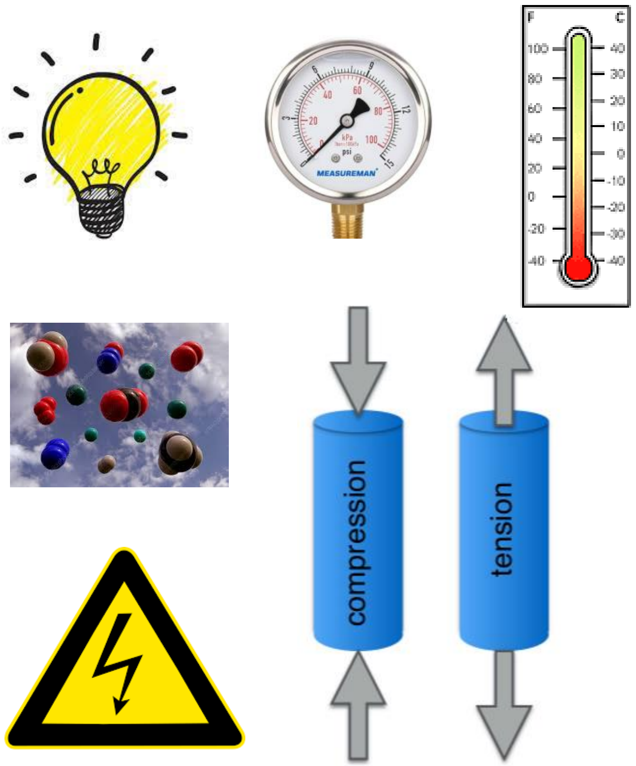
XRD & Scattering Summer School
June 18-20, 2024

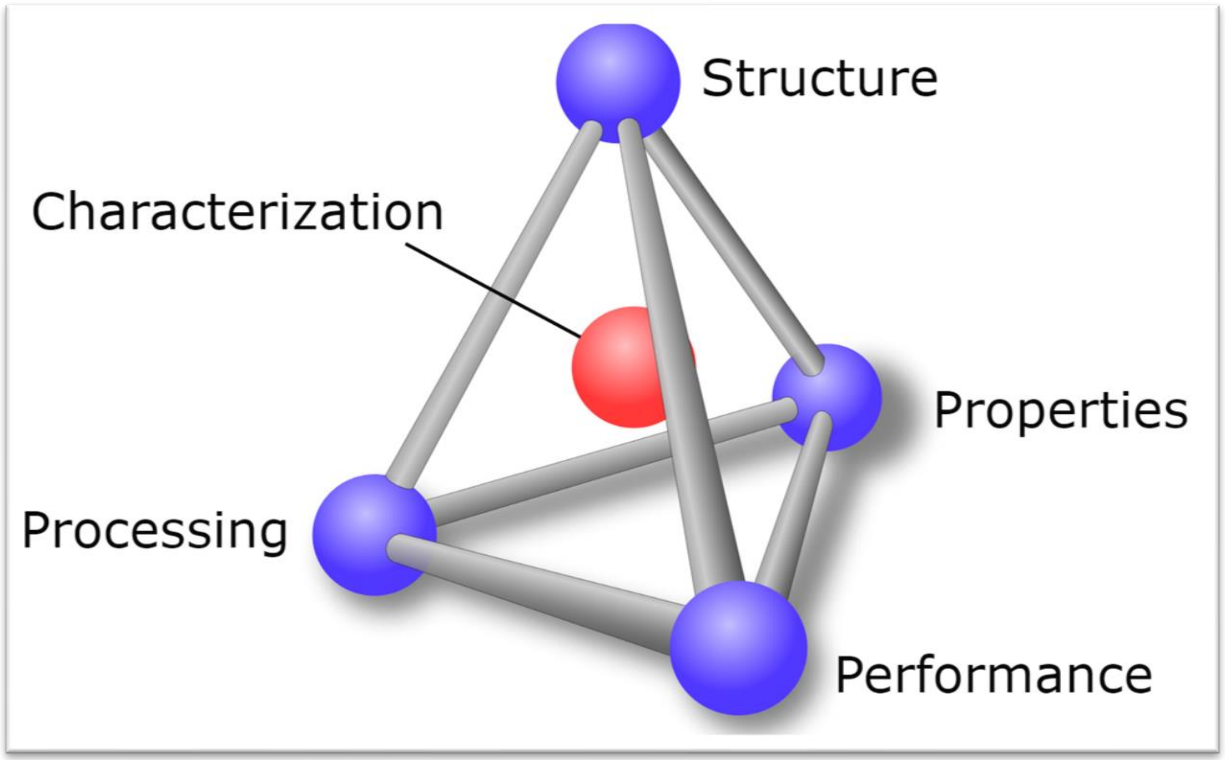
In-situ experiments

beatriz.moreno@lightsource.ca

Motivation for in-situ x-ray experiments

Studying materials under working conditions:





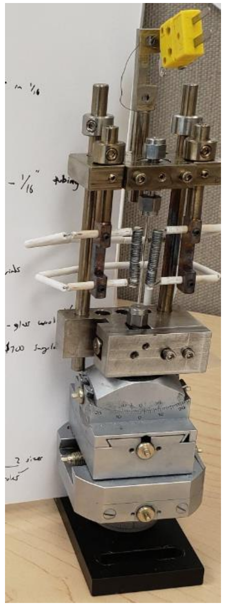
Applications:

- Microelectronics
- Batteries
- Fuel cells
- Catalysis
- Food science
- Solar cells
- New alloys and steels
- Materials under extreme conditions, etc.

Provides information on the chemical and physical properties of materials and devices under realistic processing conditions

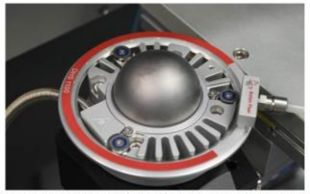
Materials Science tetrahedron. Credit: Public domain.
https://www.e-education.psu.edu/matse81/node/2094

Sample environments



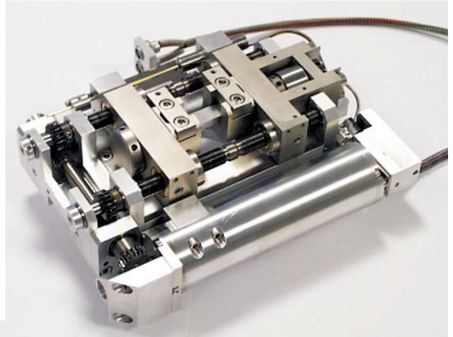
Sample environments seek to mimic the operation conditions of the materials or devices being tested

- Furnaces with controlled atmosphere and temperature
- Tensile rigs
- Temperature/humidity light chambers
- in situ cycling / temperature control for battery studies
- Customized setups

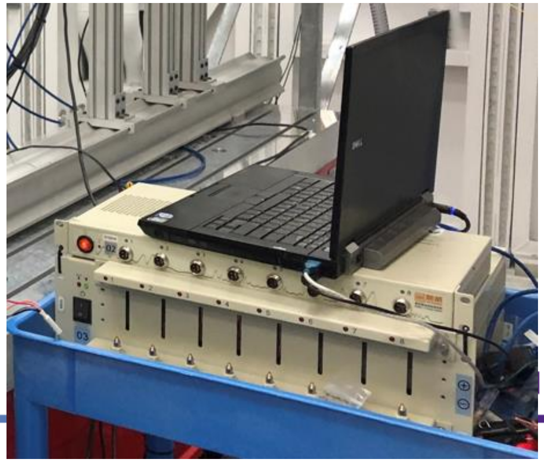


The Anton Paar domed heating stage (DHS1100) can be used to heat flat plate samples from ambient temperature to 1100 °C in a variety of inert gas atmospheres or under vacuum.

A Stoe capillary furnace can heat capillaries up to 1770K. Quartz capillaries can be used up to 1370 K, above which sapphire capillaries must be used. Users must supply their own sapphire capillaries.



(e)



Brilliant synchrotron sources

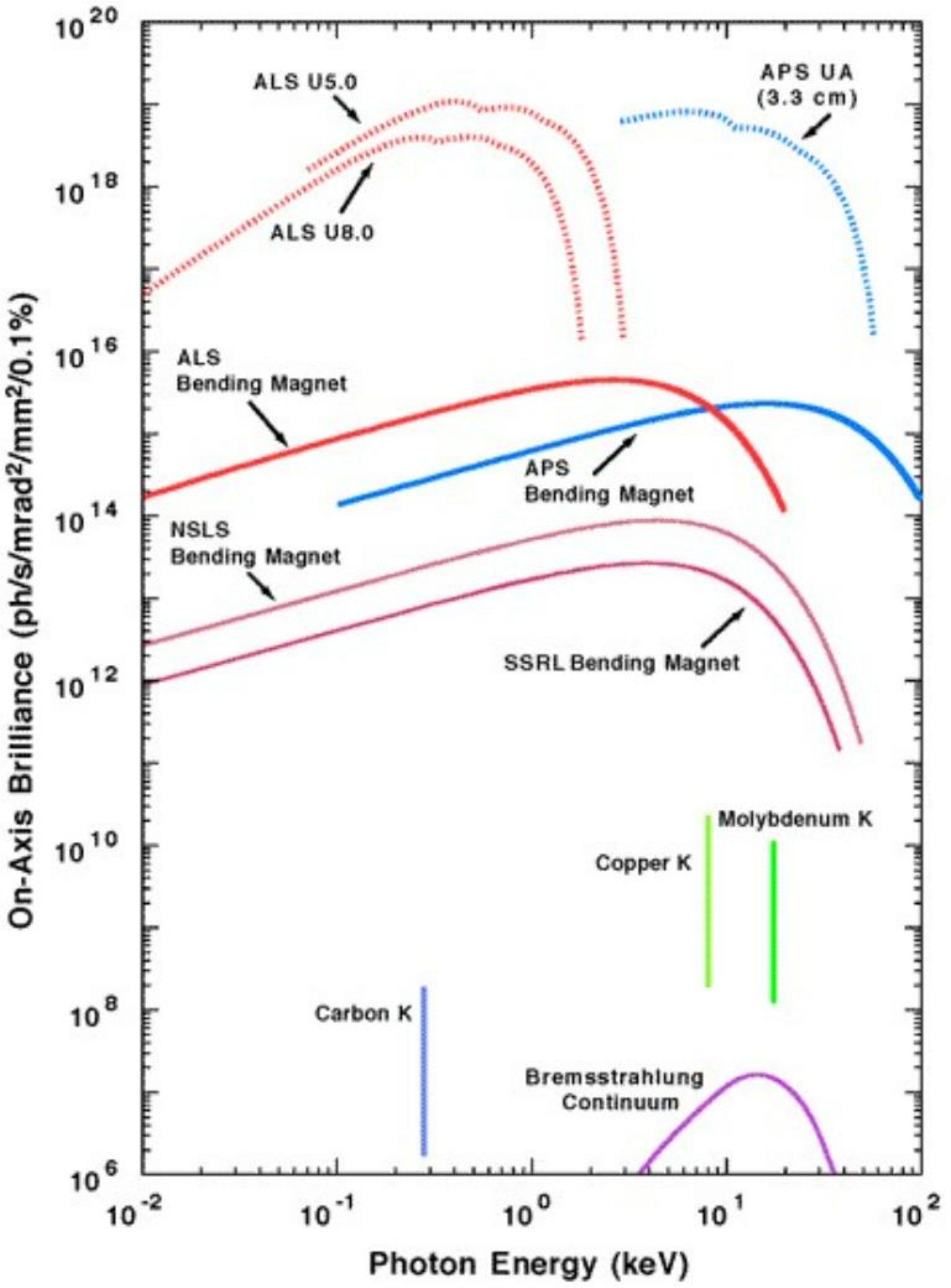
→ Fast acquisition

→ High temporal resolution

→ Many applications!

1. Phase transitions
2. Microelectronics
3. Batteries
4. Solar cells
5. Mechanical rigs
6. Catalysts
7. Corrosion
8. High pressure

https://www.nottingham.ac.uk/aspire-itn/aspire-blog/aspire-blogs-2020/synchrotron-radiation-and-synchrotron-light-sources.aspx



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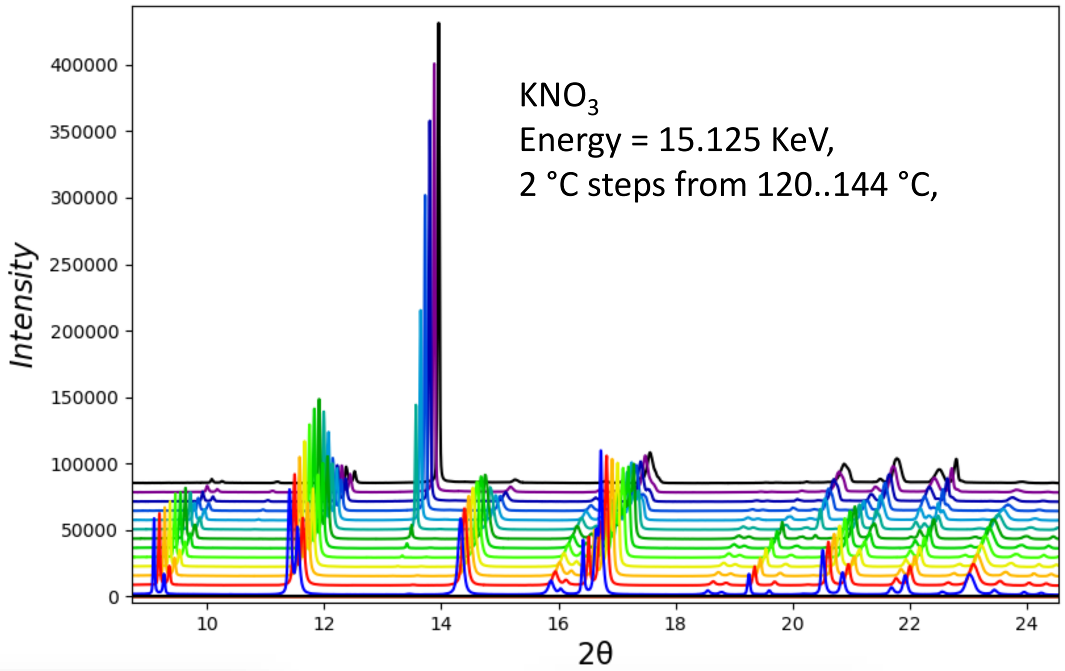
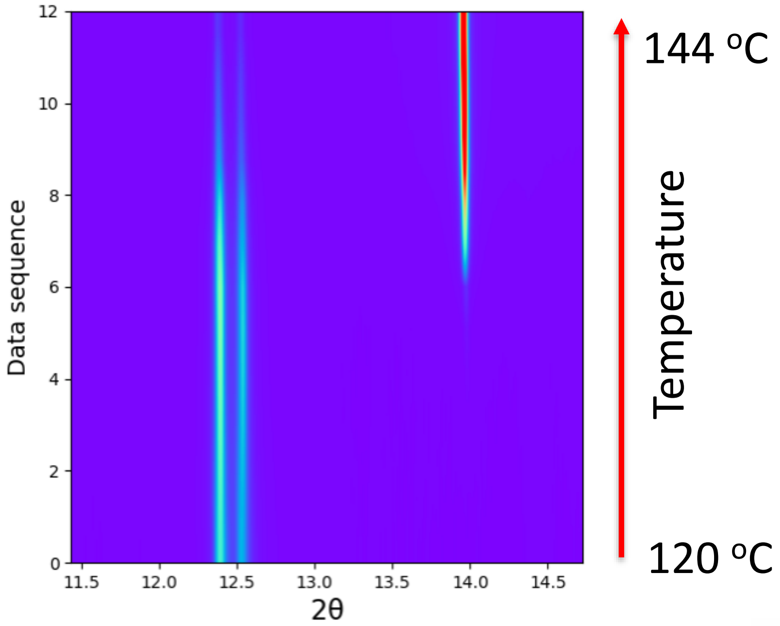
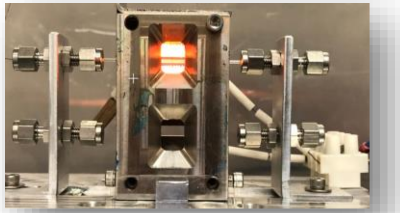
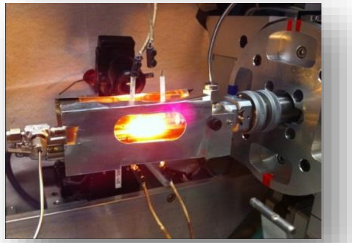
Structural phase transitions

