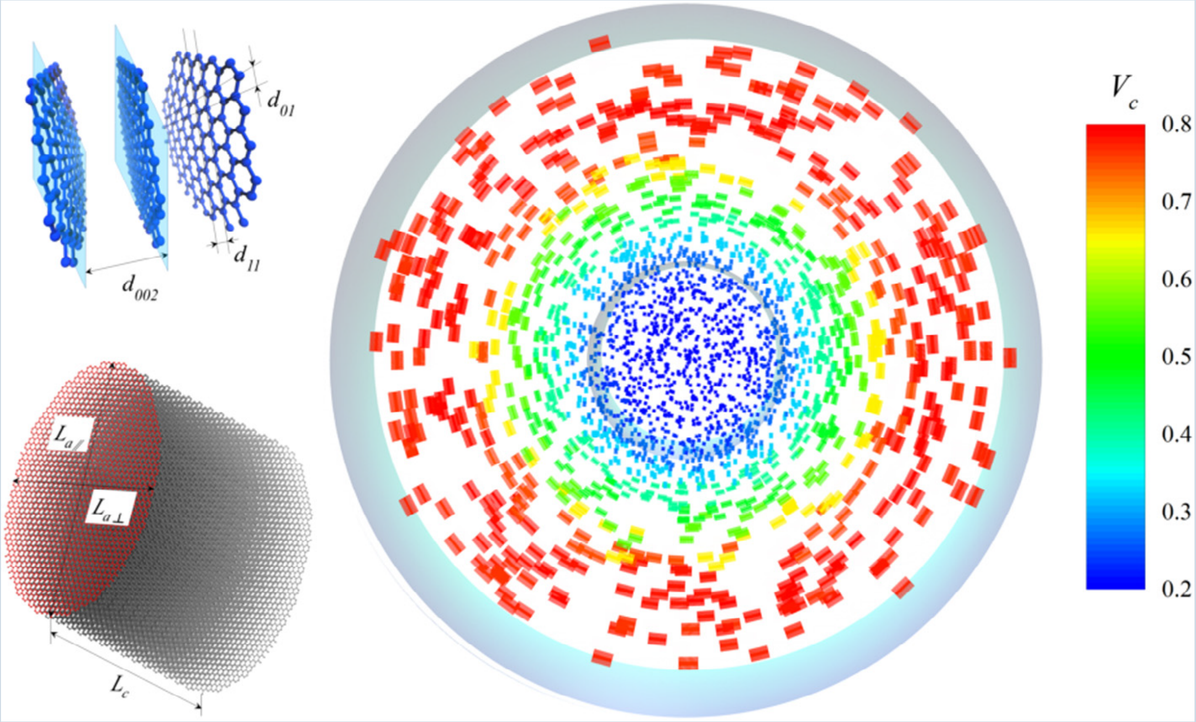
C-SiC fibre – internal stress state



N. Baimpas, A.M. Korsunsky et al., Carbon, 2014

Carbon monofilament (~35um diameter)

- Crystalline volume fraction variation (V_c)
- Crystalline aspect ratio variation (Size of markers)
- Absolute strain variation inside the fibre – Eigenstrain modelling

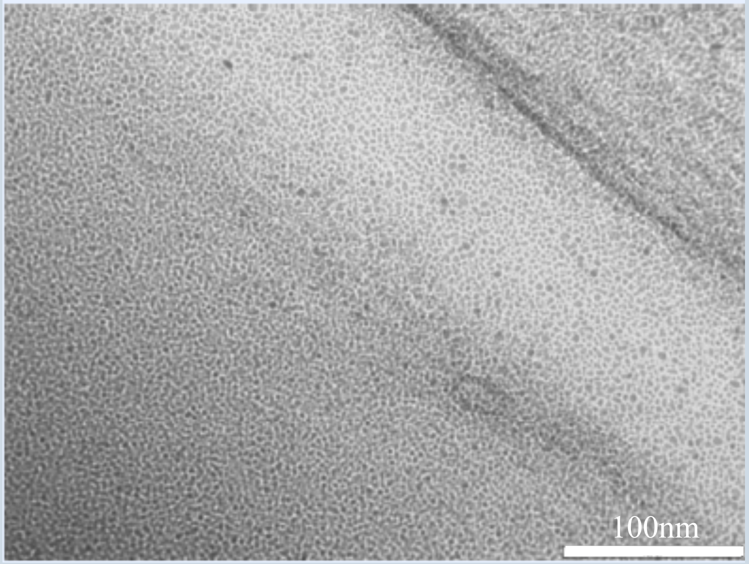


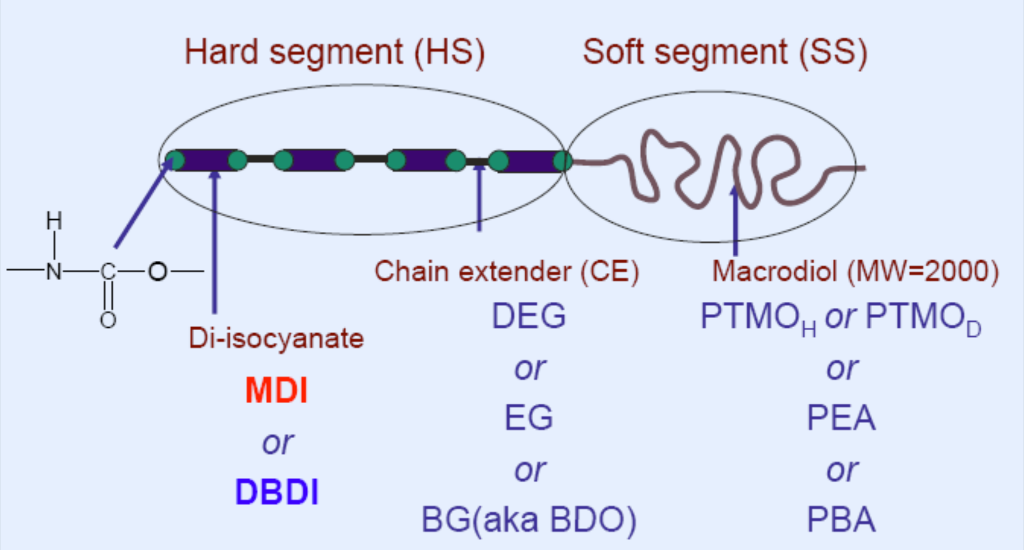
UNIVERSITY OF OXFORD

N. Baimpas, A.M. Korsunsky et al., Carbon, 2014

Multi-scale nature of strain in a thermoplastic polyurethane (TPU)

❖ A two-phase microstructure at the nm-scale





By courtesy of Dr Kayleen Campbell, University of Queensland

TEM illustration of polymer nanostructure and a schematic diagram of the hard-soft segment structure.

UNIVERSITY OF OXFORD

Tan Sui et al., A M Korsunsky, *Nature Comms*. 6, 2015.