Orthorhombic $\alpha - KNO_3$ → trigonal β - KNO_3









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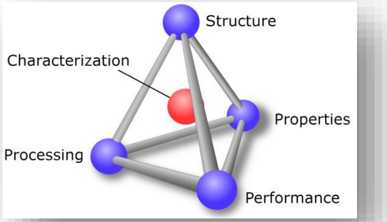
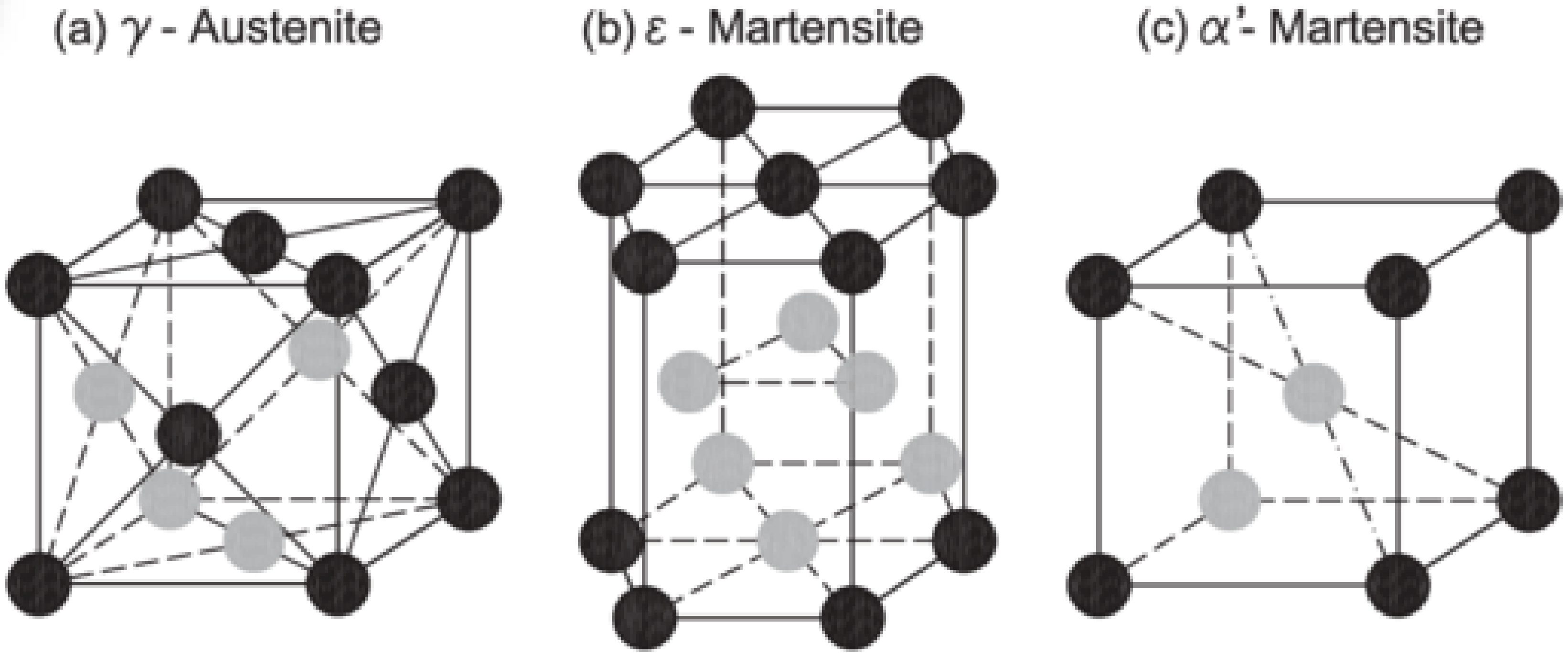
THE BRIGHTEST LIGHT IN CANAD

Structure - property relationship
Steels





Austenitic Stainless Steel is highly corrosion-resistant, ductile, and formable.

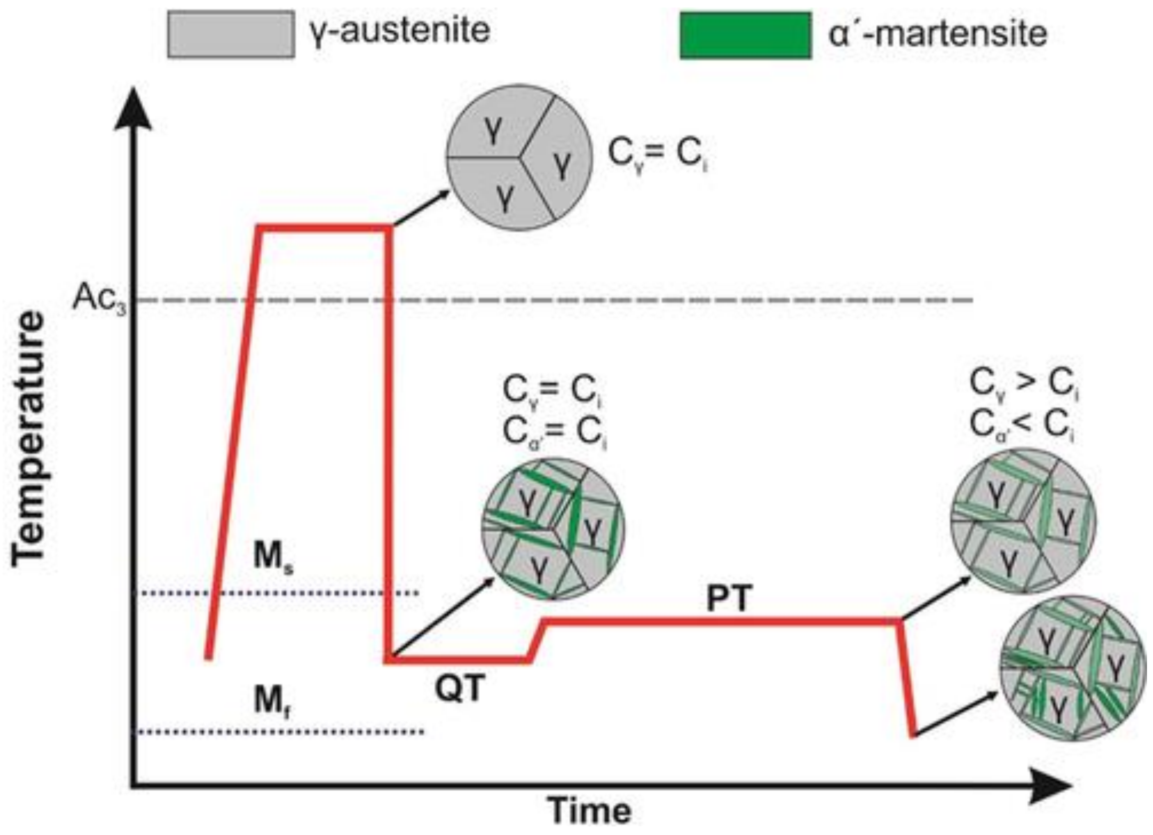
Martensitic Stainless Steel is highly wear-resistant, hard, and strong

Iron-based shape memory alloys for civil engineering structures: An overview

Designing and synthesizing high strength alloys

Quenching and partitioning (Q&P)

- Multi step heat treatment
- Q&P generates microstructures containing retained austenite stabilised by carbon partitioning from martensite.
- austenite/martensite mixtures with desirable combinations of strength, ductility, and toughness.
- Q&P steels yield an excellent balance of high tensile strength and good elongation



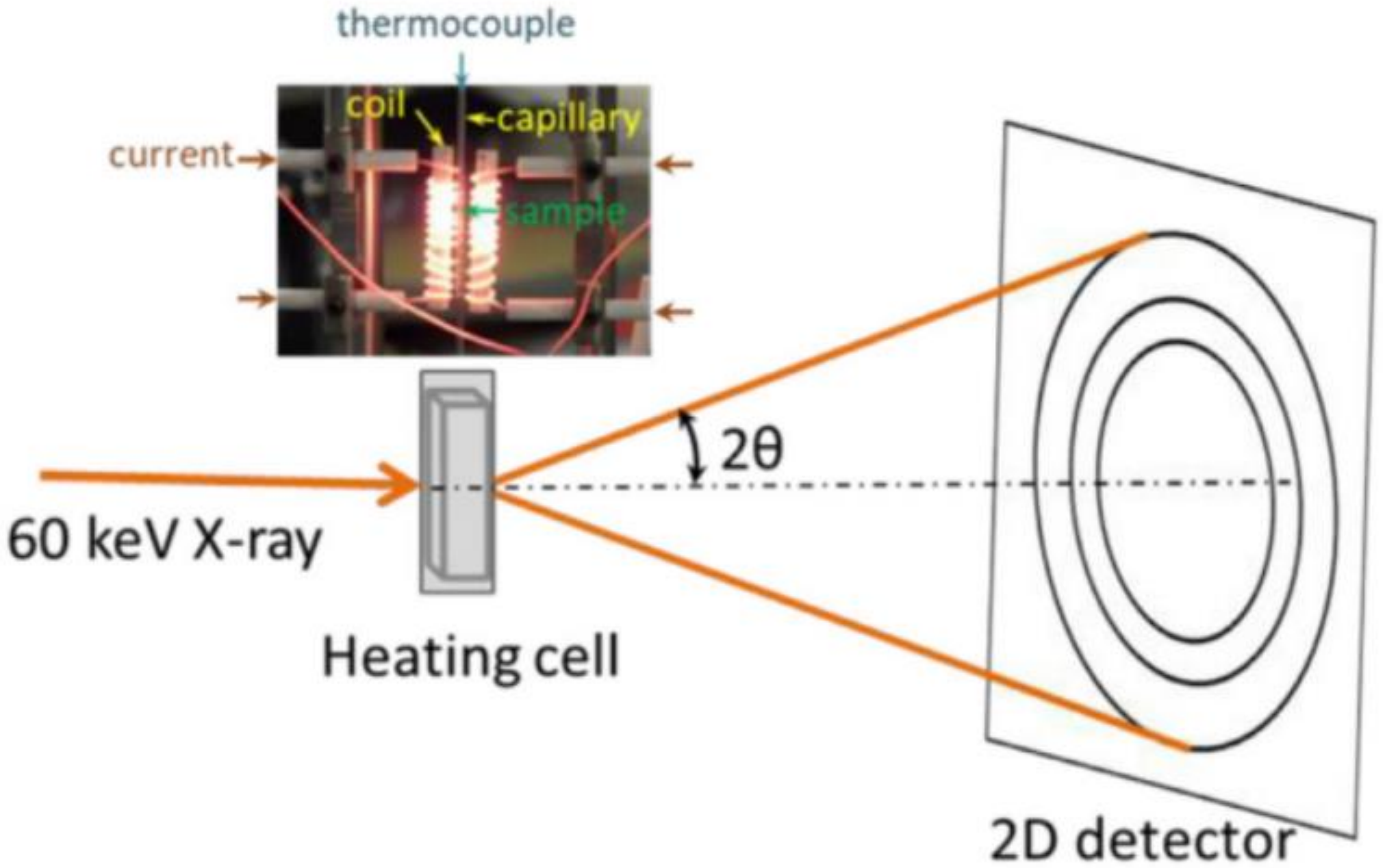
Schematic illustration of the Quenching and Partitioning (Q&P) process

https://www.dierk-raabe.com/martensite-alloys-and-transformations/quench-partitioning-steels

https://onlinelibrary.wiley.com/doi/10.1002/srin.201700218#srin201700218-bib-0161

Structural phase transformations in steels

"In-situ quantification and density functional theory elucidation of phase transformation in carbon steel during quenching and partitioning." Acta Materialia **221**: 117361, 2021. Wang et al.



Phase transformations in carbon steel during Q&P

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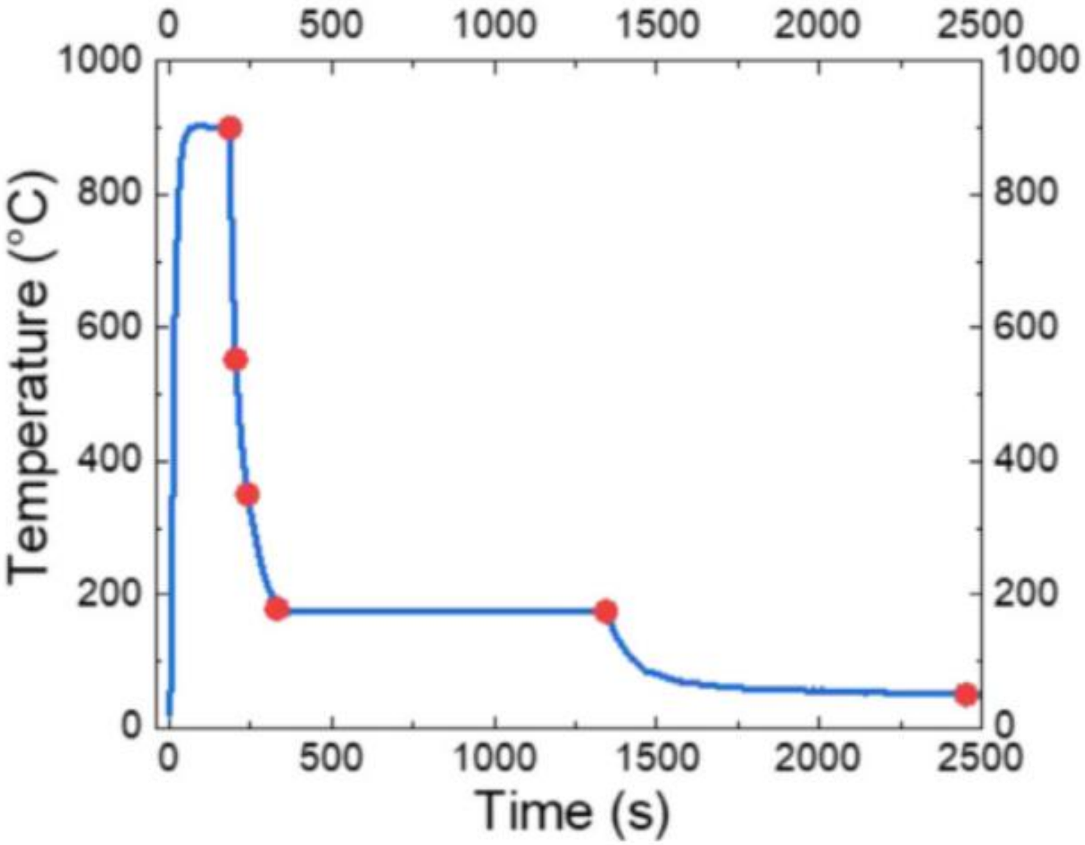