Experimental Techniques

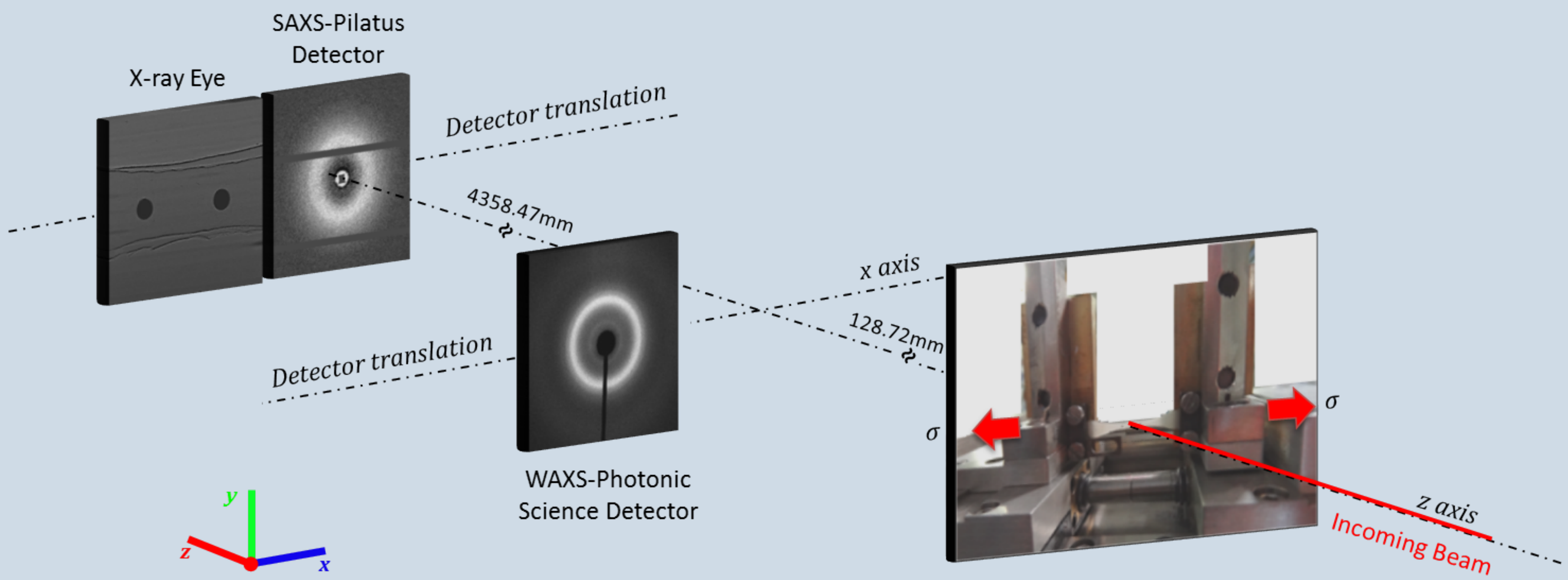


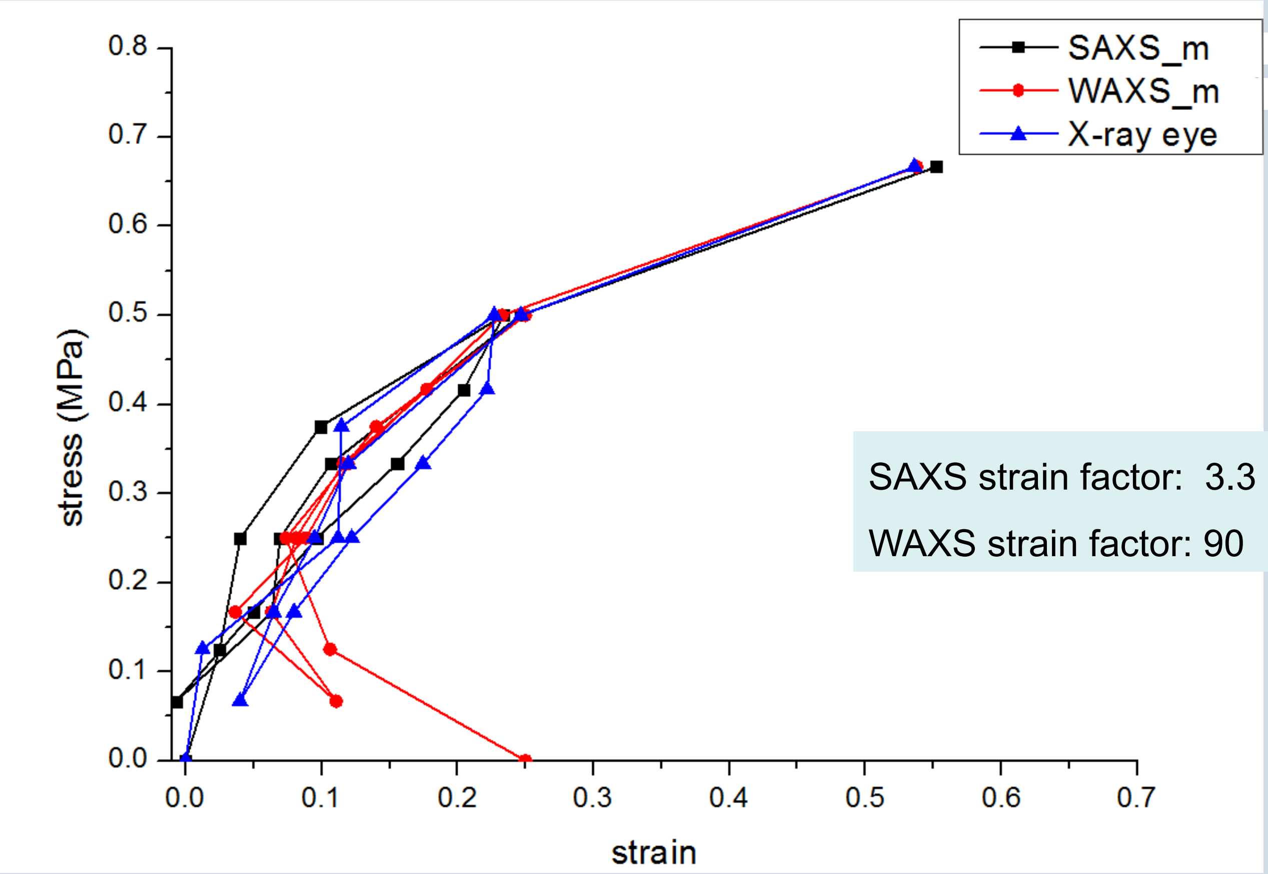
Figure 2: A schematic diagram of *in situ* cyclic tensile loading experimental setup.

Beamline:	**Energy**:	**Beam size**:
B16 (DLS, U.K.)	18 keV monochromatic	0.7×0.7 mm^2

UNIVERSITY OF OXFORD

Tan Sui et al., A M Korsunsky, *Nature Comms*. 6, 2015.

Bringing it all together …



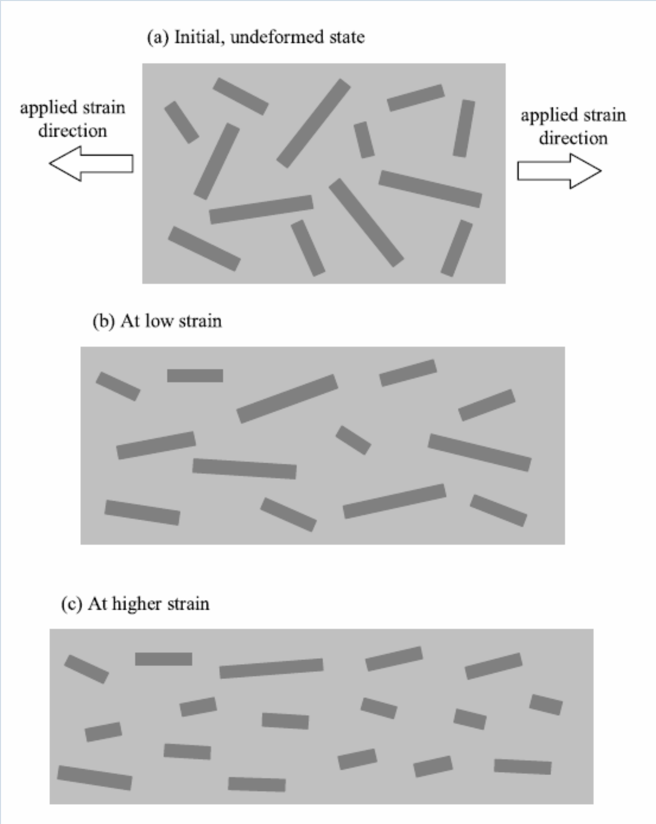
SAXS strain factor: 3.3

WAXS strain factor: 90

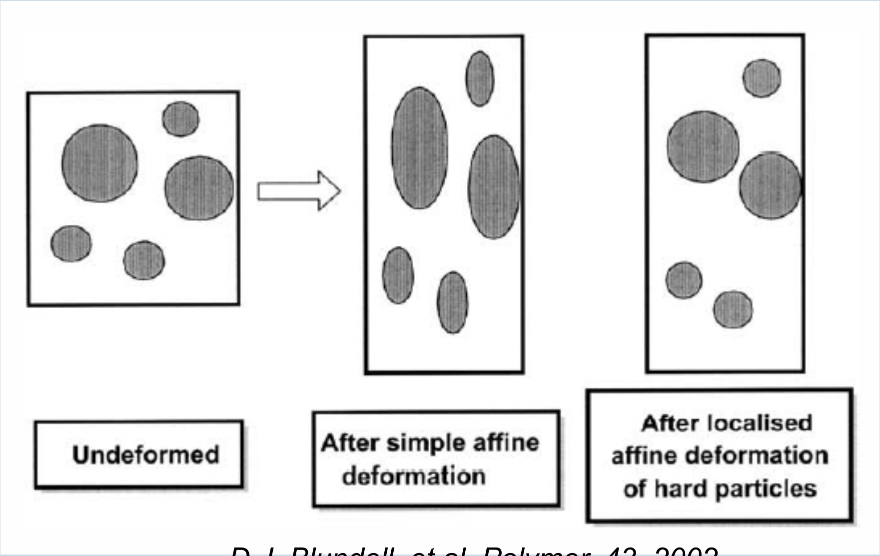
UNIVERSITY OF OXFORD

Tan Sui et al., A M Korsunsky, *Nature Comms*. 6, 2015.

How is that possible? …looking to explain



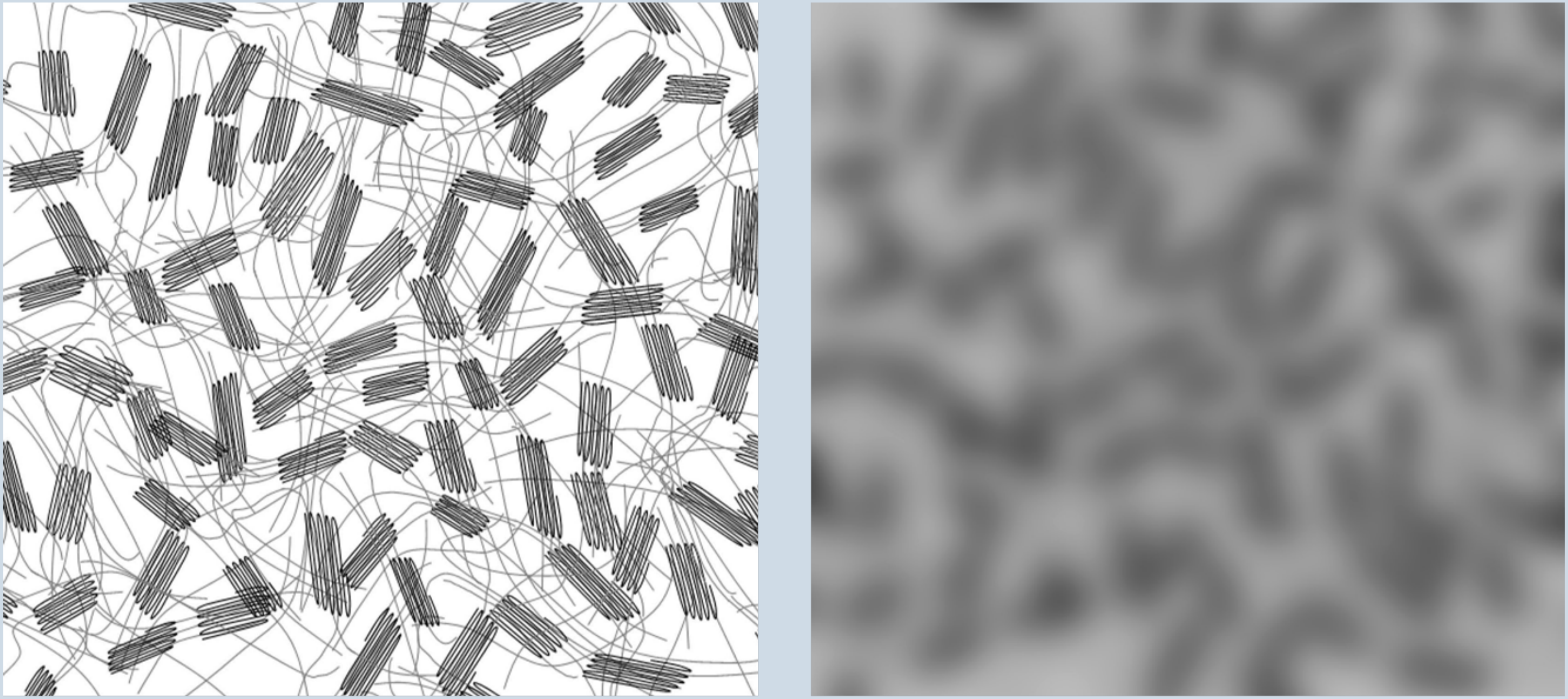
P.R. Laity, et al. Polymer, 45, 2004



D.J. Blundell, et al. Polymer, 43, 2002

Tan Sui et al., A M Korsunsky, *Nature Comms*. 6, 2015.

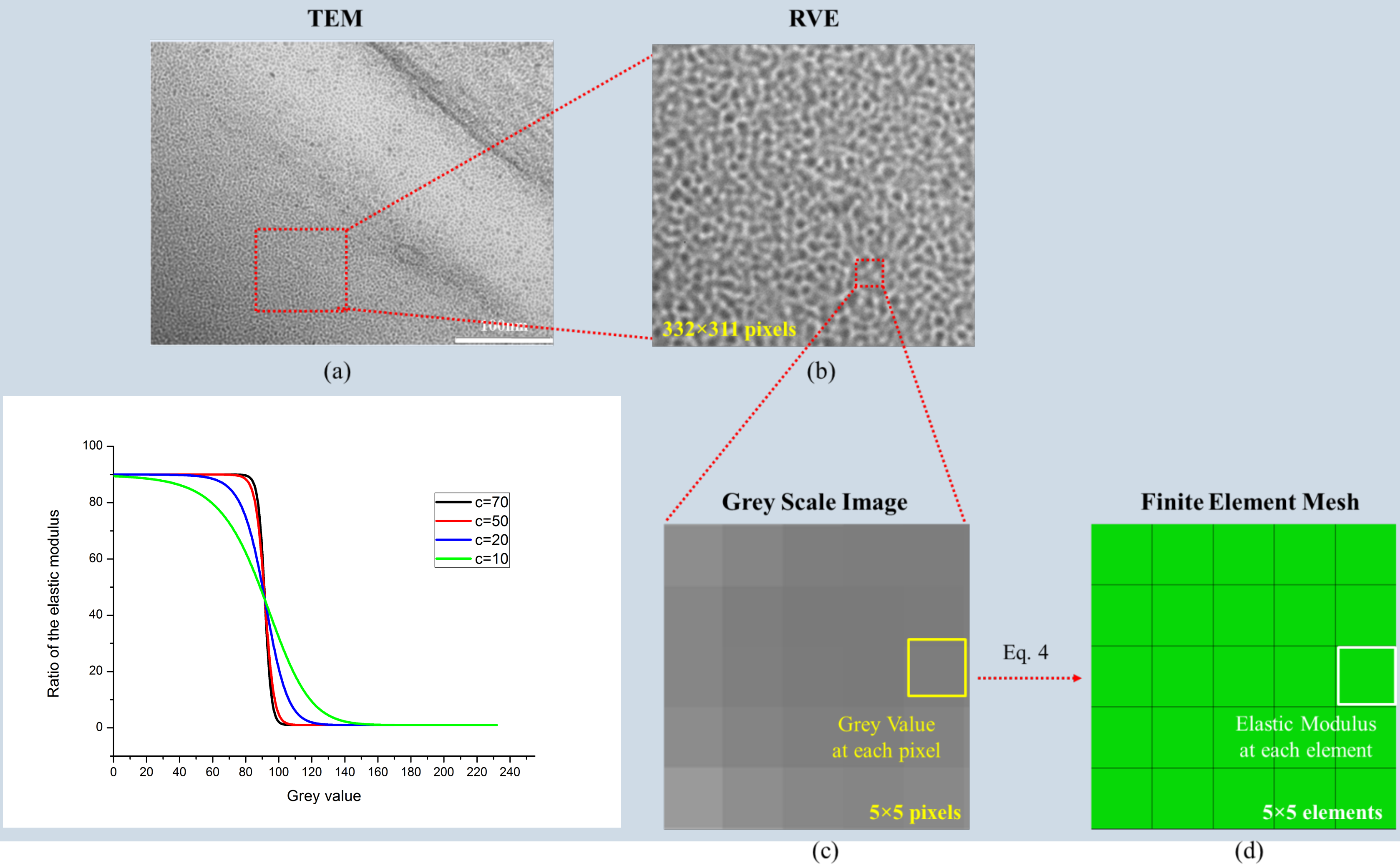
"Fuzzy" interfaces



(a) (b)

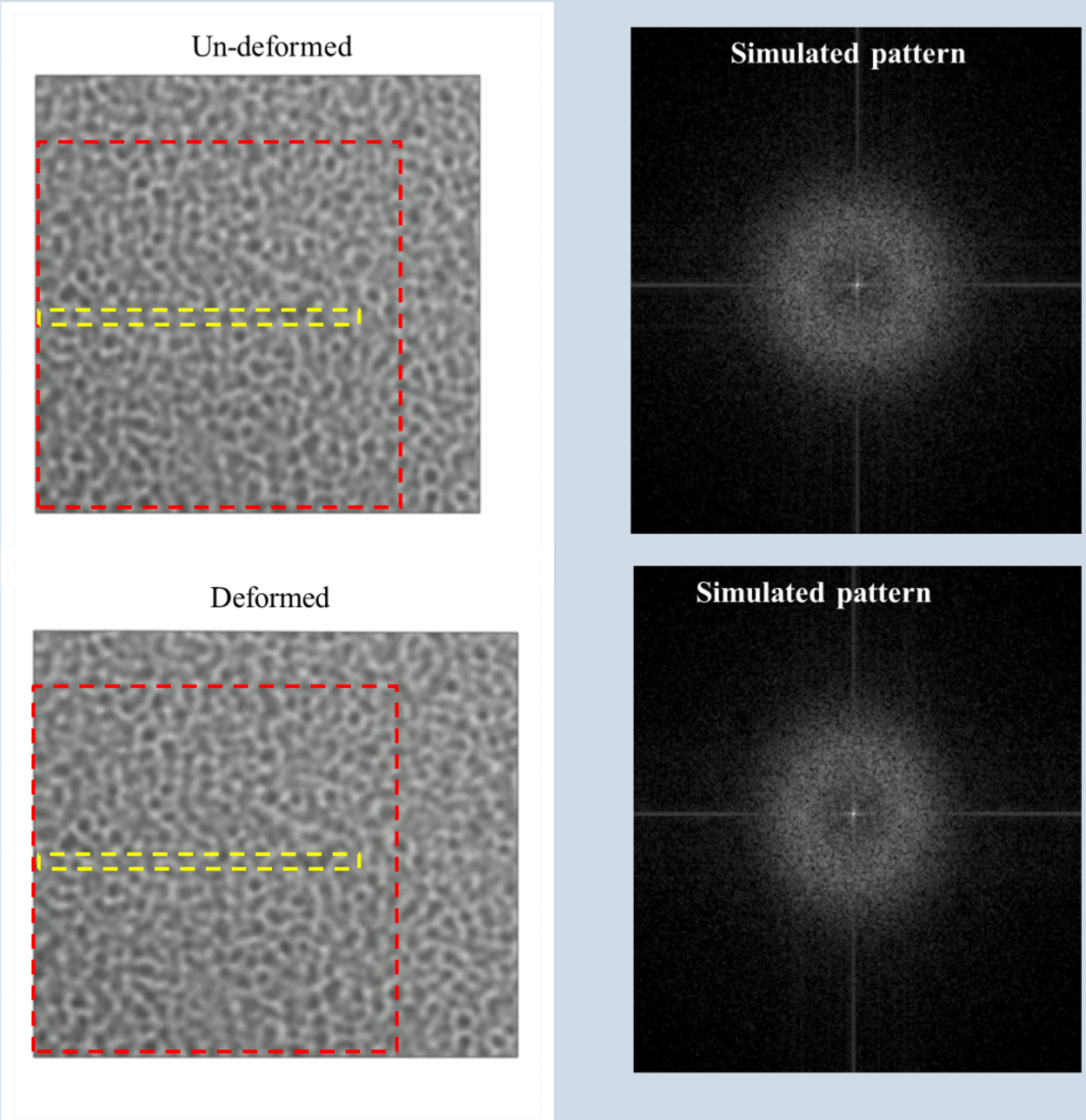
Tan Sui et al., A M Korsunsky, *Nature Comms*. 6, 2015.