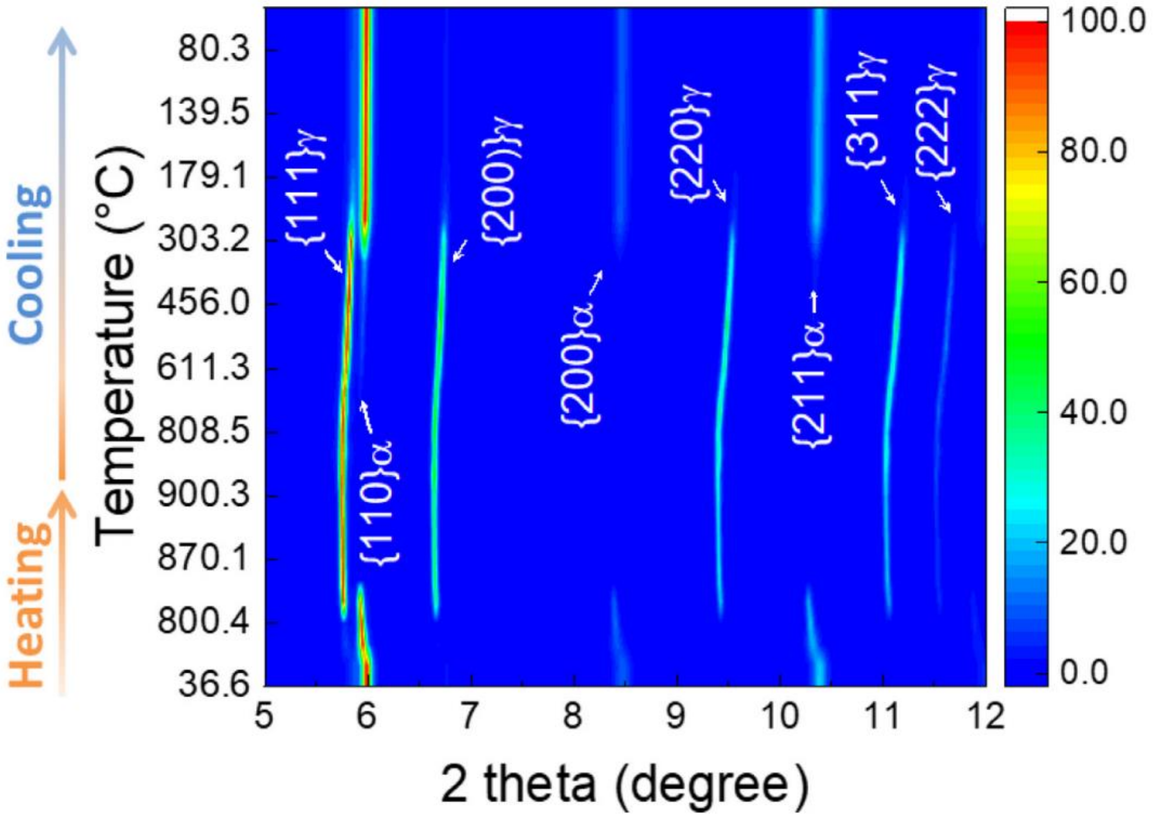

γ - austenite α - martensite

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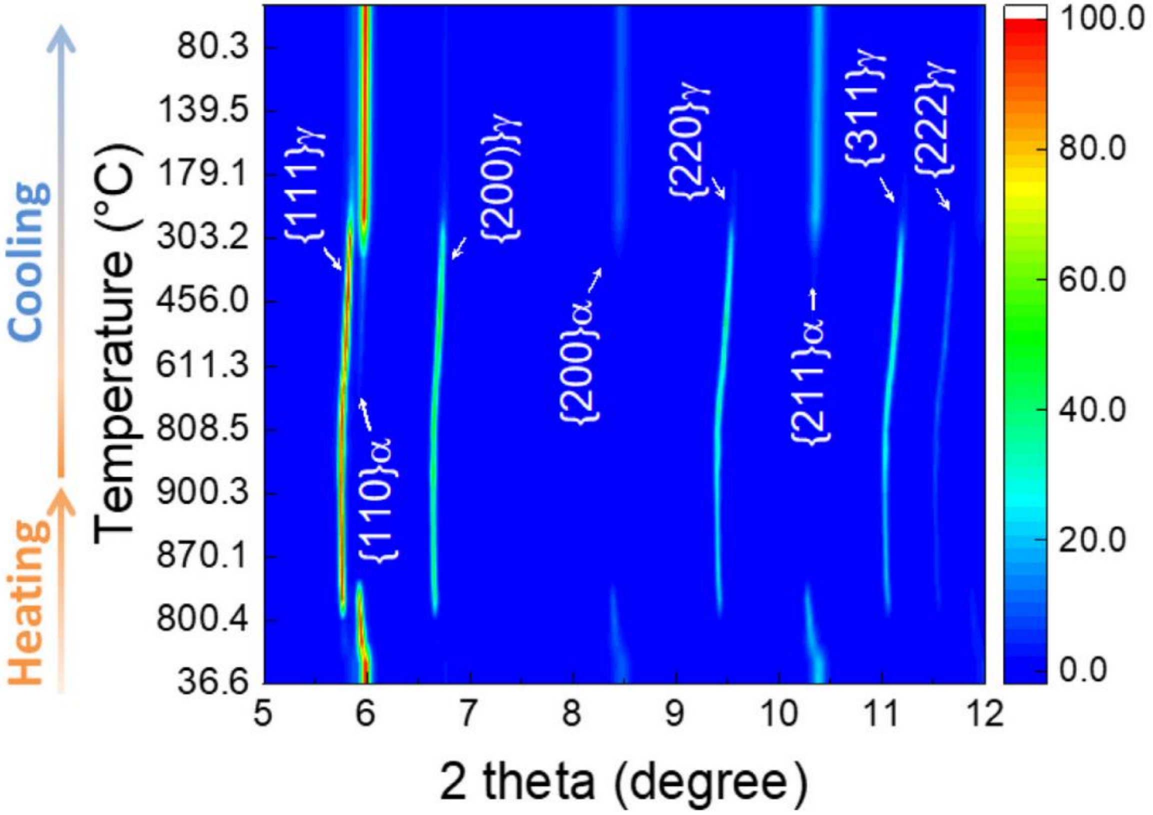
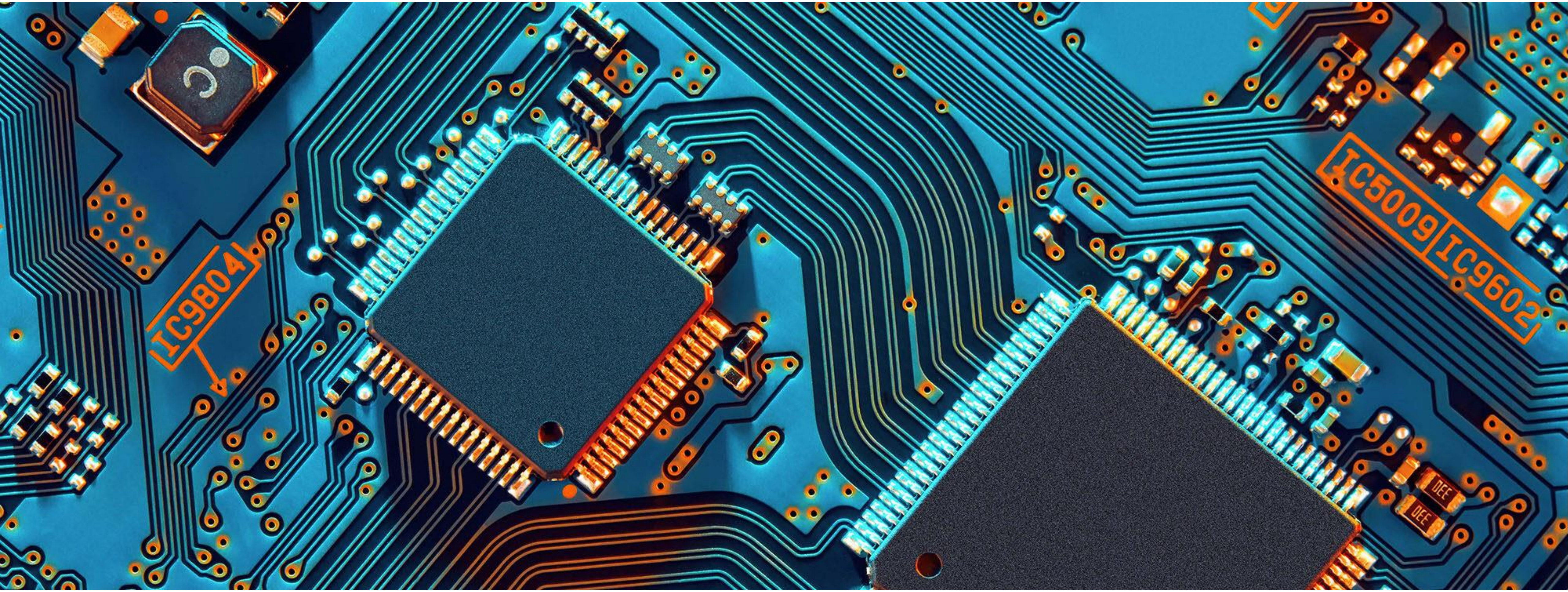


\+ DFT →

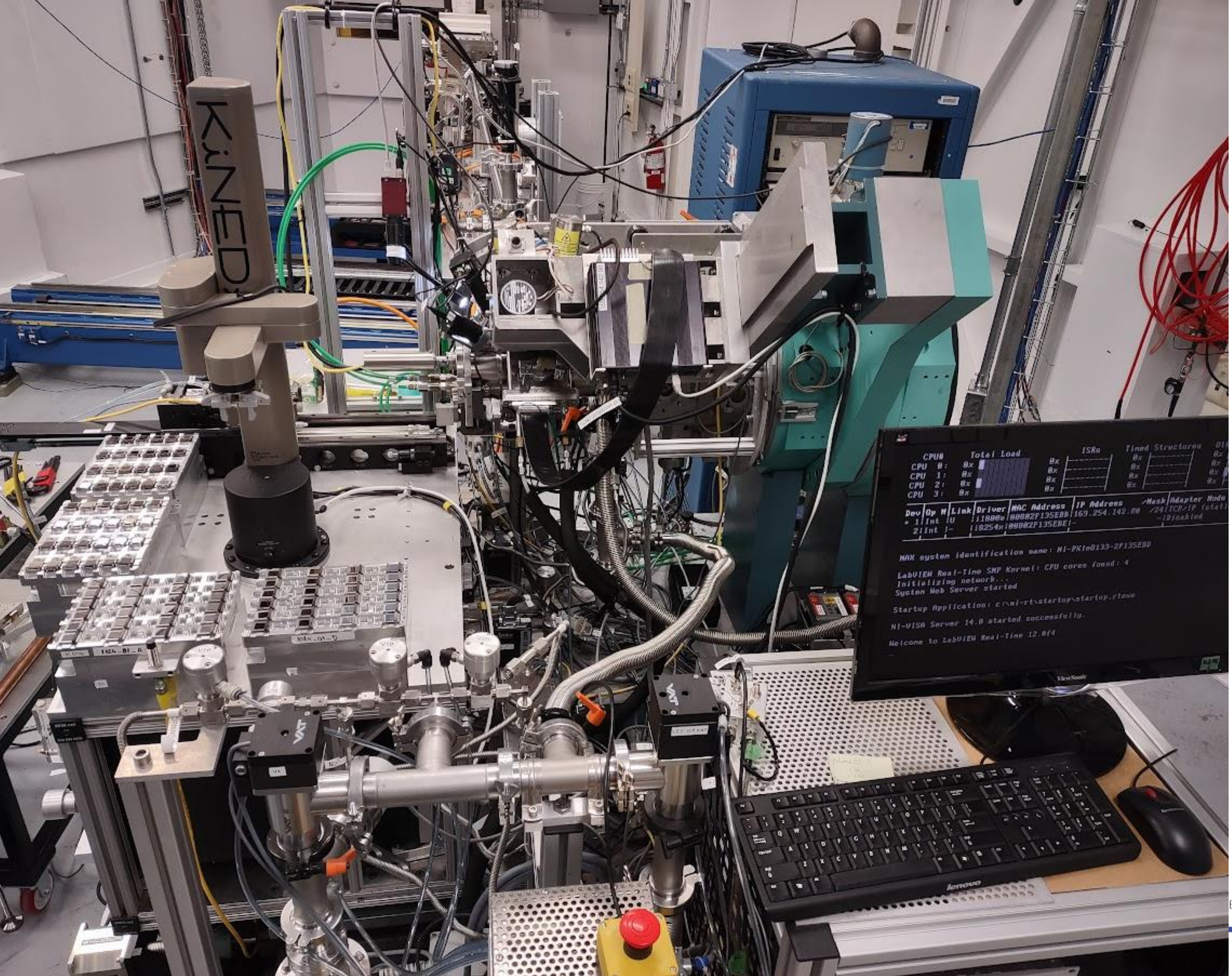
- ✓ Quantifying microstructural evolution
- ✓ Unveiling the mechanisms of phase transformation
- ✓ Elucidating carbon diffusion paths

γ - austenite α - martensite

Applications to Microelectronics



https://www.lbl.gov/research/microelectronics-and-beyond/



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In-situ characterization
- thin films
- microelectronic materials
- semiconductors

Rapid thermal annealing (up to ~ 1,000^{o}C)

Techniques

✓ X-Ray diffraction

✓ Four point probe to measure film resistivity

✓ Optical light scattering to measure surface morphology

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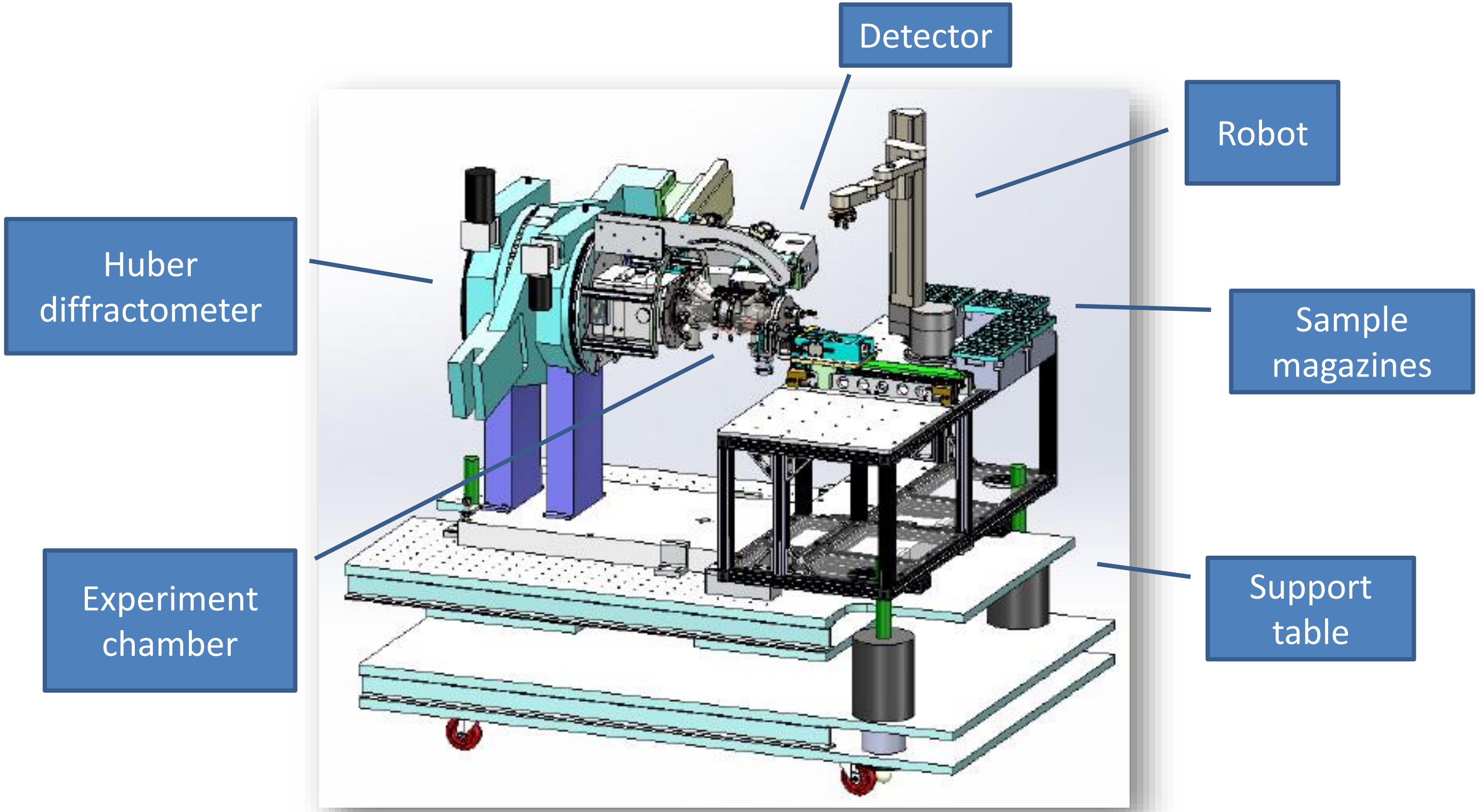
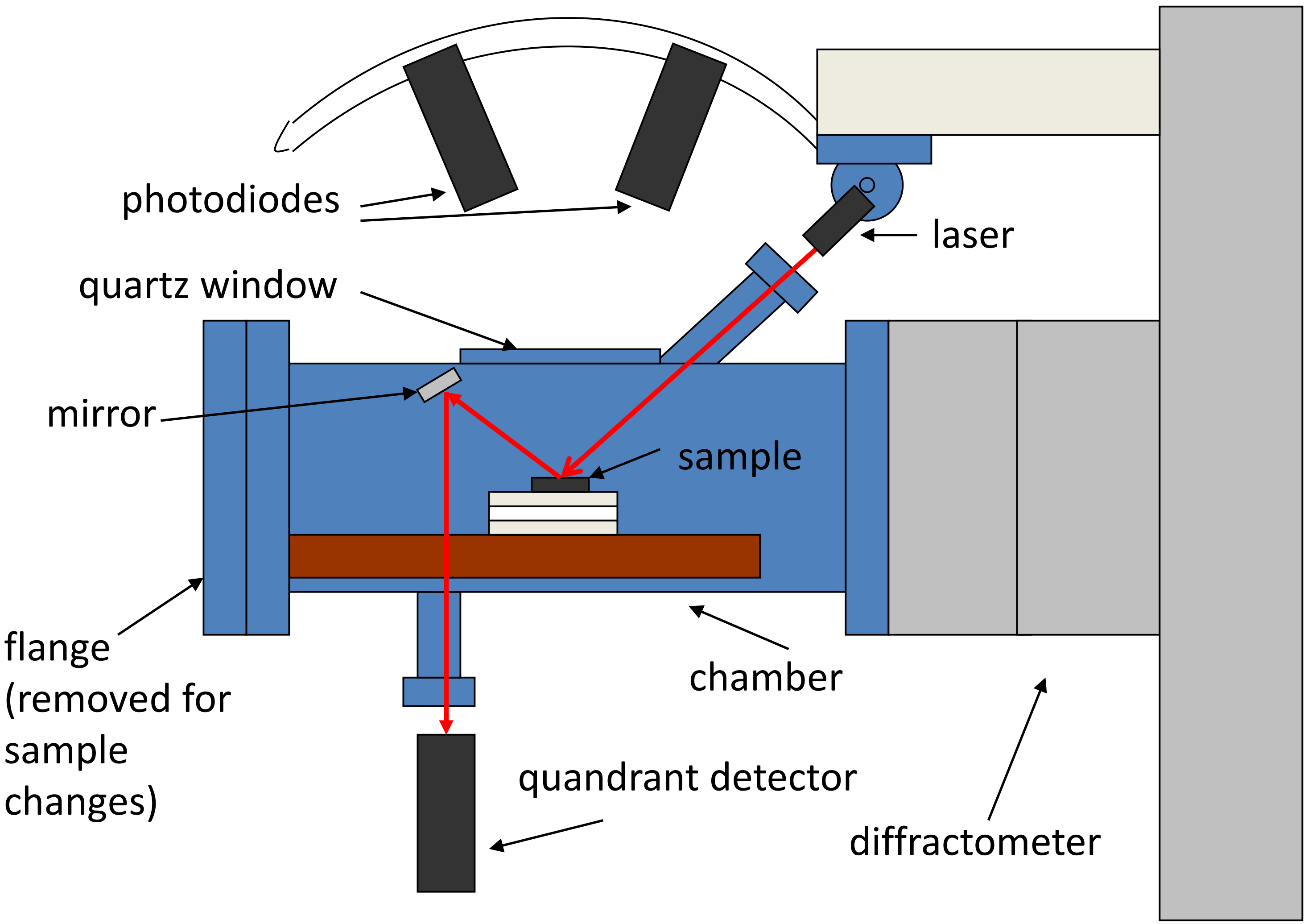


Experiment chamber



Sample size and format

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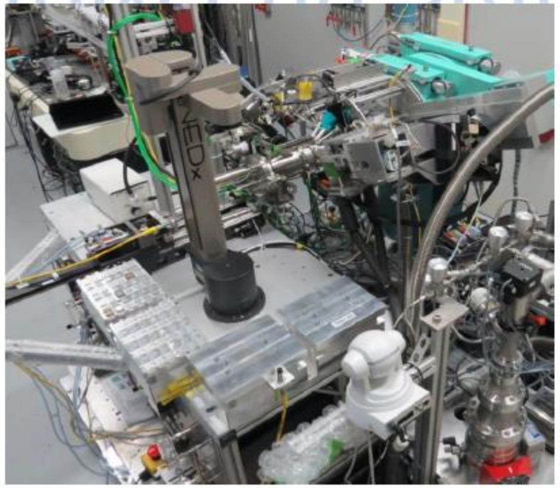
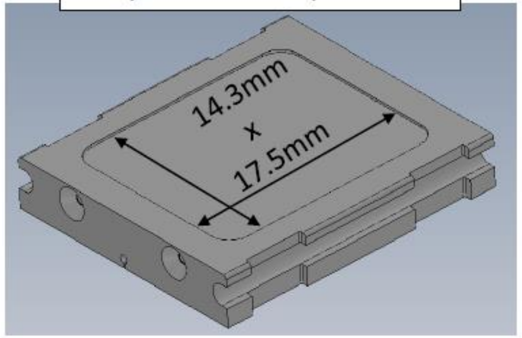


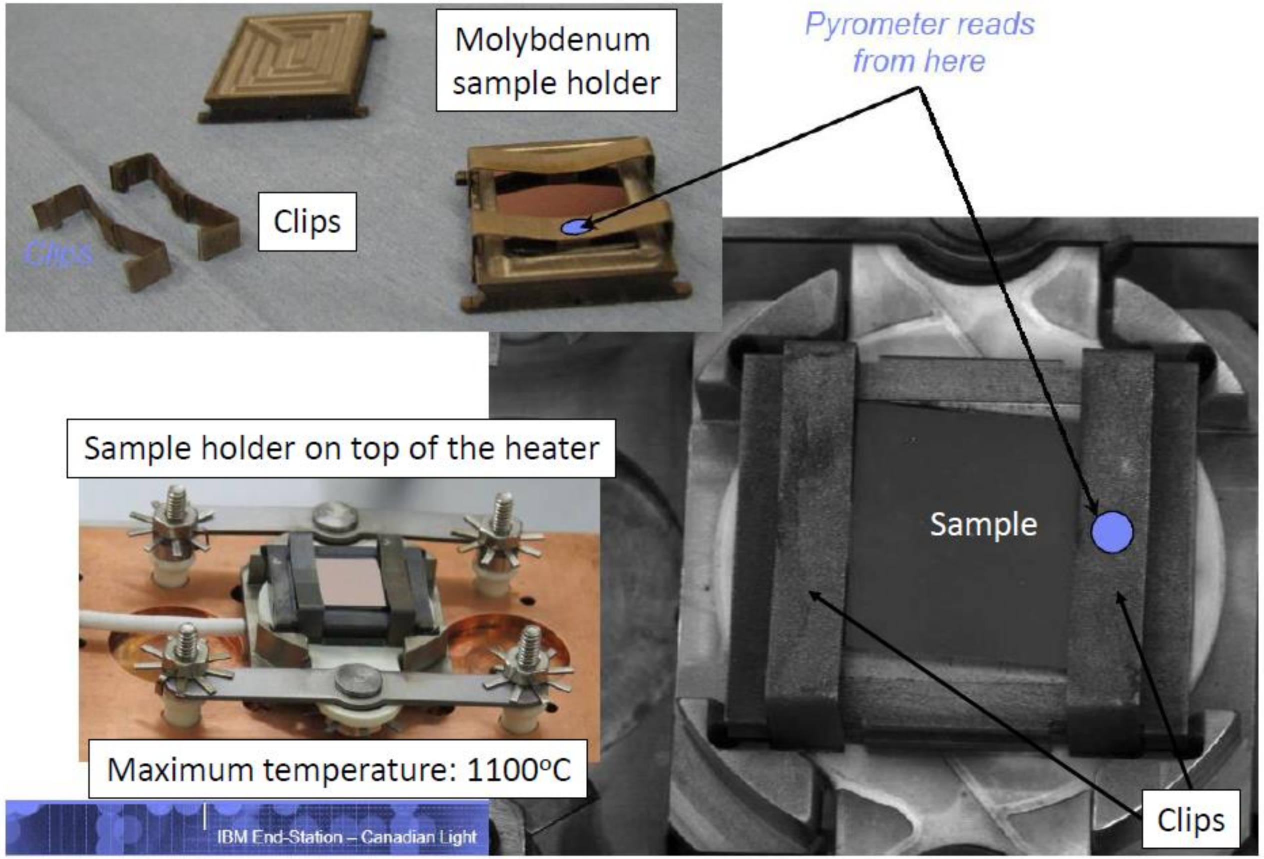
Thin films studies

Combined diffraction,
resistivity and roughness measurements
under ultra high purity N_2 or He.
Temperature up to 1100 °C.

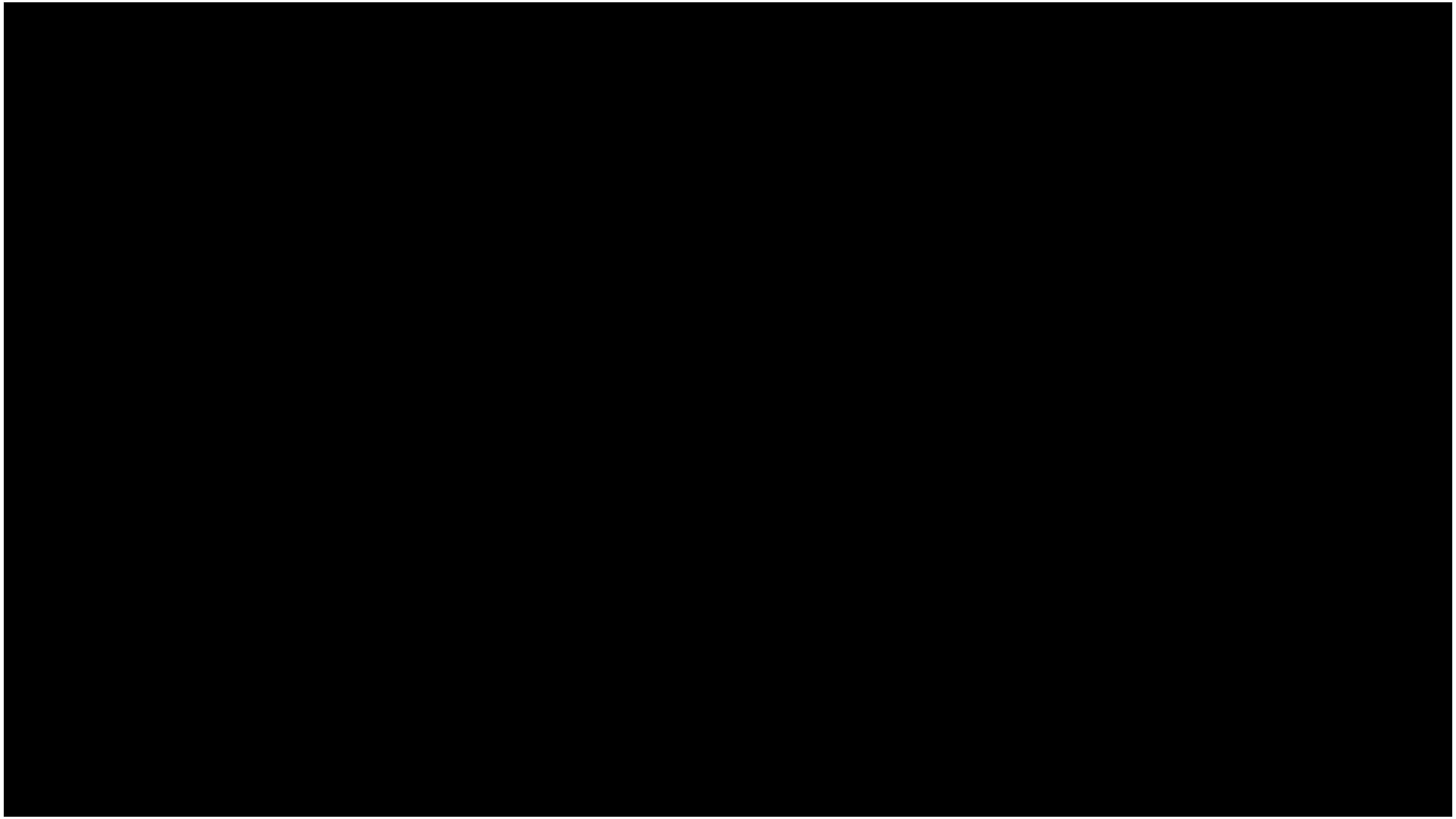
Molybdenum sample holder



Sample size should be approximately 12mm x 15 mm



IBM end-station in action



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- ✓ Quick investigation of different growth conditions
- ✓ Better nucleation processes
- ✓ Improved film stability at higher temperatures
- ✓ Lower interface roughness

Microelectronic Engineering **83**, 2042-2054 (2006)

C. Lavoie et al.

Effects of additive elements on the phase formation and morphological stability of nickel monosilicide films

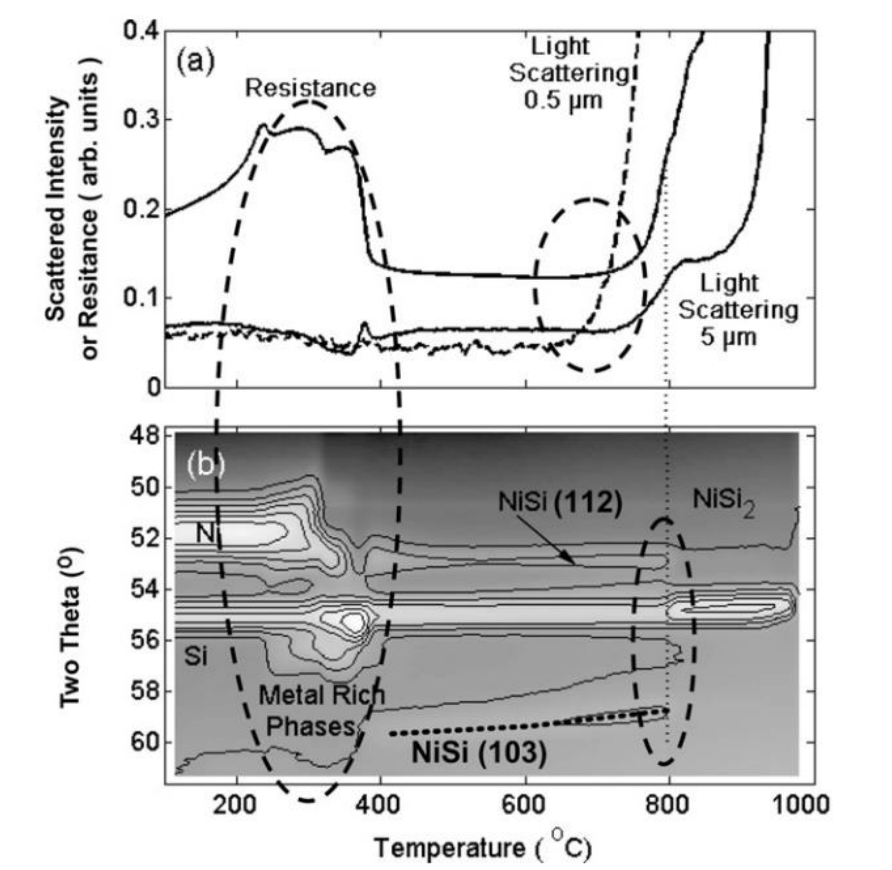
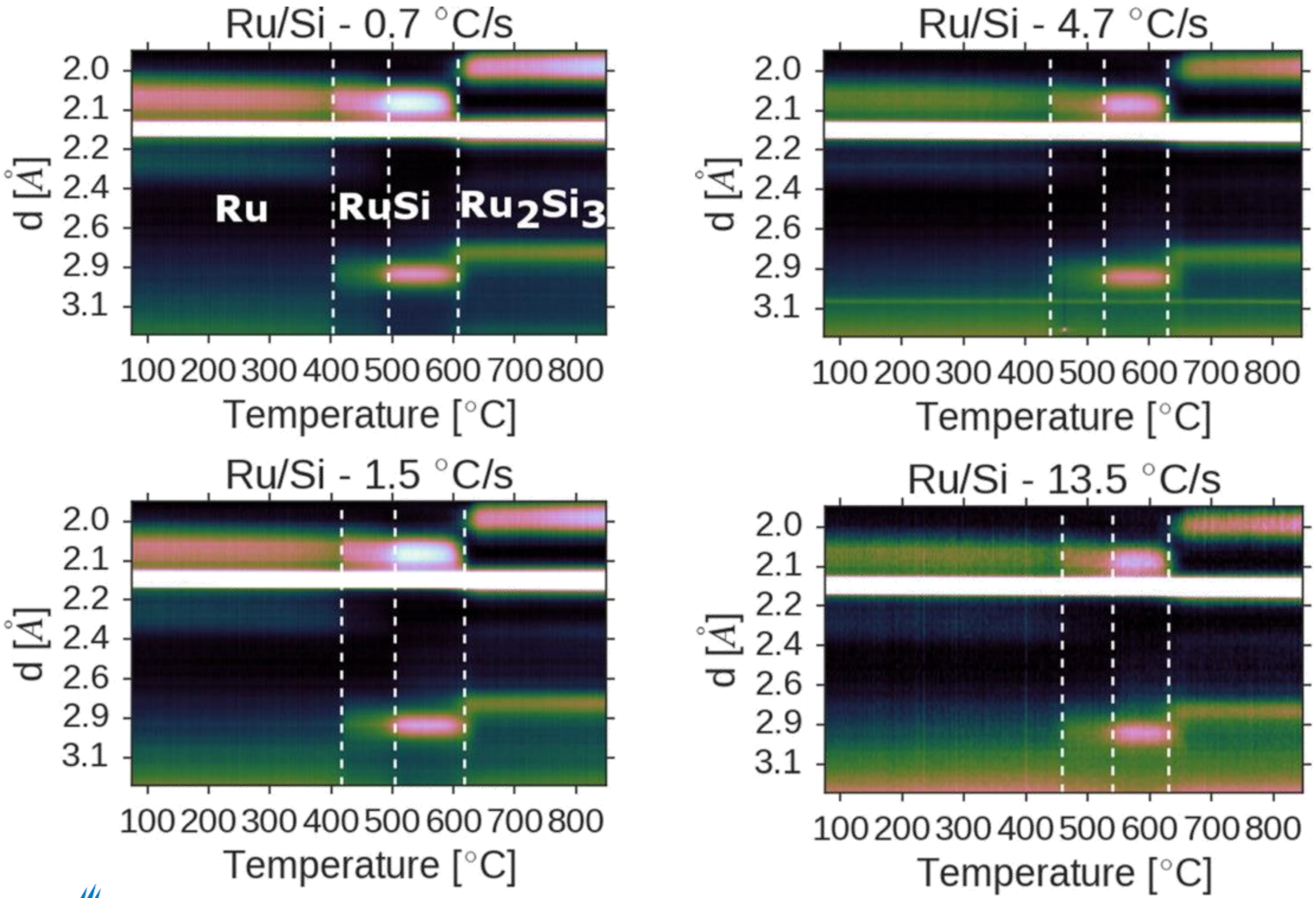


Fig. 4. (a) Elastic light scattering at 0.5 µm and 5 µm length scales and resistance measurements together with (b) X-ray diffraction measurements performed *in situ* during annealing in purified He of a 15 nm Ni layer deposited on a 100 nm poly-Si film (3 °C /s). The three ellipse also refer to the challenges discussed using the phase diagram in Fig. 1.