Setting up the model



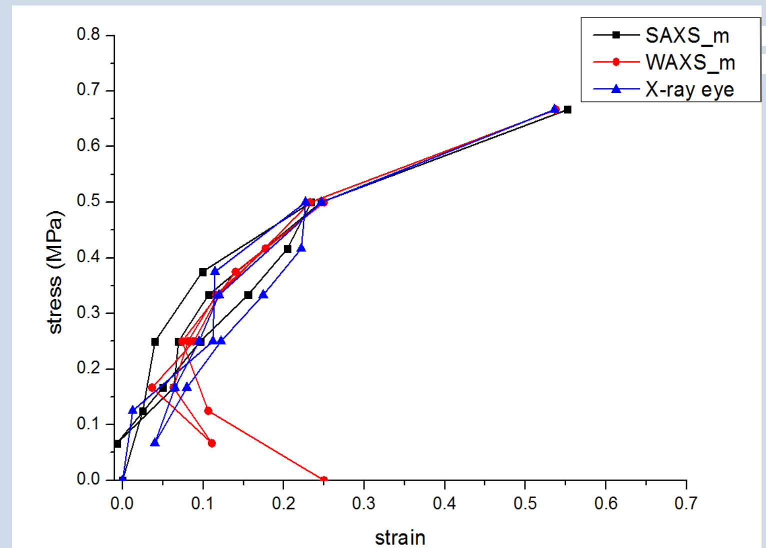
Tan Sui et al., A M Korsunsky, *Nature Comms*. 6, 2015.

FEM **2D-FFT**



(a) (b)

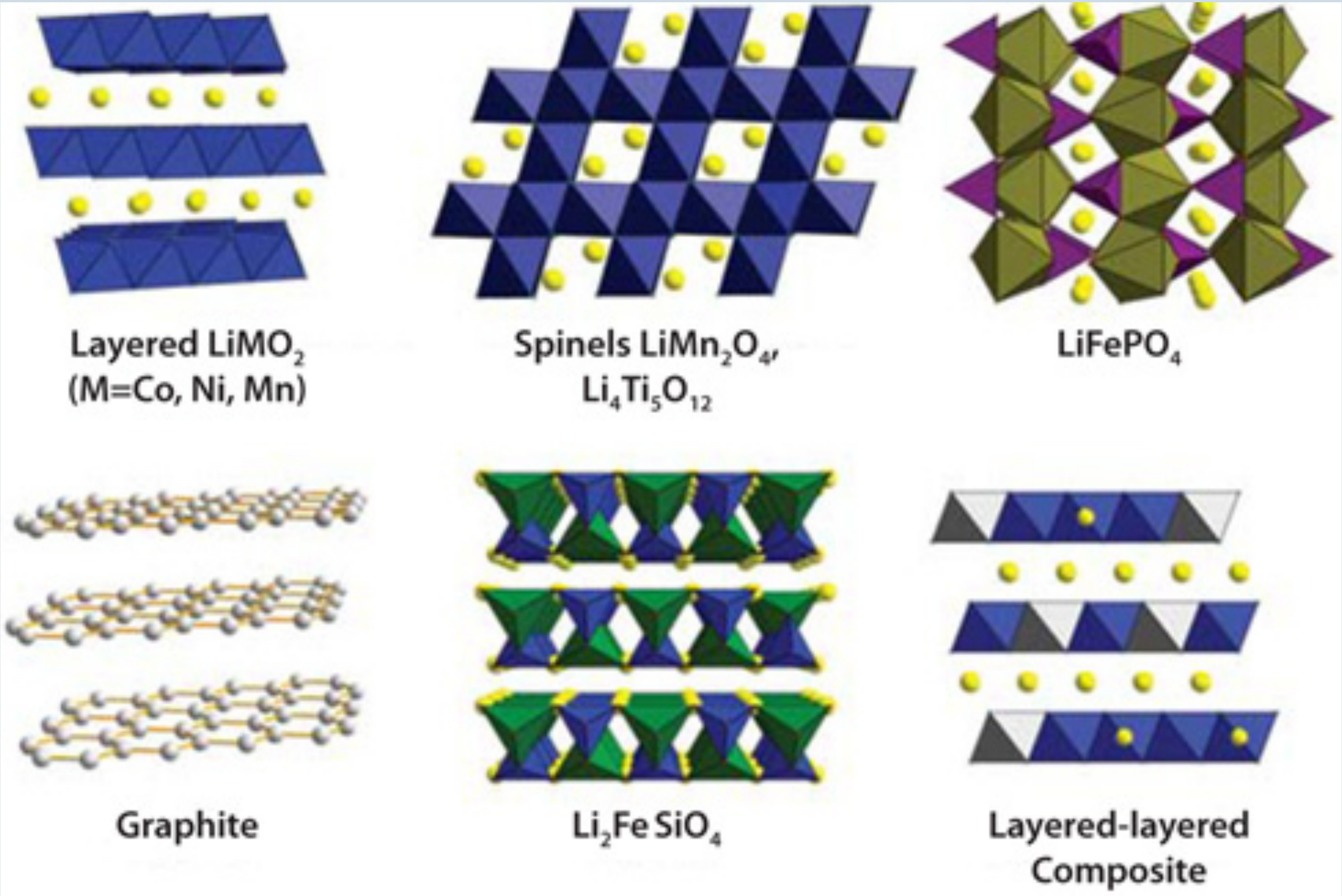
Model validation - FFT



UNIVERSITY OF OXFORD

Tan Sui et al., A M Korsunsky, *Nature Comms*. 6, 2015.

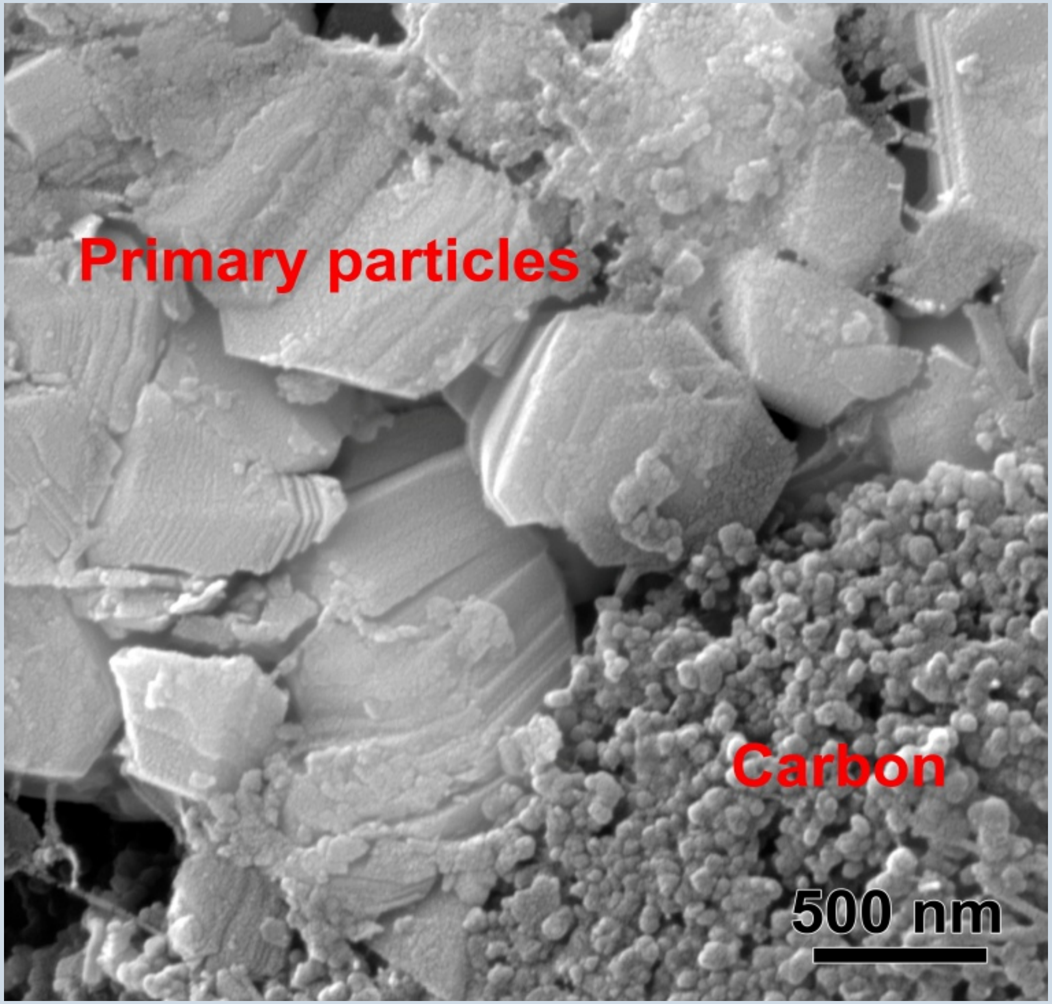
Multi-modal X-ray and FIB-SEM analysis of Li-ion batteries