Atomic layer deposited ultrathin metal nitride barrier layers for ruthenium interconnect applications.



- Search of alternative materials to Cu interconnects.
- Synchrotron XRD was used to investigate the thermal stability.
- Determining activation energies of metal nitride (TiN, TaN) barrier failure, leading to ruthenium monosilicide formation.

Journal of Vacuum Science & Technology A **35**, 03E109 (2017)

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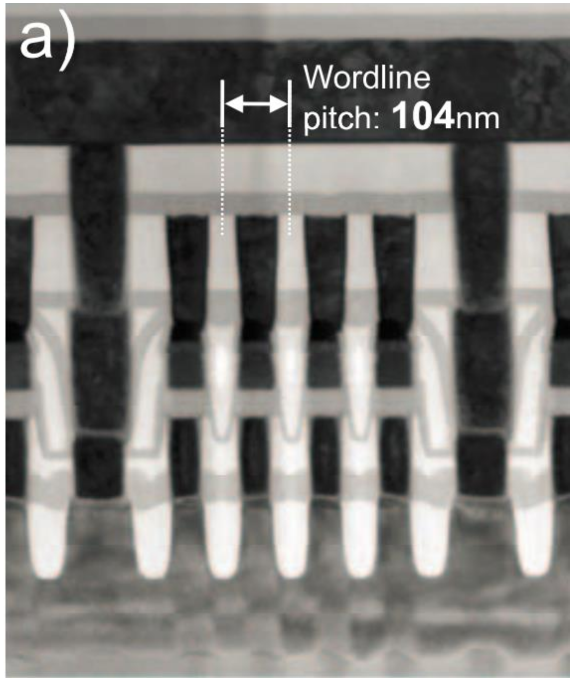
Investigating materials for Phase Change Memory (PCM) technology.
Suitable materials have:

- High electrical resistivity in the amorphous phase
- Low electrical resistivity in the crystalline phase

TEM cross-section for a 1 Gbit PCM cell array

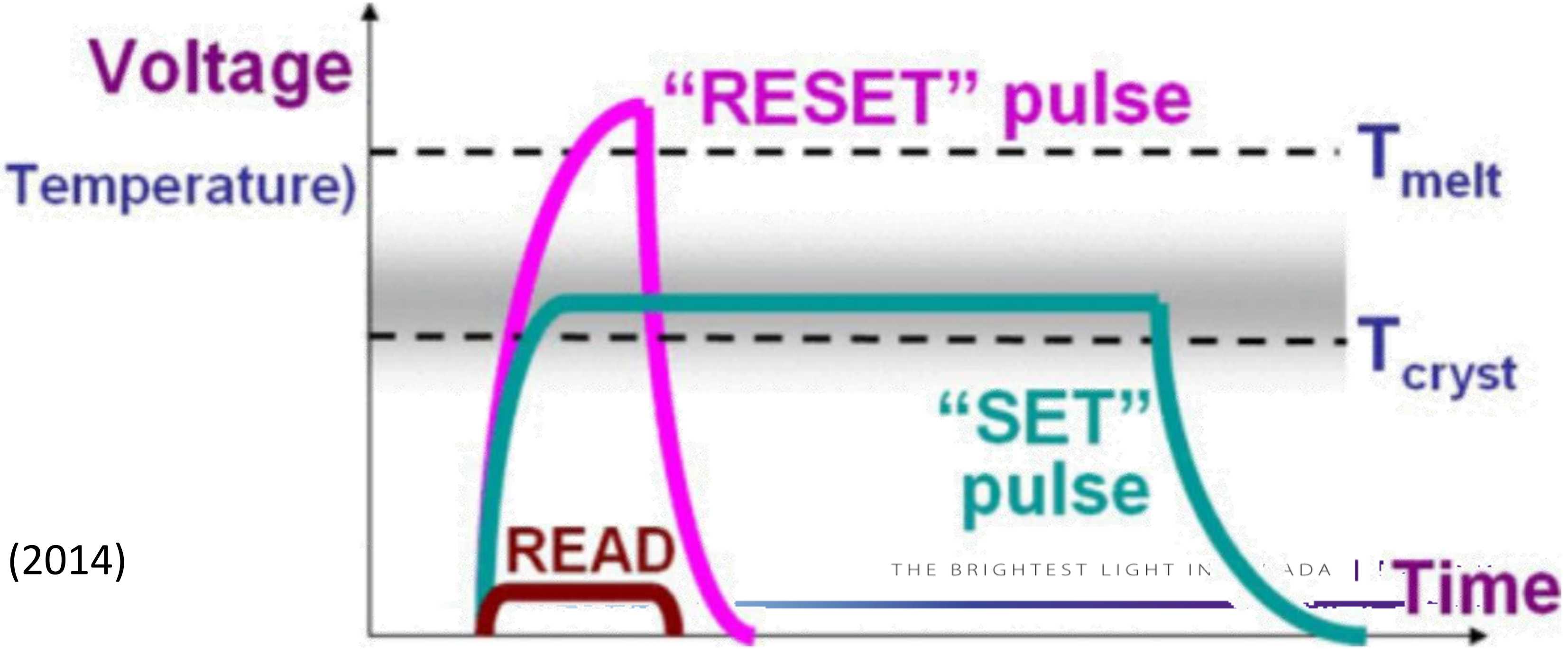


Heating and cooling at different rates can set and reset the amorphous and crystalline states back and forth.

Read operations are performed by measuring the device resistance at low voltage so that the device state is not perturbed.

Non volatile → lasts for years

https://ieeexplore.ieee.org/abstract/document/7453199



Journal of Applied Physics **115**, 093101 (2014)
Huai-Yu Cheng et al.

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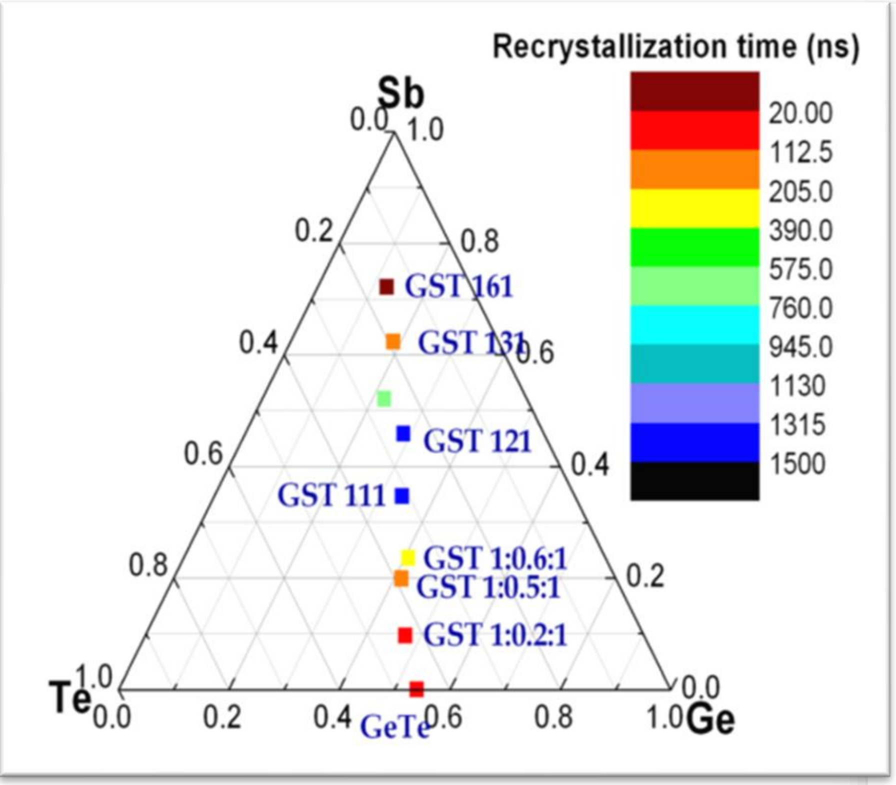
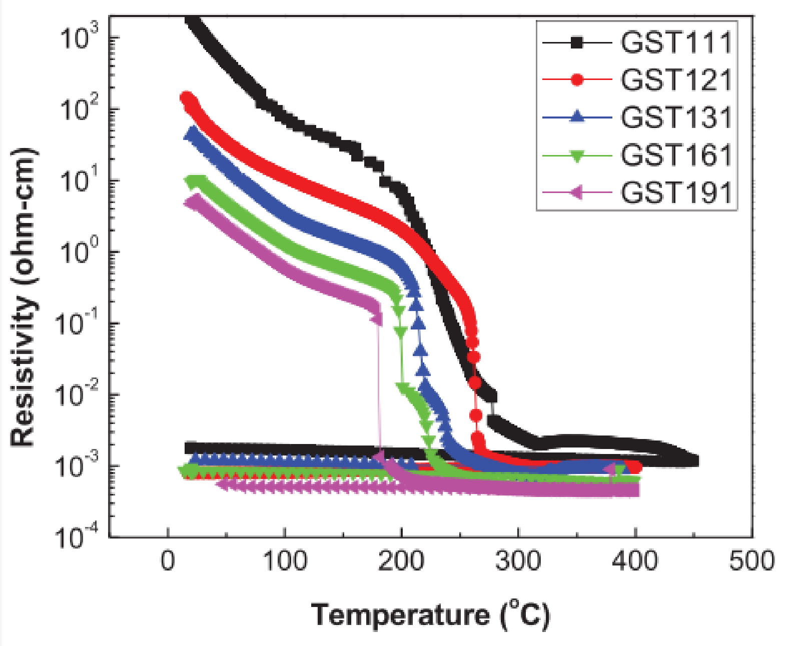
Crystallization properties of materials along the pseudo-binary line between GeTe and Sb





Resistivity as a function of temperature for $Ge_1Sb_xTe_1$ films for $x > 1$ during a heating ramp to 300–450 °C at 5 °C/min and subsequent cooling back to room temperature.

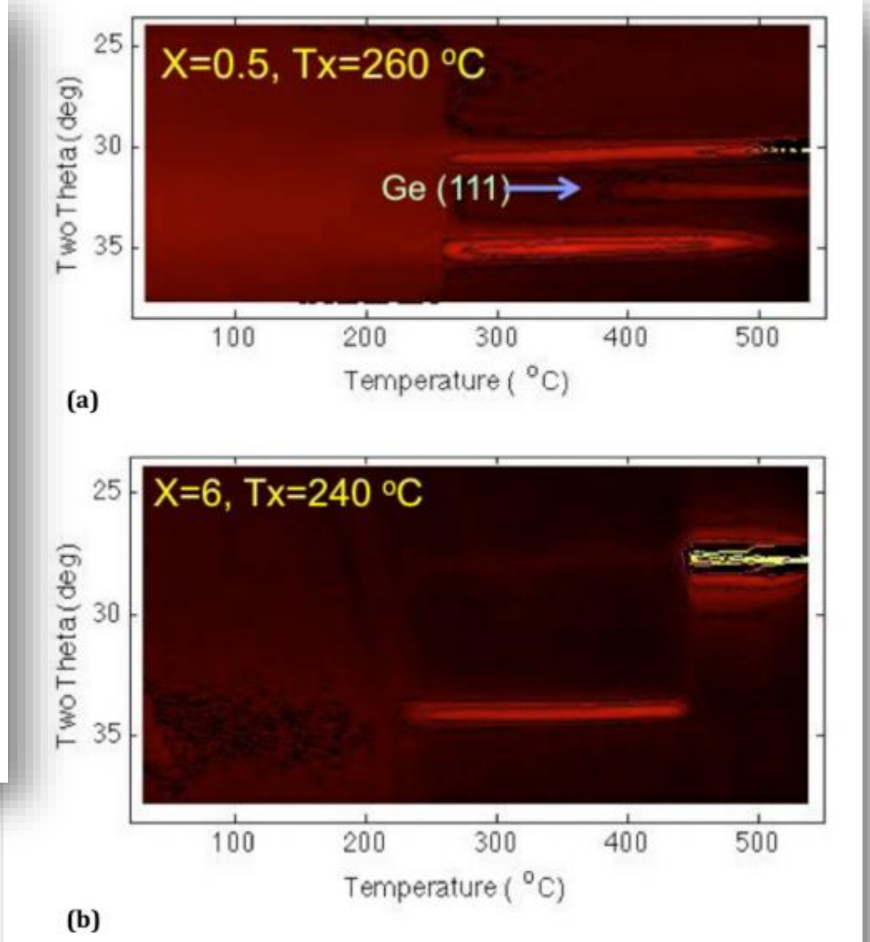
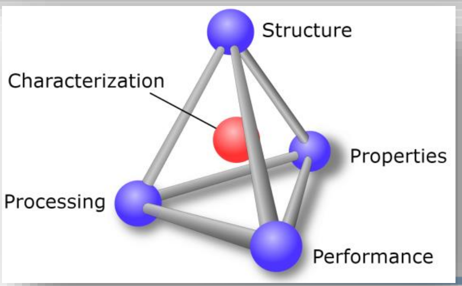


FIG. 2. XRD peak intensity as a function of temperature T during heating at 3 °C/s to 550 °C of a $Ge_1Sb_xTe_1$ film with (a) $x = 0.5$ and (b) $x = 6$, respectively.



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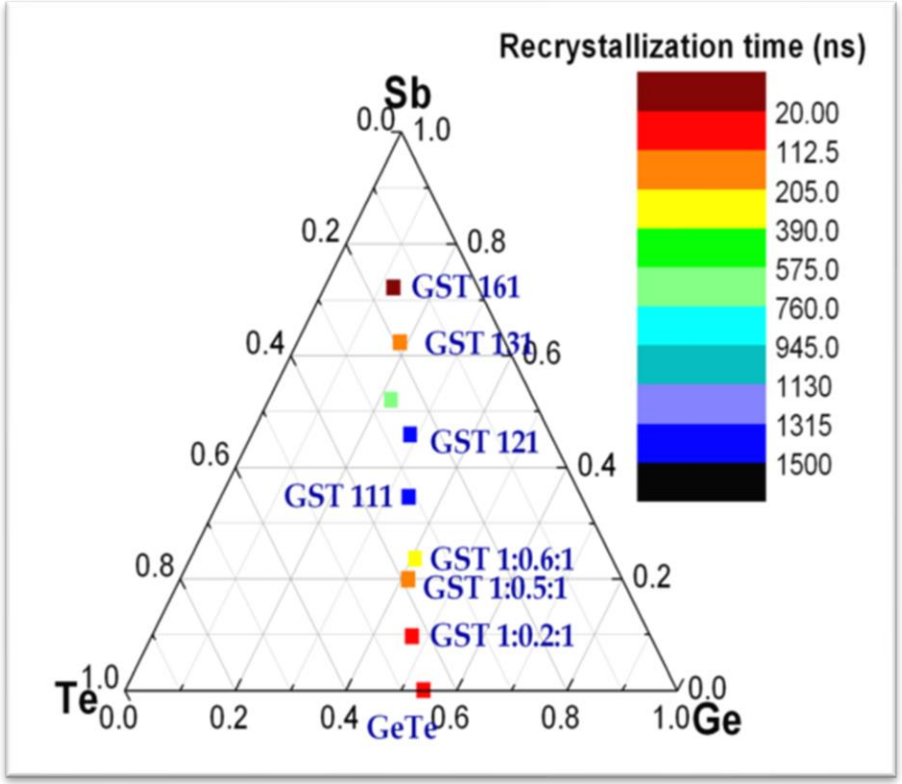
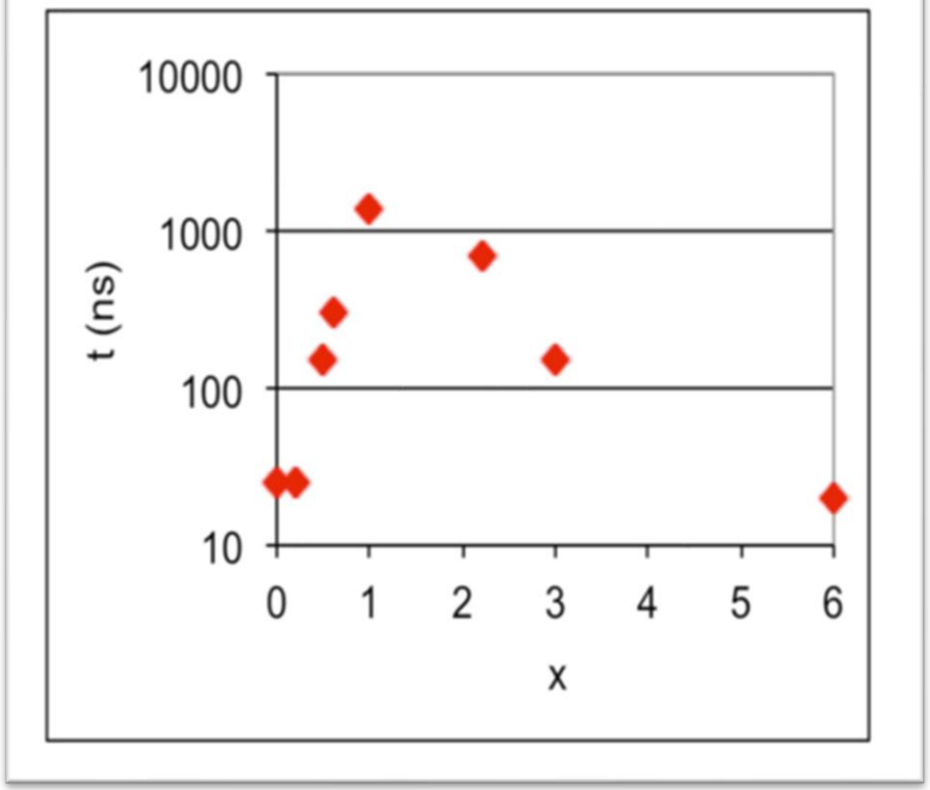


Re-crystallization times of Ge1SbxTe1



Characterization of key parameters:

- ✓ Crystallization temperature
- ✓ Crystallization speed
- ✓ Resistance
- ✓ Thermal stability

Journal of Applied Physics **115**, 093101 (2014)
Huai-Yu Cheng et al.