UNIVERSITY OF OXFORD

Cathode materials

MNC Li battery cathodes

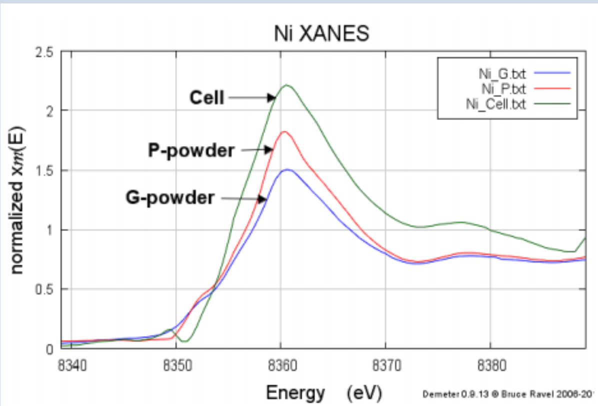


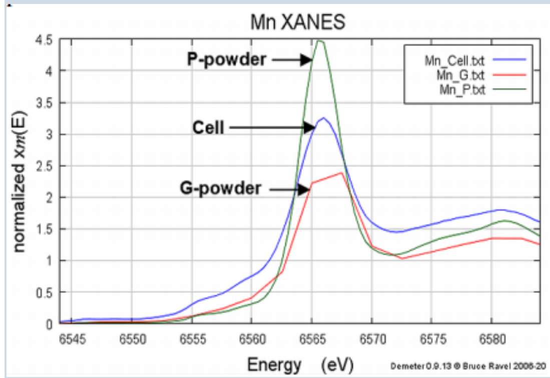
High magnification SEM image of primary particles of active material that reveals the details of their morphology. Hexagonal habit platelets of oxides can be clearly recognised in the small stack to the top right of image centre, whilst elsewhere the multi-layer nature of the particles composed of laminae ~50 nm in thickness

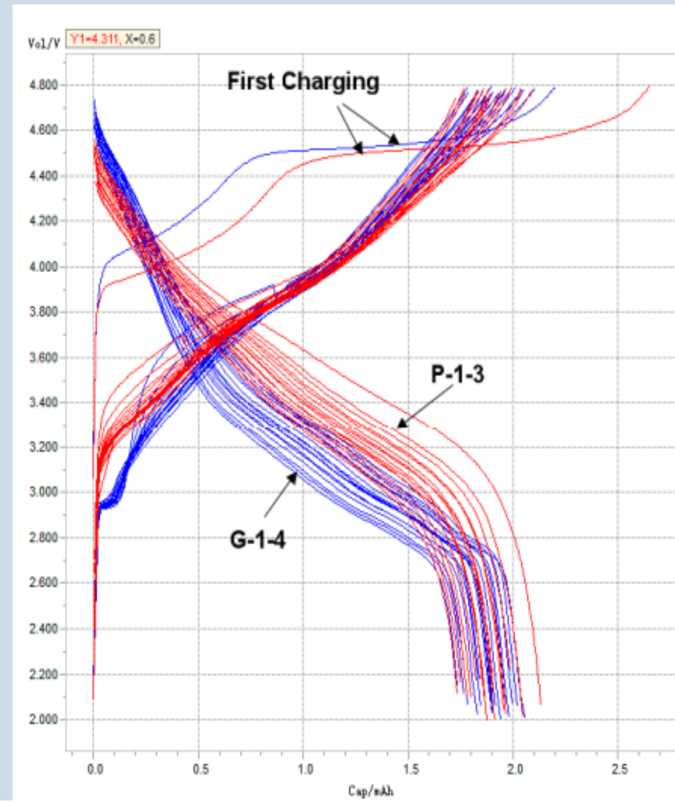
X-ray studies of Li-ion batteries: imaging, diffraction, XAS

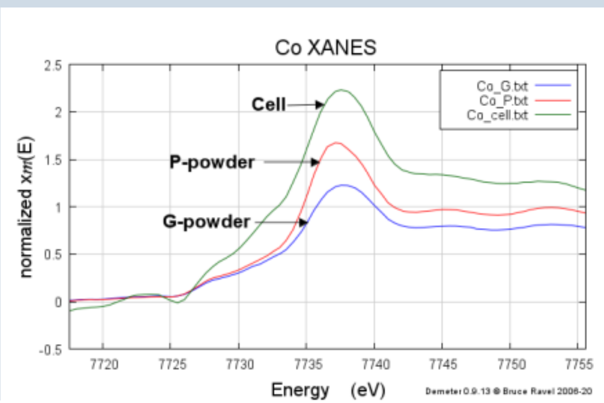
Absorption Spectroscopy for the Characterisation of NMC oxides for **Li-ion Battery Cathodes**