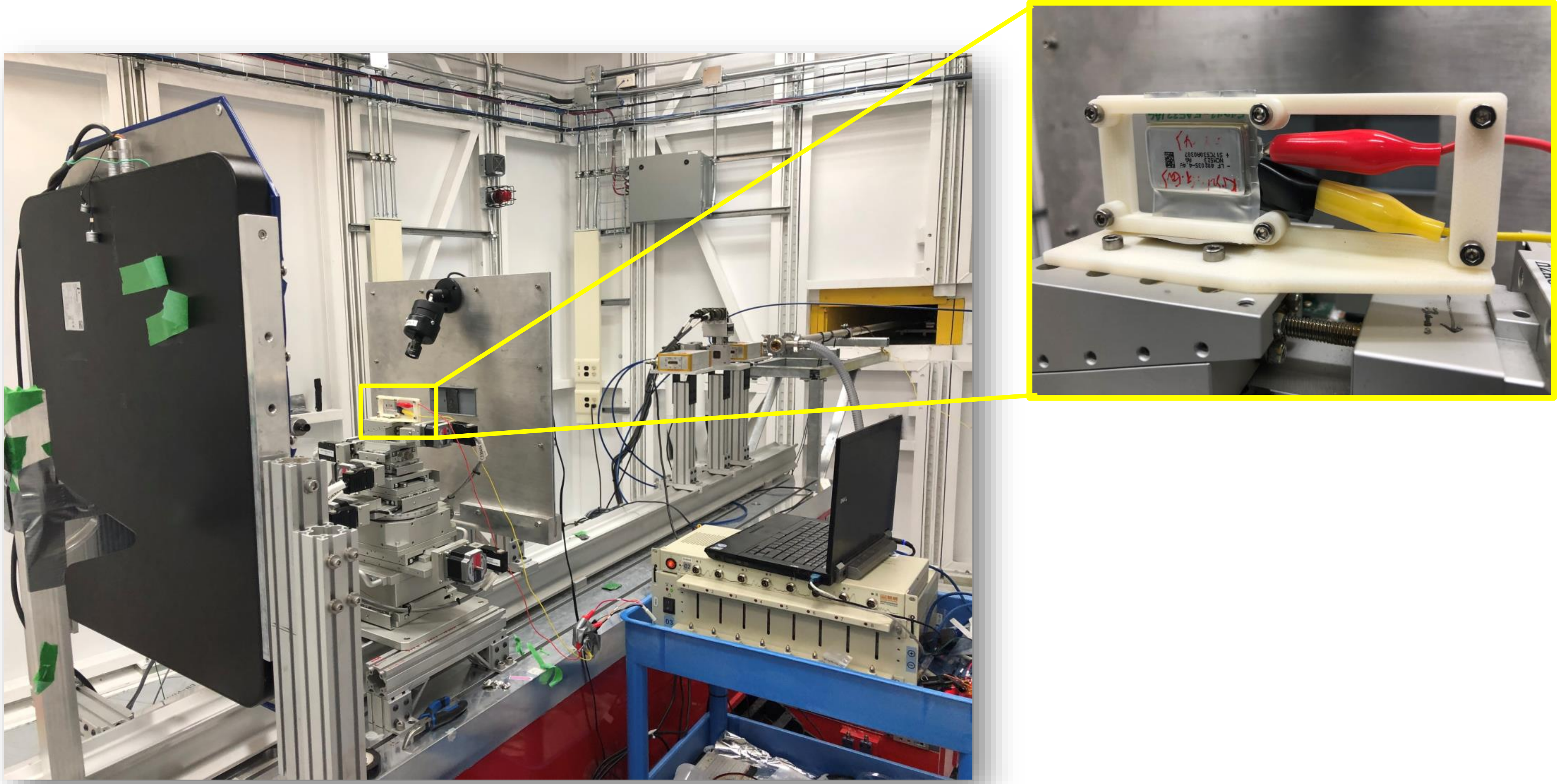
Battery experiments

Canadian Light Source Centre canadien de rayonnement synchrotron

https://www.dreamstime.com/illustration/stick-man-question-mark.html

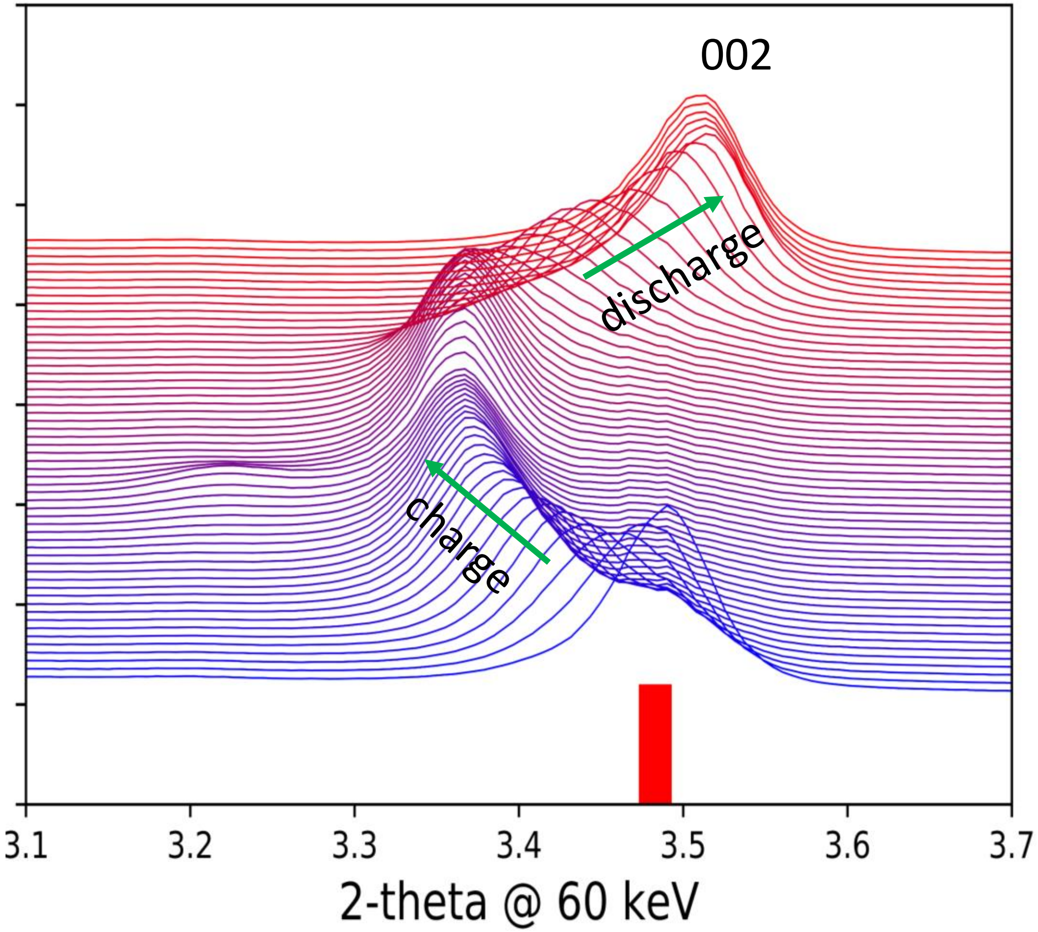
https://www.intechopen.com/chapters/84482

In-situ battery research

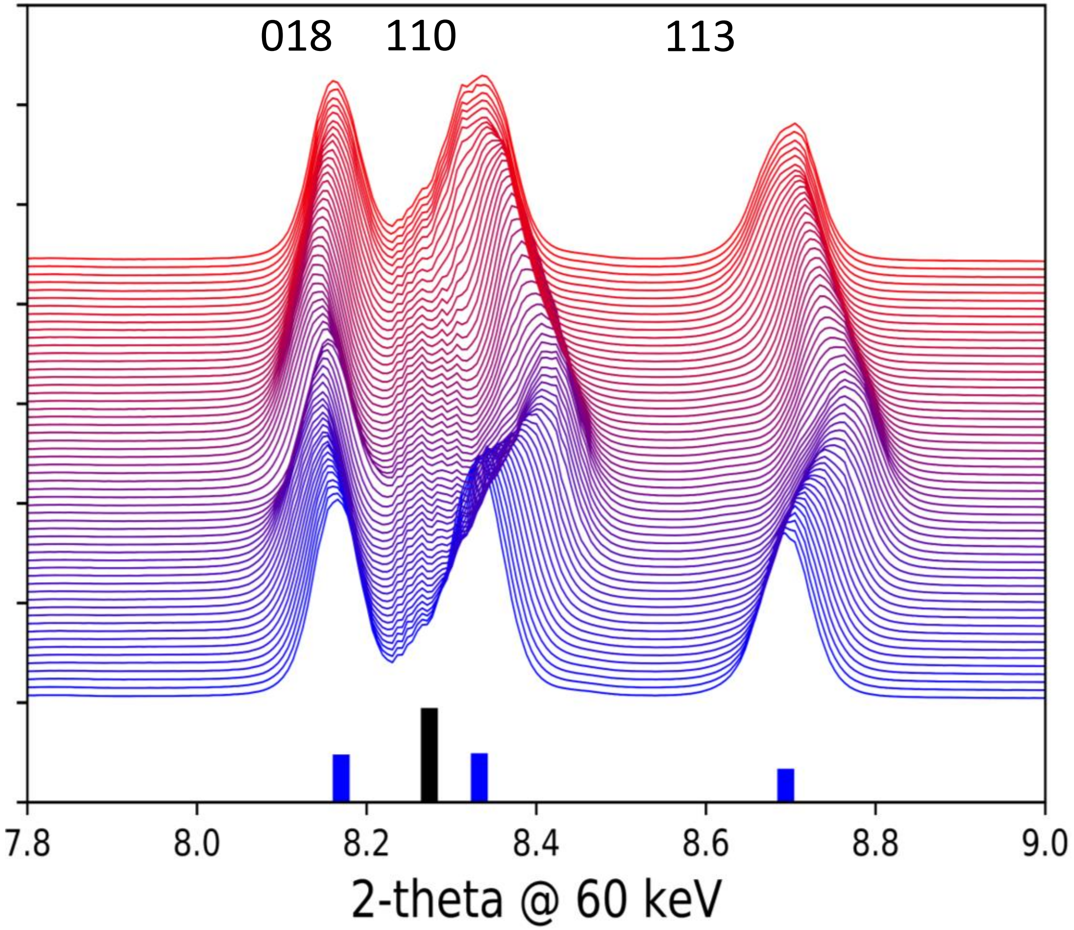


In-situ battery research

Anode (Graphite)



Cathode (Transition Metal Oxide)



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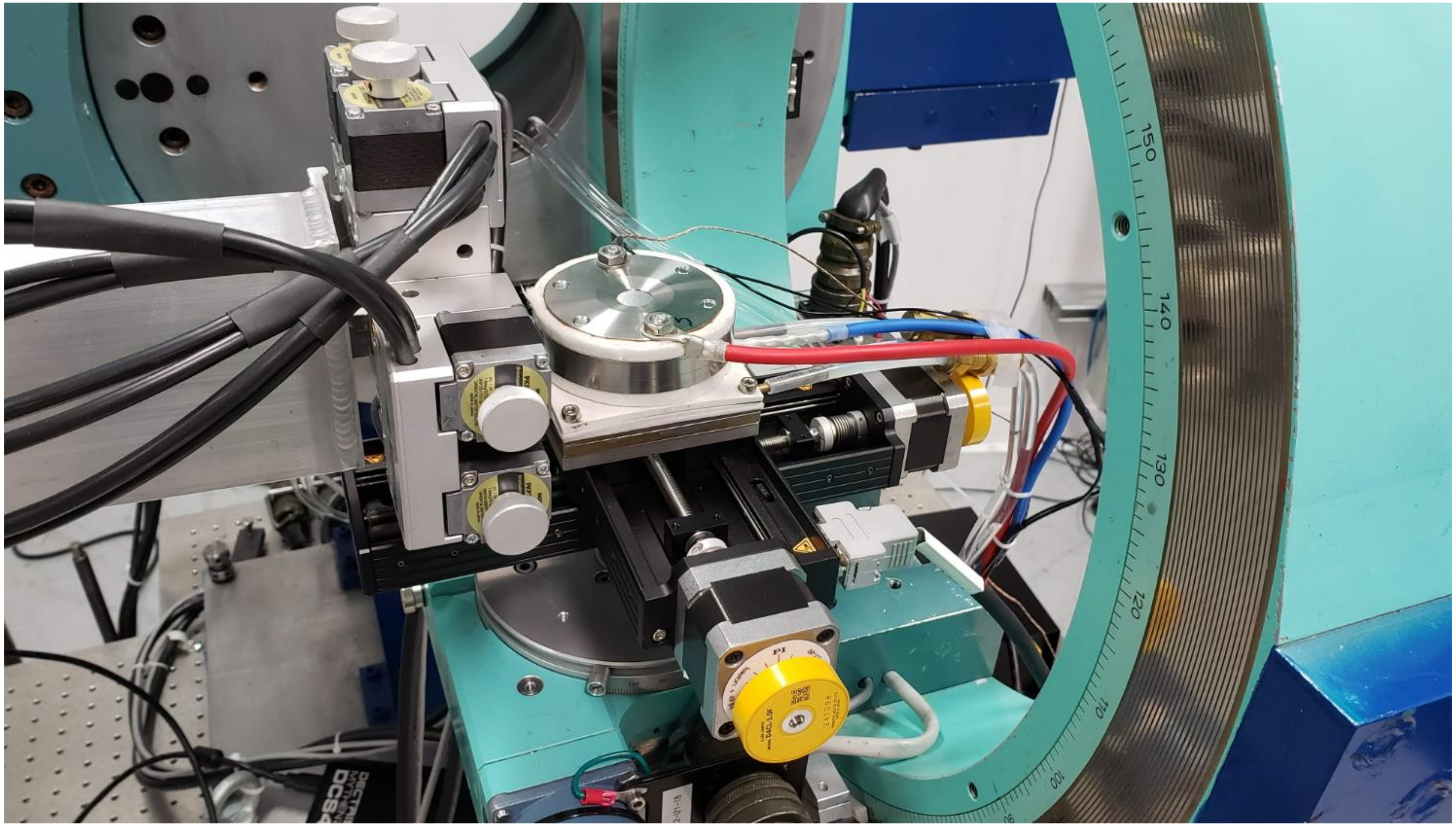
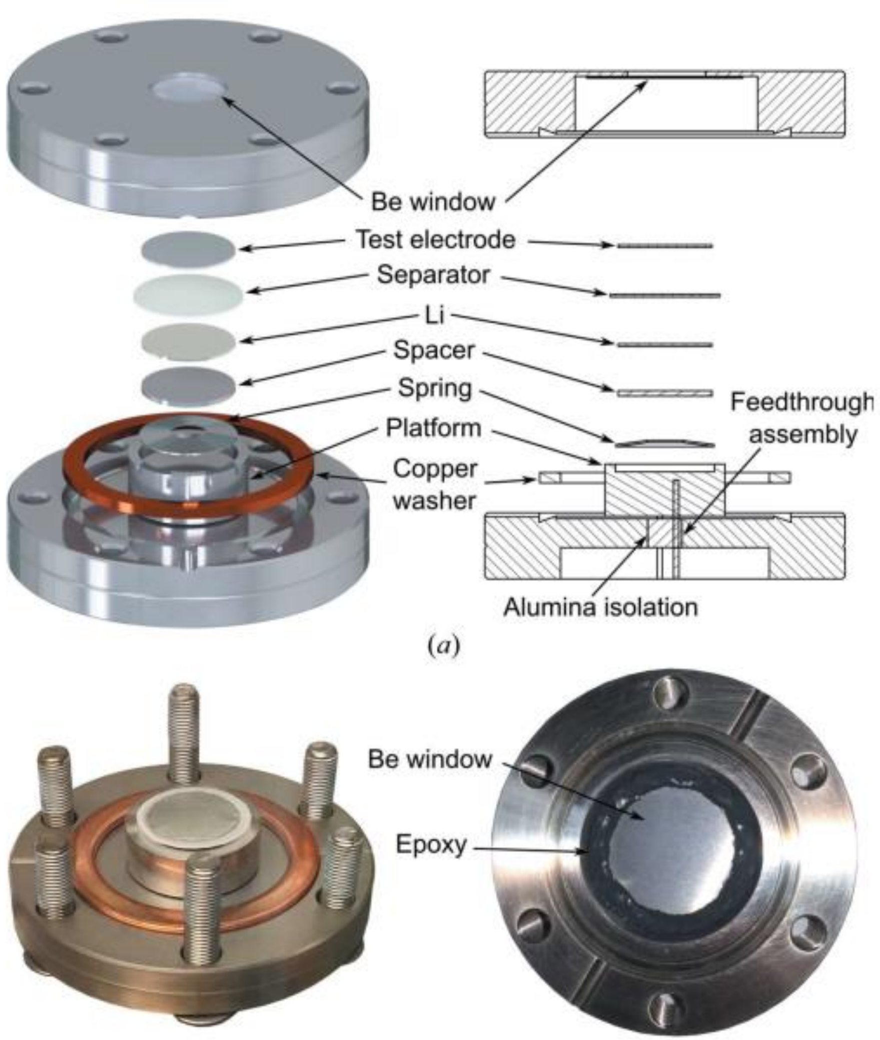
In-situ battery research

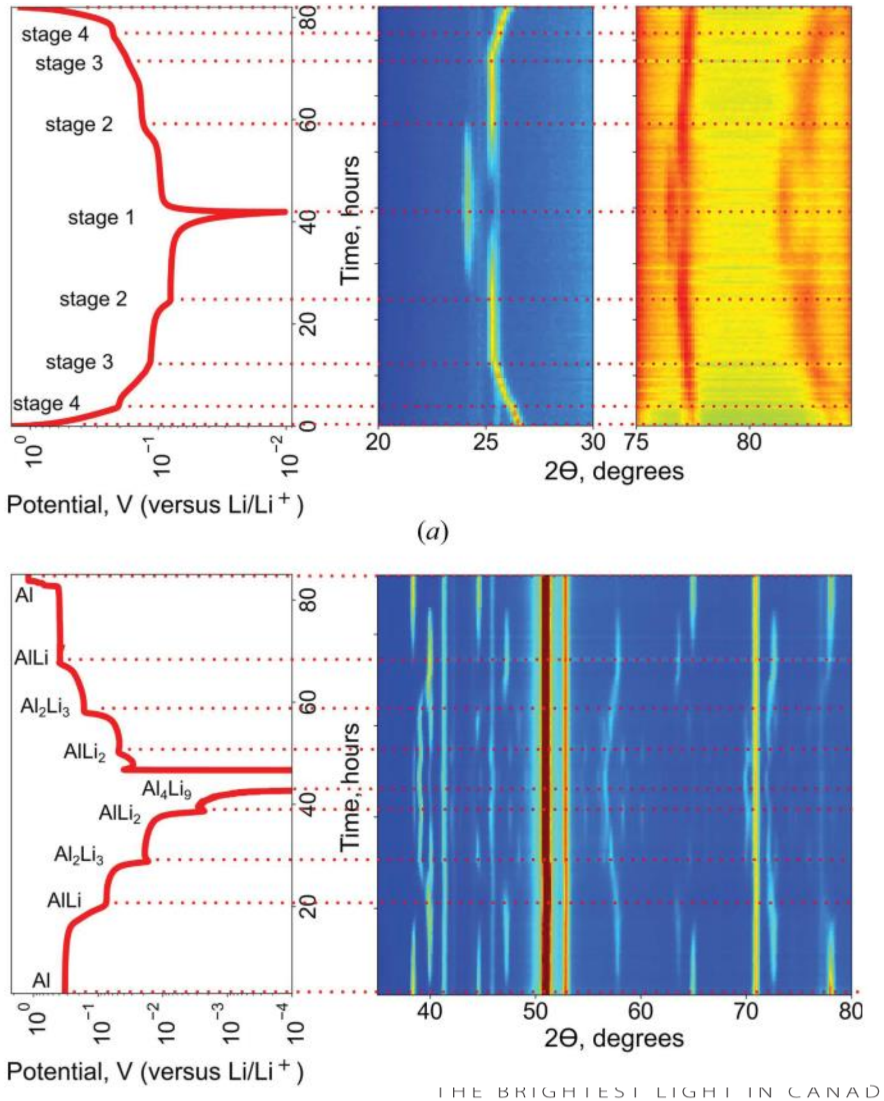
High Temperature Compatible Conflat Cell with Adjustable Stack Pressure for
In-Situ and Operando X-Ray Studies of Lithium-Ion Battery Materials



Michael Fleischauer - NRC / University of Alberta

In-situ battery research

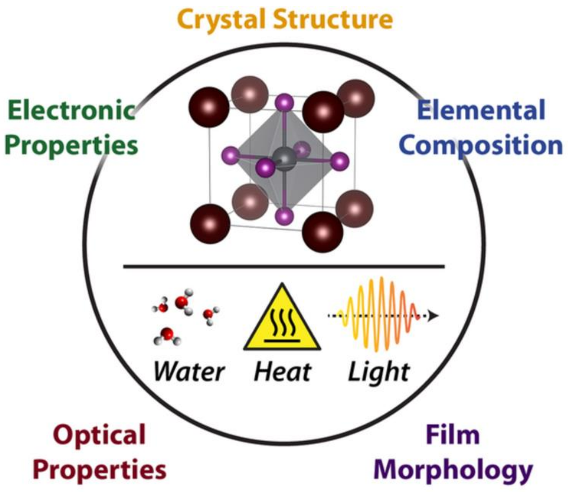


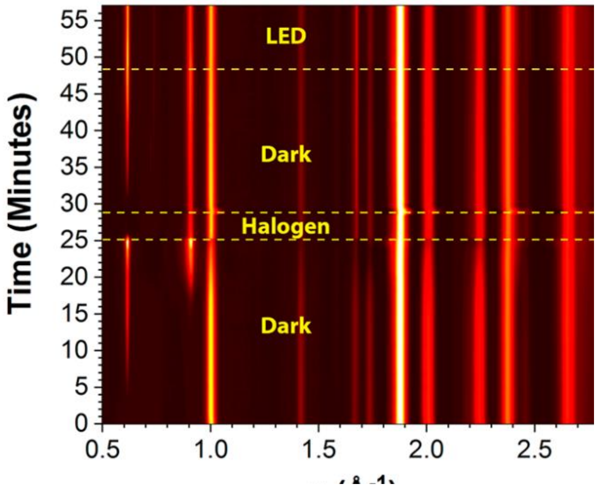


J. Appl. Cryst. (2021). **54**, 1416–1423

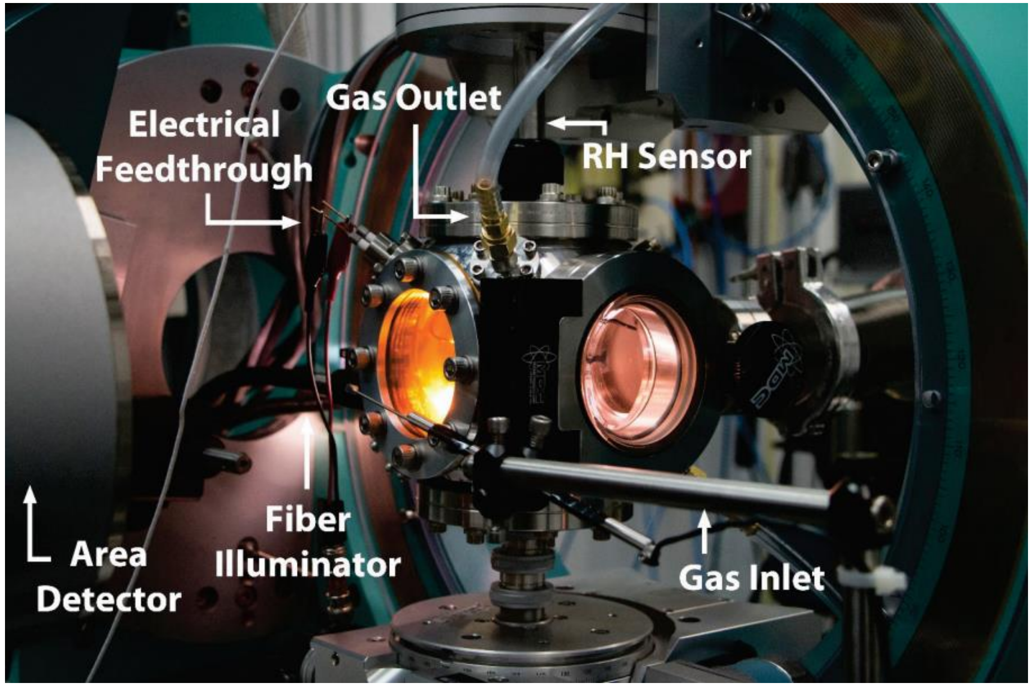
Solar cell research

In situ studies of the degradation mechanisms of perovskite solar cells





GIWAXS pattern of an ITO/ZnO/$CH_3NH_3PbI_3$/P3HT/Ag device exposed to a nitrogen atmosphere with RH ≈ 90%.



Elucidating the Failure Mechanisms of Perovskite Solar Cells in Humid Environments Using In Situ GI-WAXS

Tim Kelly - USASK

Corrosion studies

Corrosion can lead to failure involving personal injuries, fatalities, unscheduled shutdowns and environmental contamination.

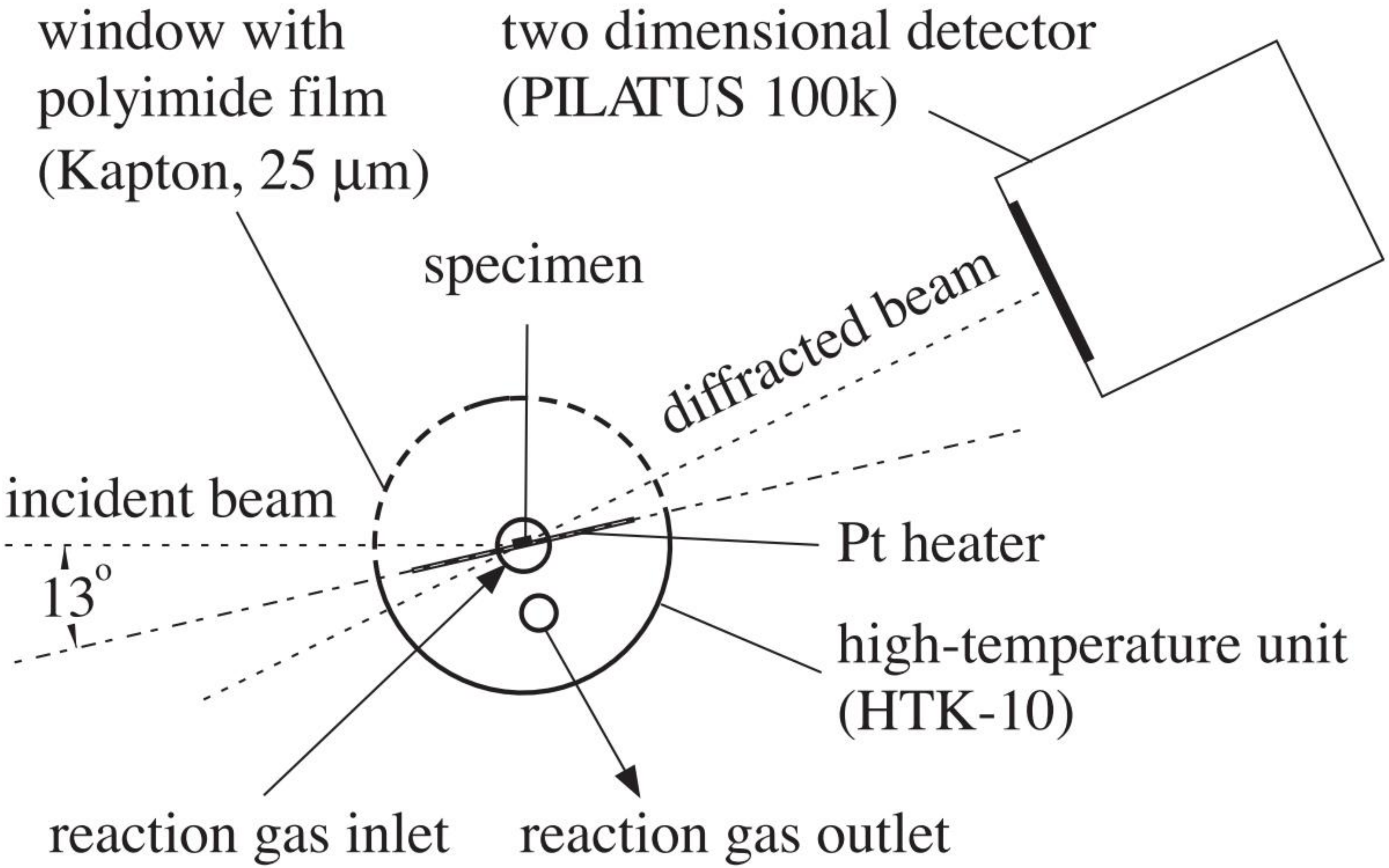
The annual direct cost of corrosion to an industrial economy is approximately 3.1% of the country's Gross National Product (GNP).

In the United States, this amounts to over $276 B per year.