T. Kim, *et al.*, IMECS 2013

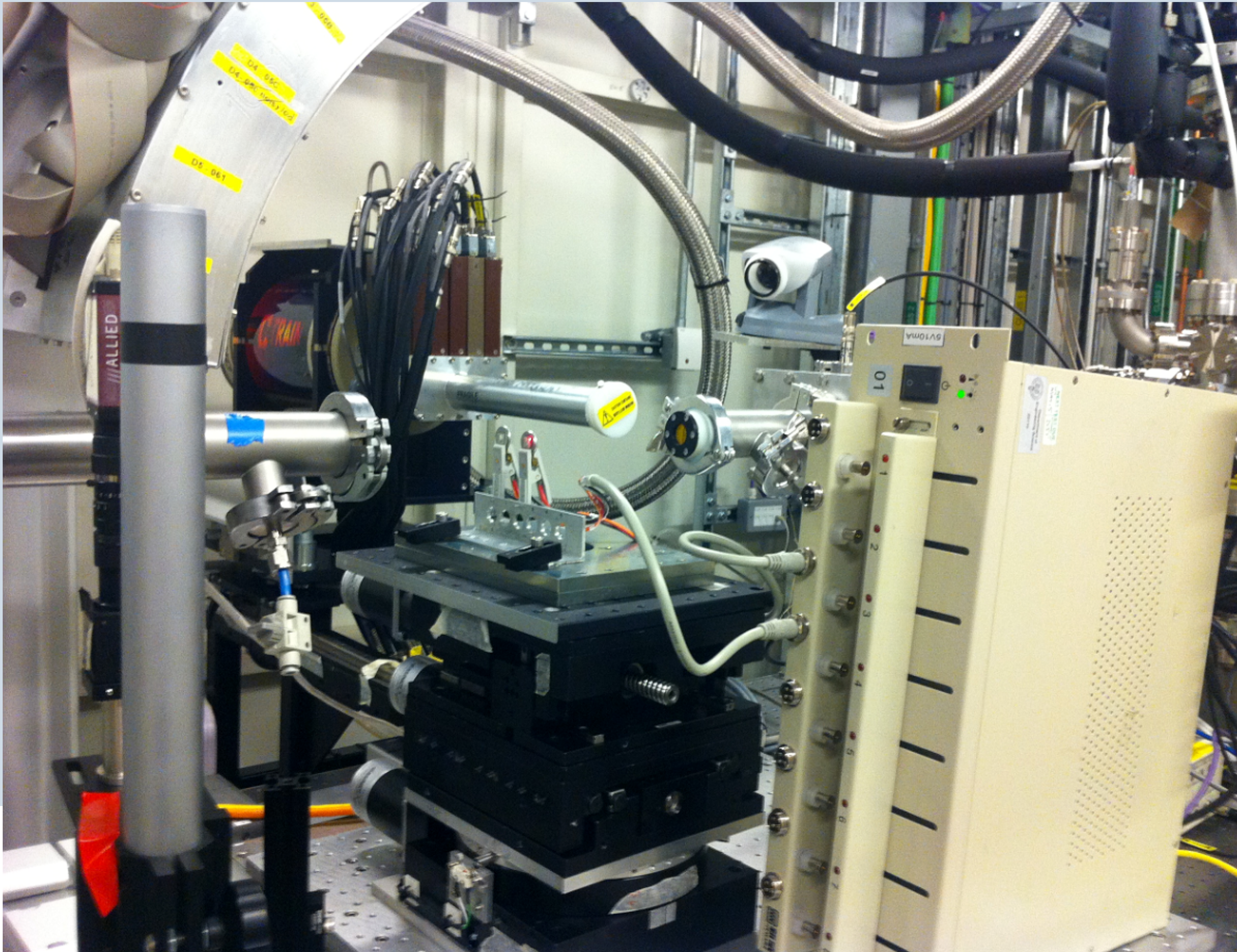




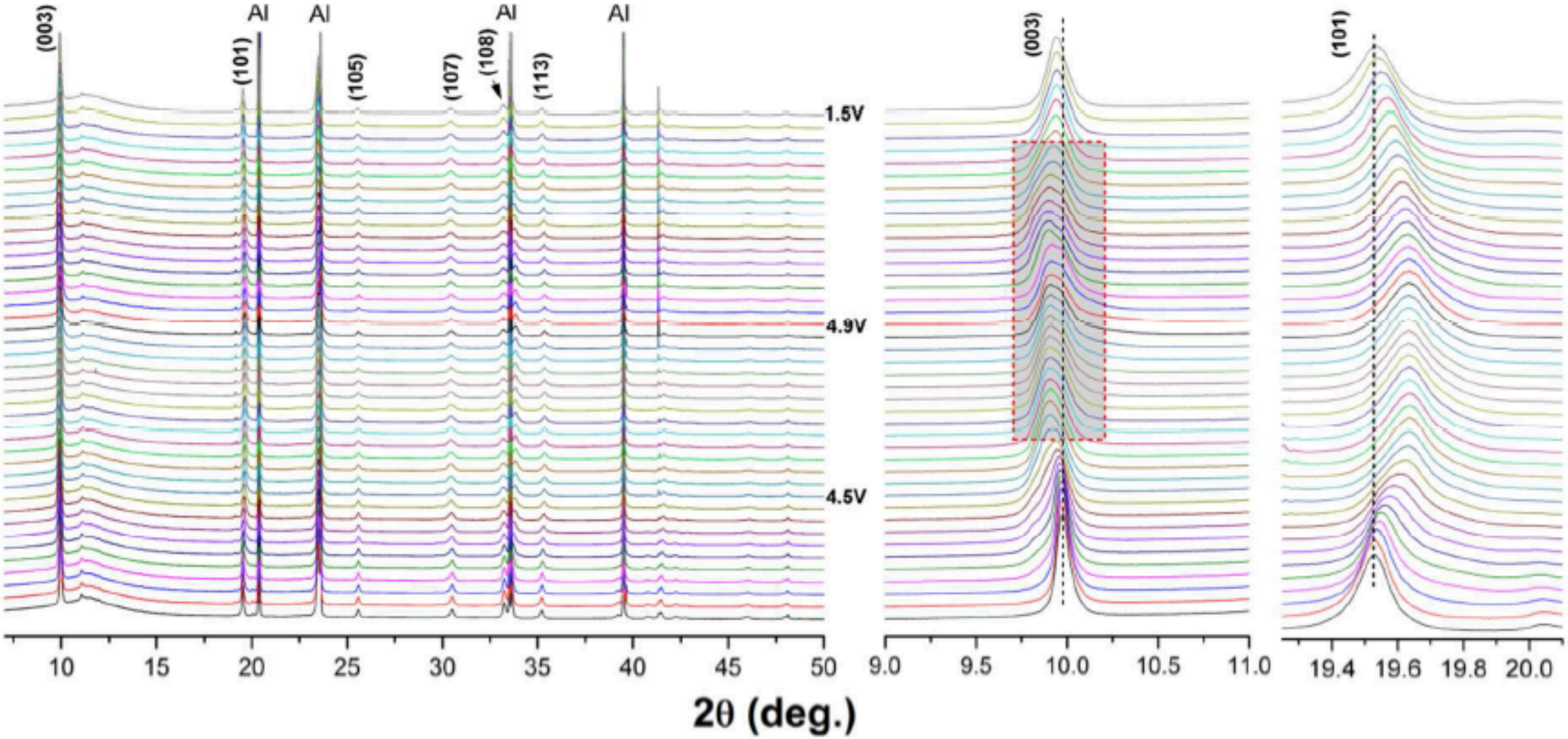




UNIVERSITY OF OXFORD


ALLIED
01

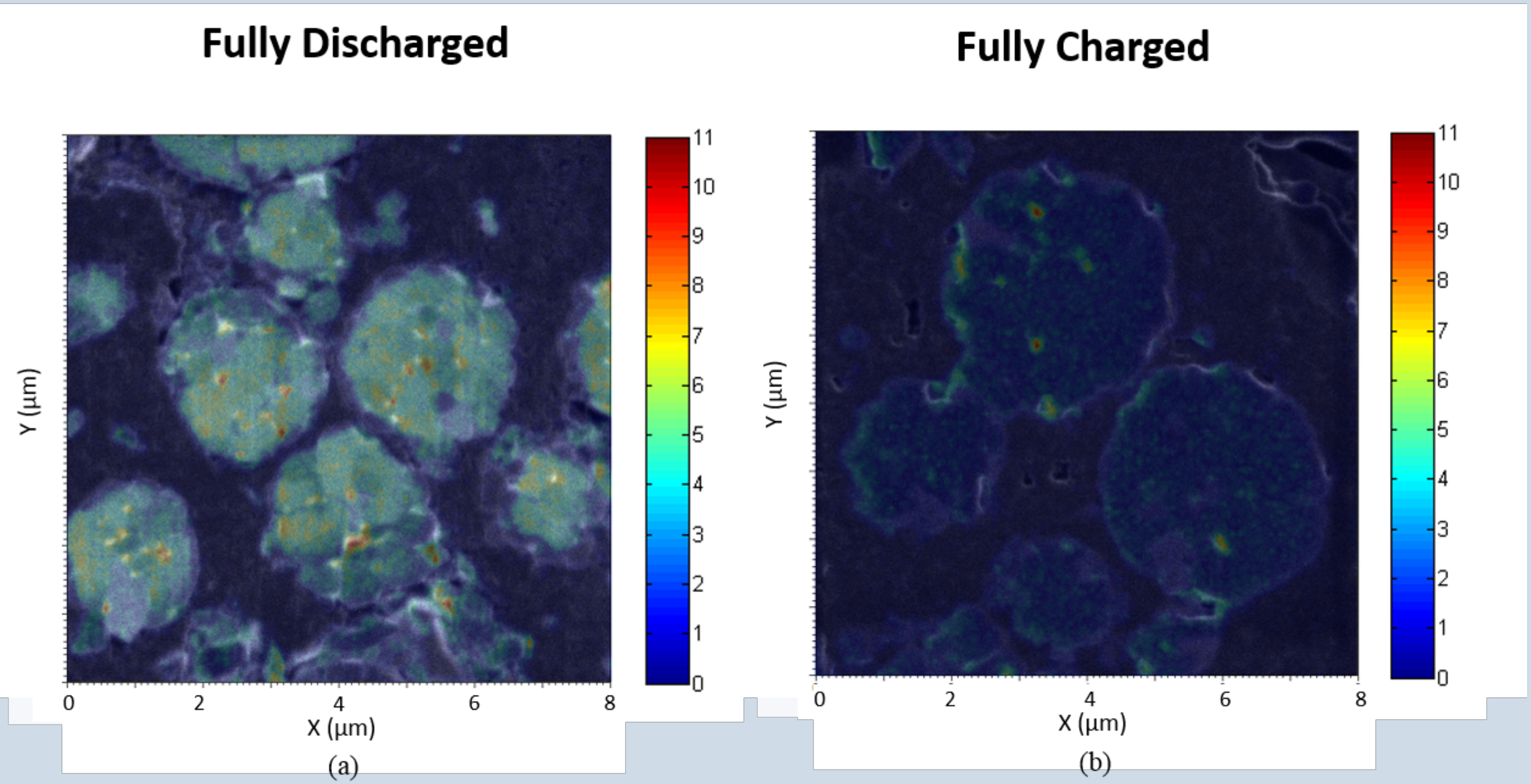
In situ Li-battery XRD



Insights obtained

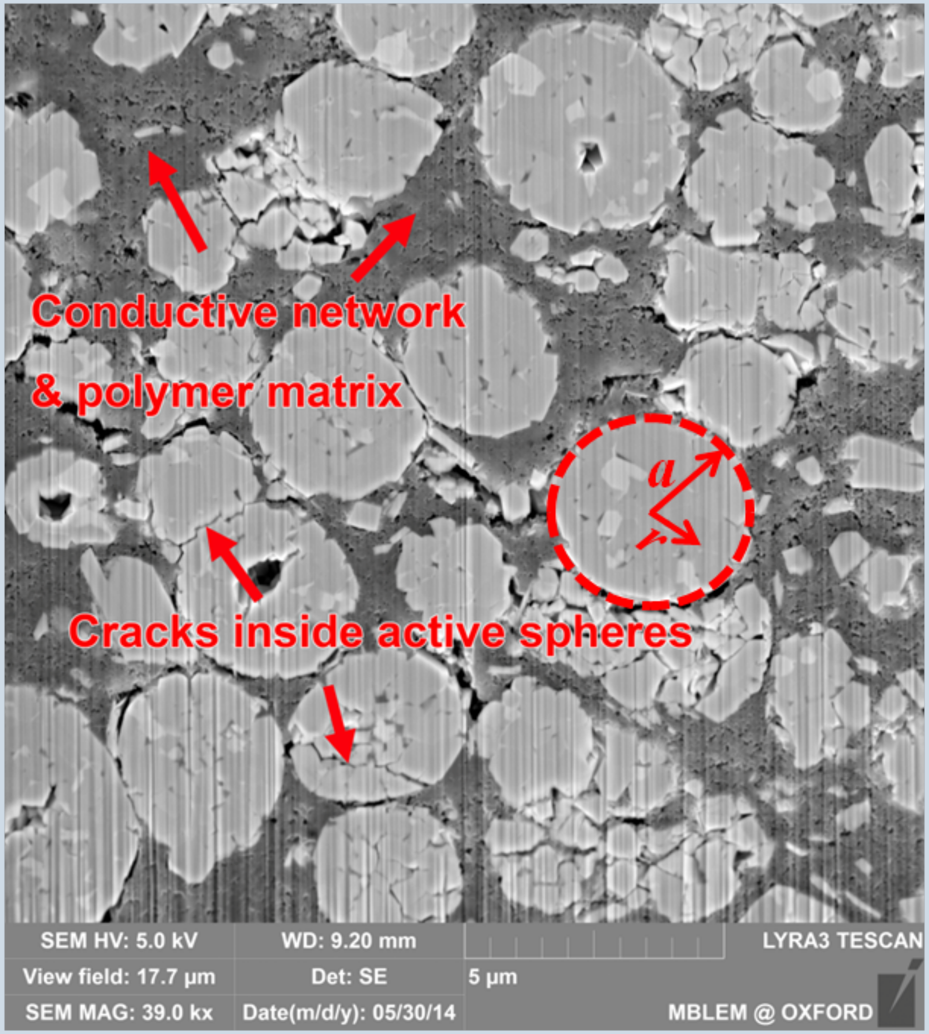
- Li diffusion is accompanied by changes in the chemical state of transition metals
- Lattice strains of the order of a few percent occur during lithium (de)intercalation
- The system is however highly inhomogeneous at the nano-scale: the relatively large beam (~70um) used in the experiment gives integral across the sample
- Local “hot spots” may lead to higher strains, causing fragmentation, loss of connectivity, and thus battery degradation and capacity fading
- What approach may reveal nano-scale inhomogeneity of Li+ migration?

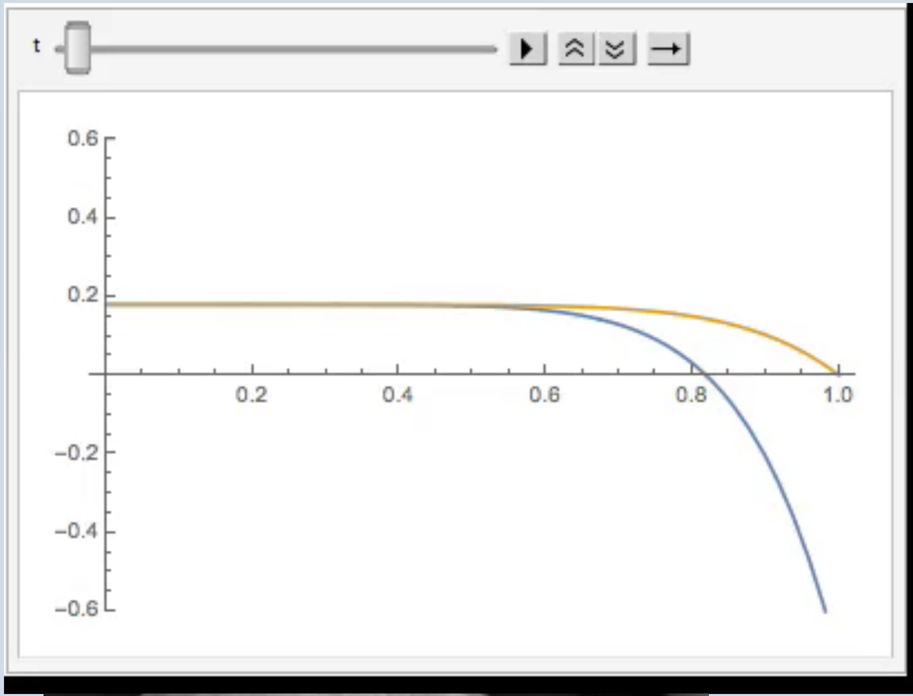
TOF-SIMS

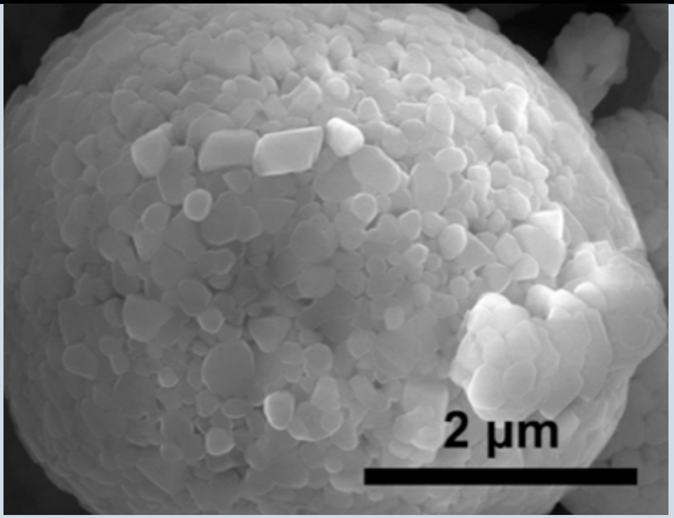


- FIB-SEM TOF-SIMS enables quantitative Li mapping in battery cathodes
- The ratio of Li concentration in discharged and charged states is ~ 4:1 (theoretical ~5:1)
- Li "trapped" at grain boundaries and particle-matrix interfaces

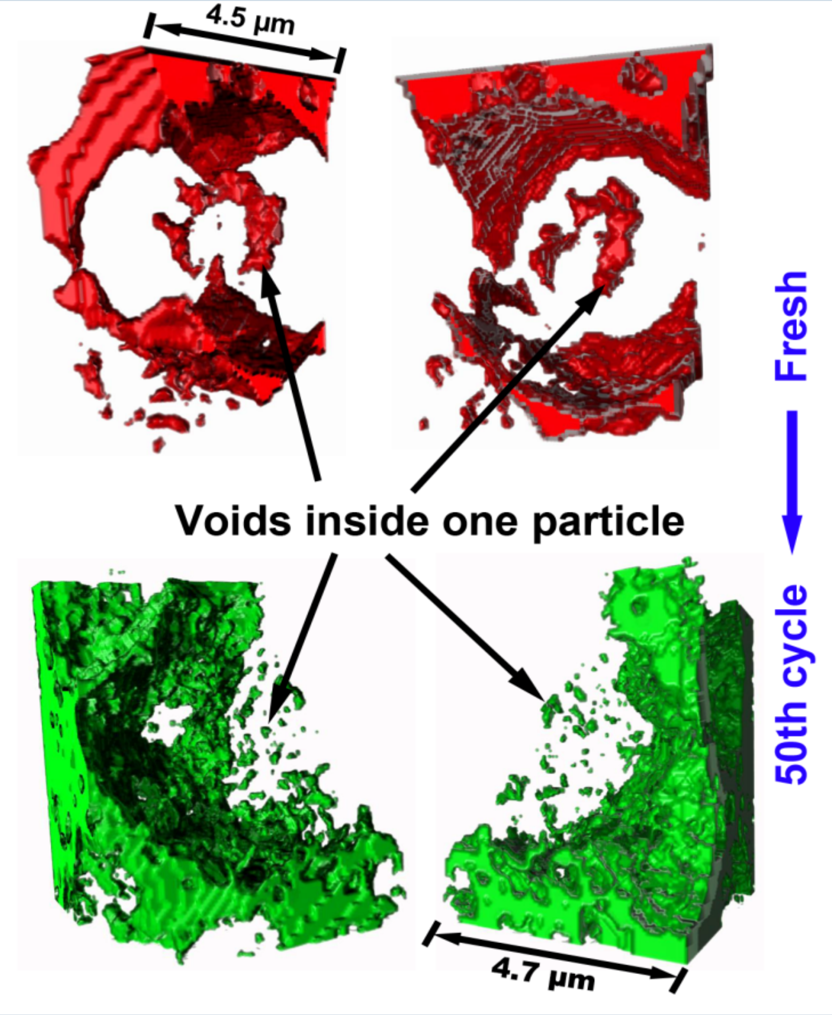
Particle fragmentation

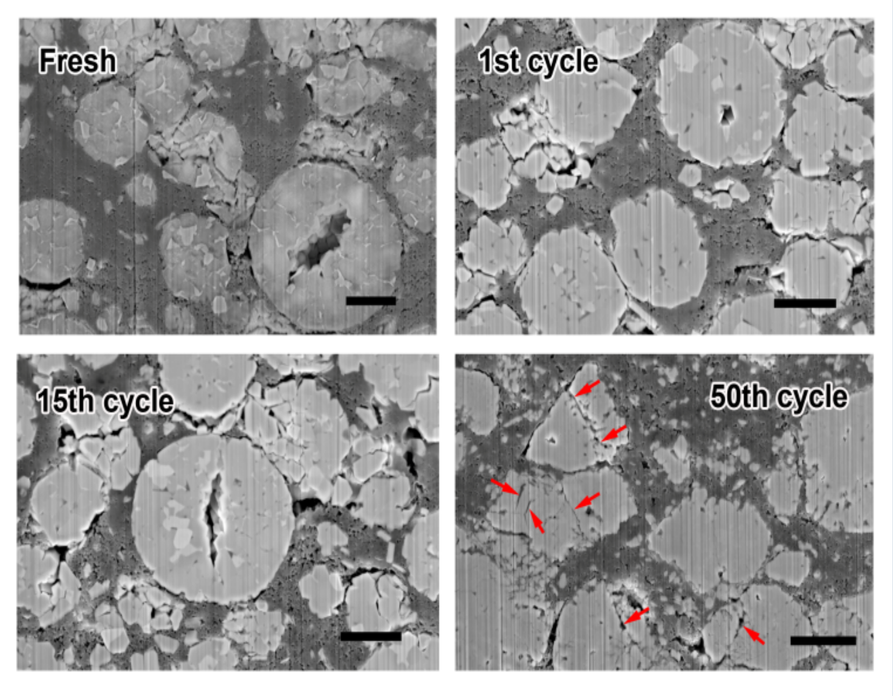






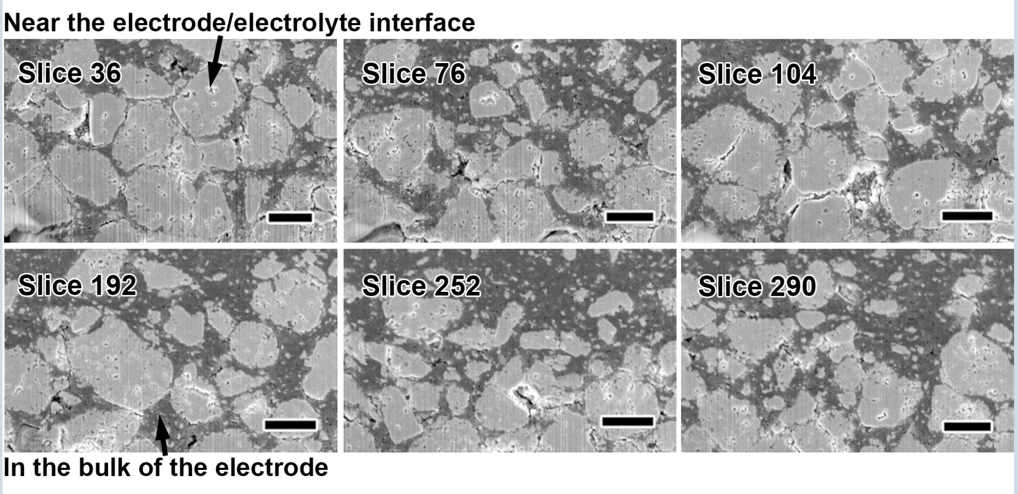
Fragmentation

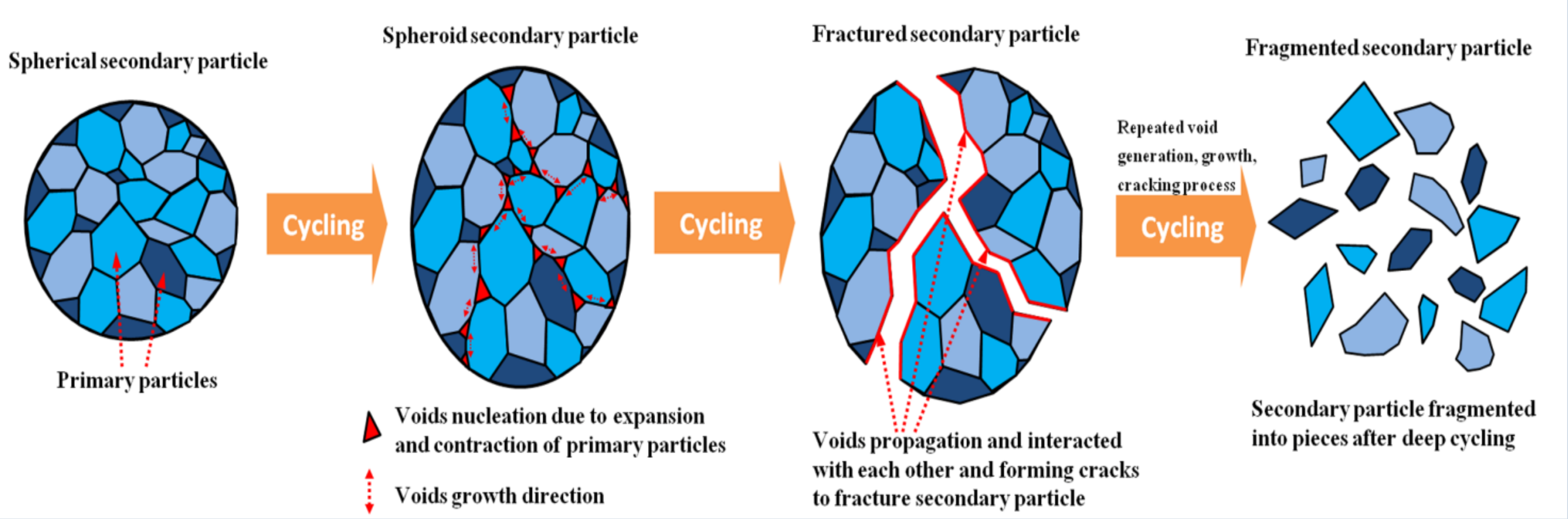




Tan Sui, A.M. Korsunsky et al. (2015) J Materials Chemistry A

Fragmentation

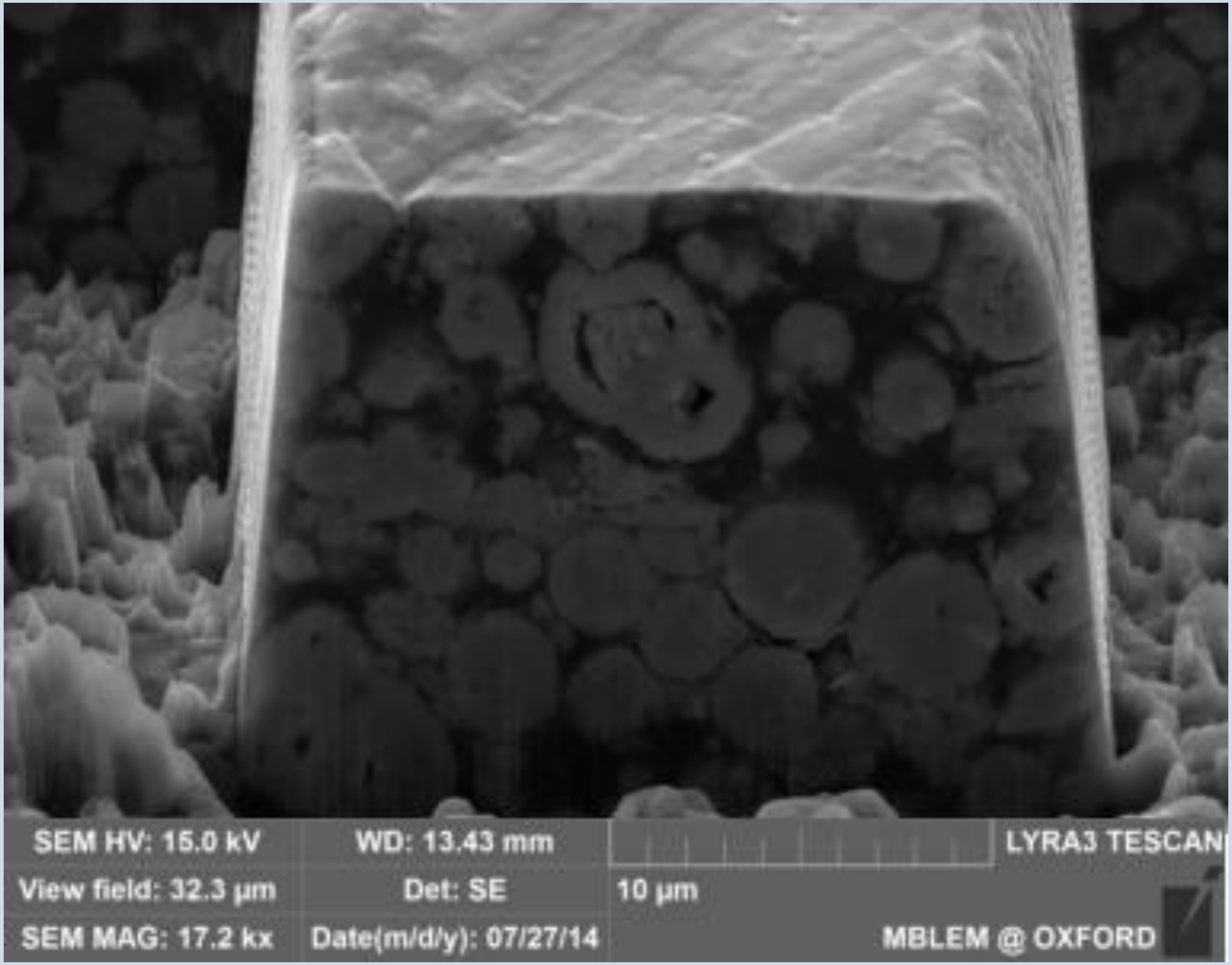


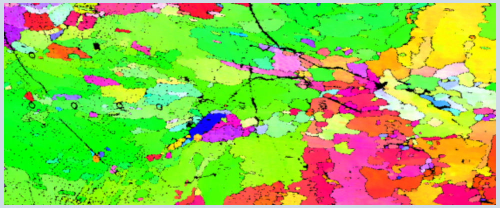
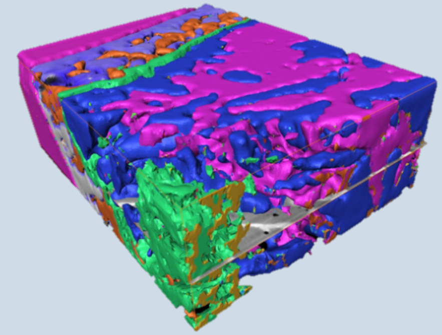


UNIVERSITY OF OXFORD

Tan Sui, A.M. Korsunsky et al. (2015) J Materials Chemistry A

FIB serial sectioning for 3D vis of fragmentation



MBLEM @ Oxford