For Canada, $60 B per year.

https://www.wermac.org/

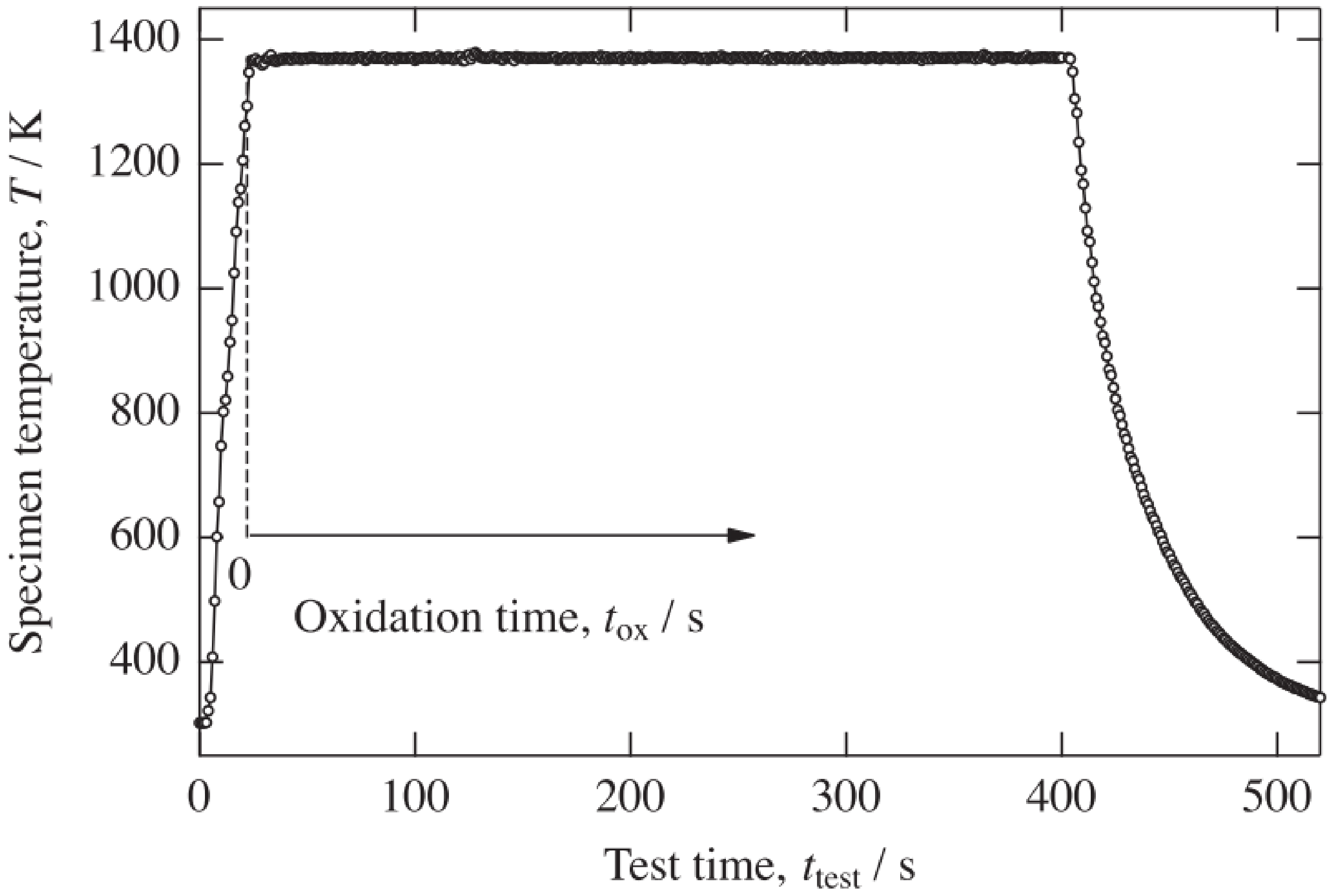
In situ studies of breakaway oxidation in type 430 stainless steel



BL-46XU in SPring-8

Saeki et al. Corrosion Science ***55****, 219, 2012*

In situ studies of breakaway oxidation in type 430 stainless steel



These specimens were heated at a rate of 50 K/s and kept at 1373 K for ~400 s;

They were then cooled in the high-temperature unit.

Gas mixture:

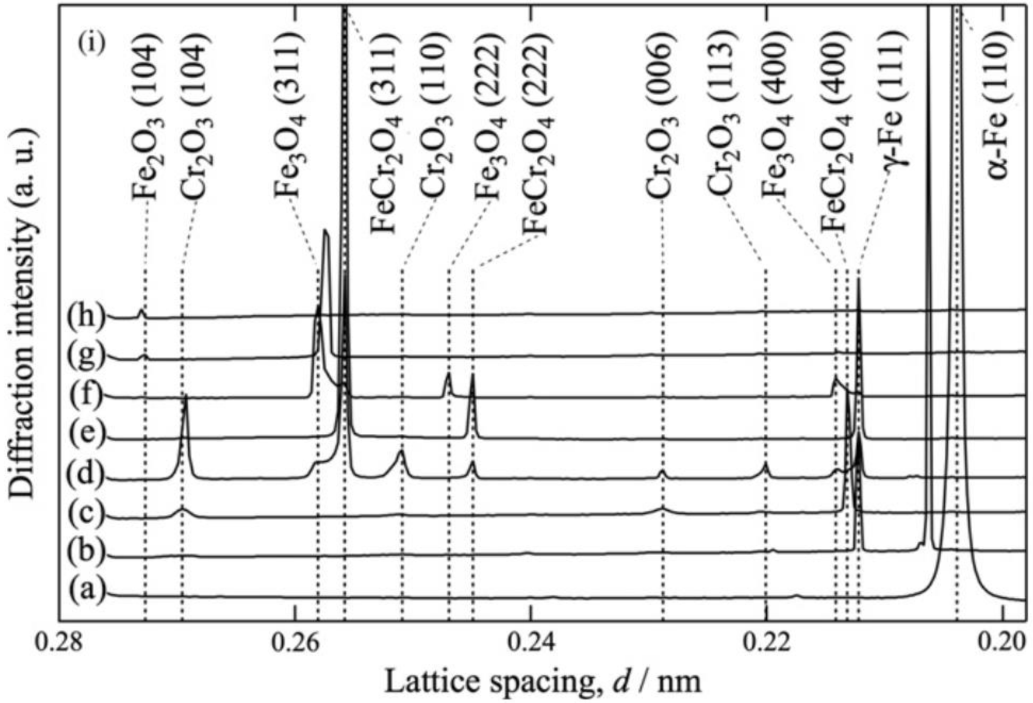
- 17 vol.% O2
- 20 vol.% H2O
- N2 gas

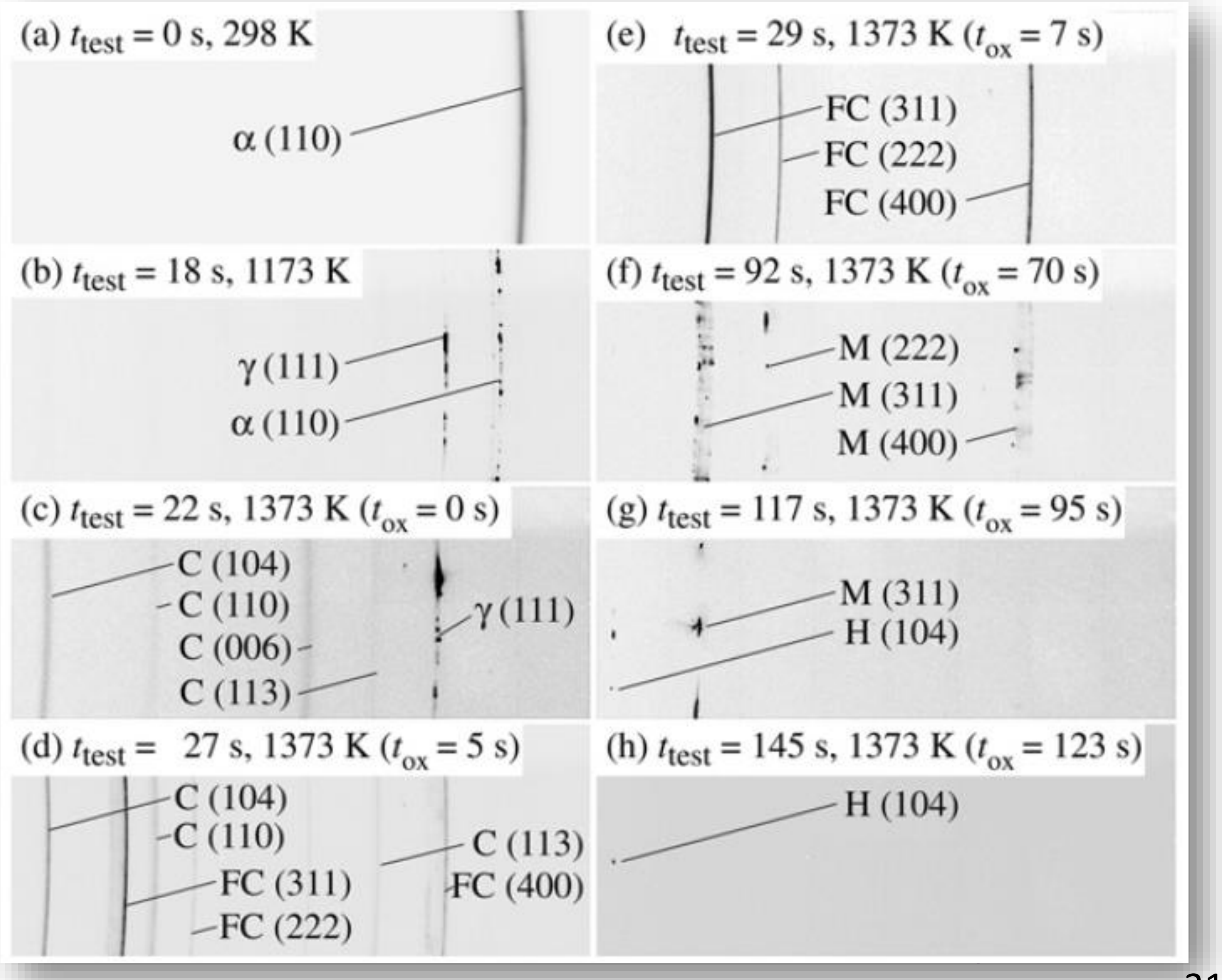
Rate of 8.3 cm^3/s

In situ studies of breakaway oxidation in type 430 stainless steel

Commercial type 430 stainless steel was used.
The composition of the steel was:

- 0.054 mass% C
- 0.55 mass% Si
- 0.09 mass% Mn
- 0.004 mass% S
- 0.13 mass% Ni
- **16.1 mass% Cr**
- and Fe!





*Saeki et al. Corrosion Science **55**, 219, 2012*

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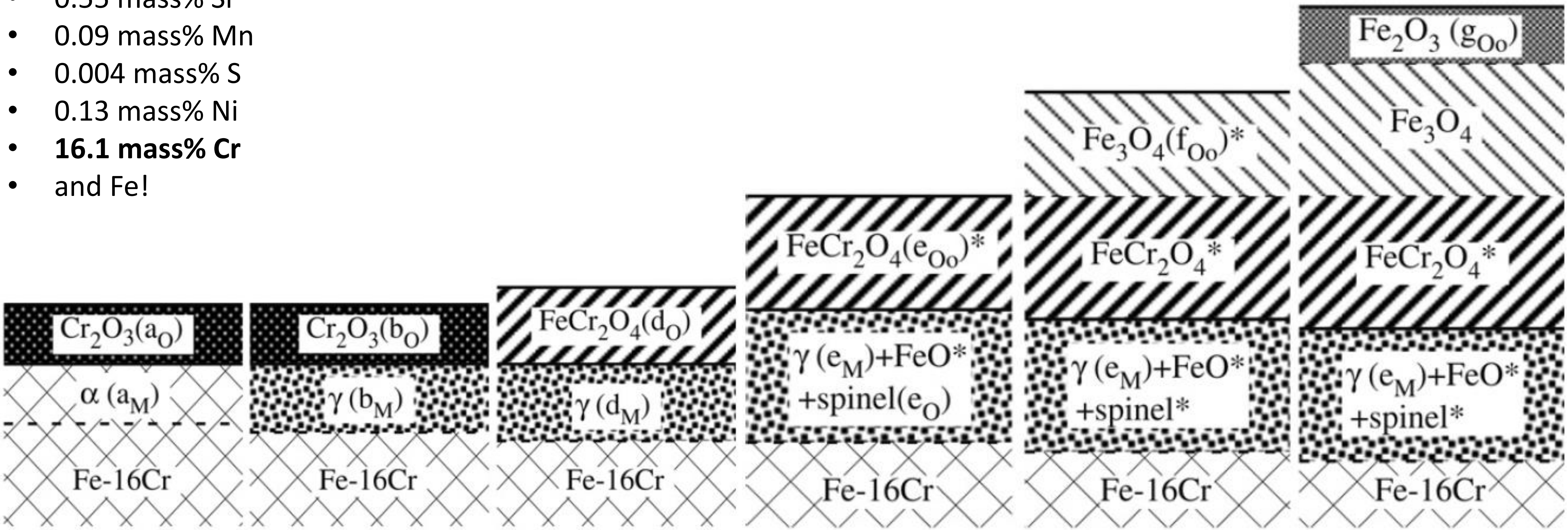
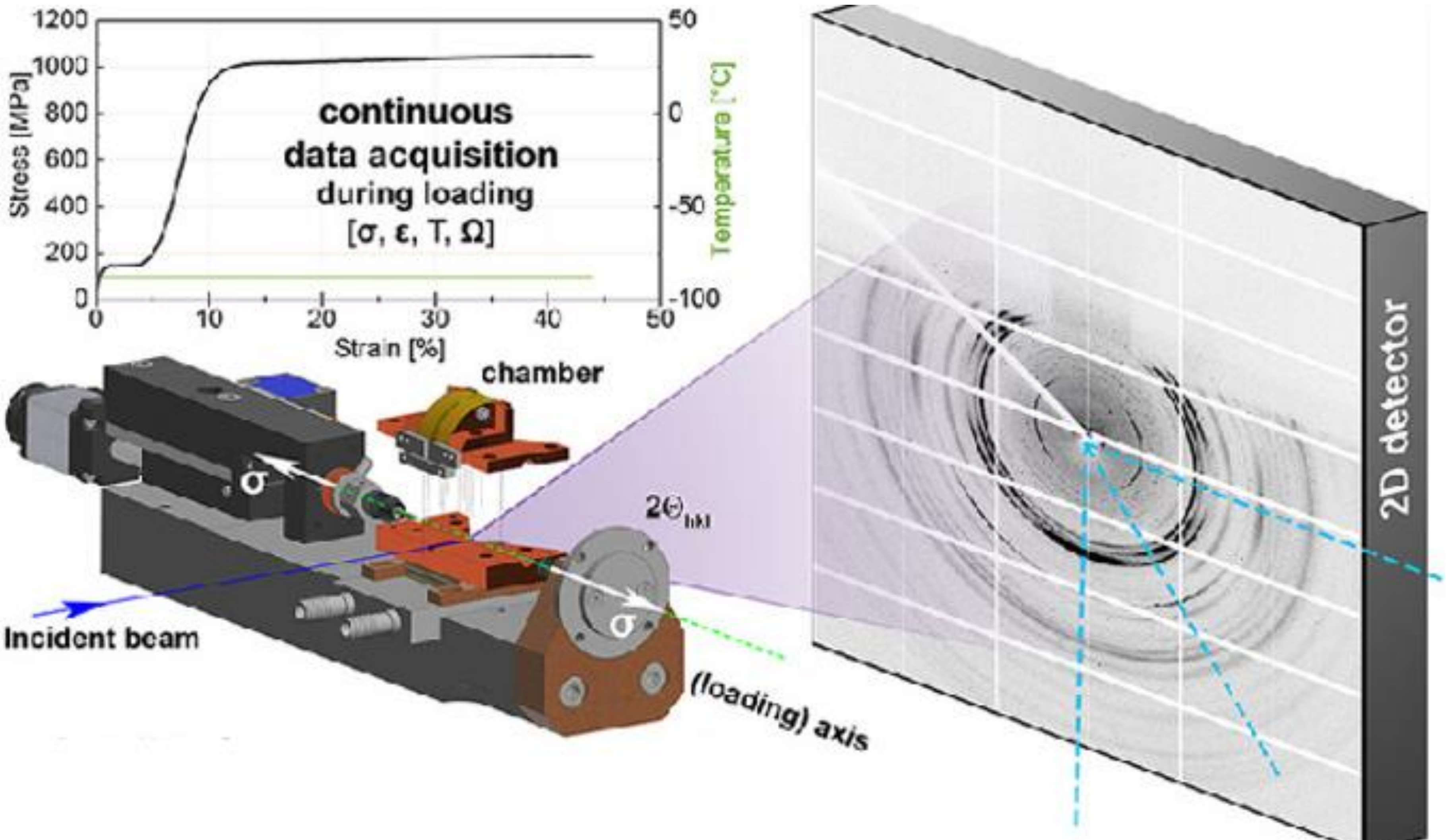


Saeki et al. Corrosion Science ***55****, 219, 2012*

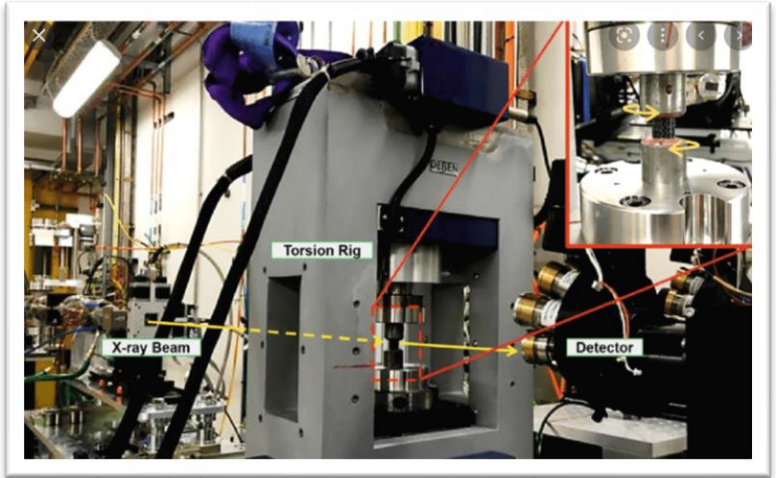
In-situ mechanical testing



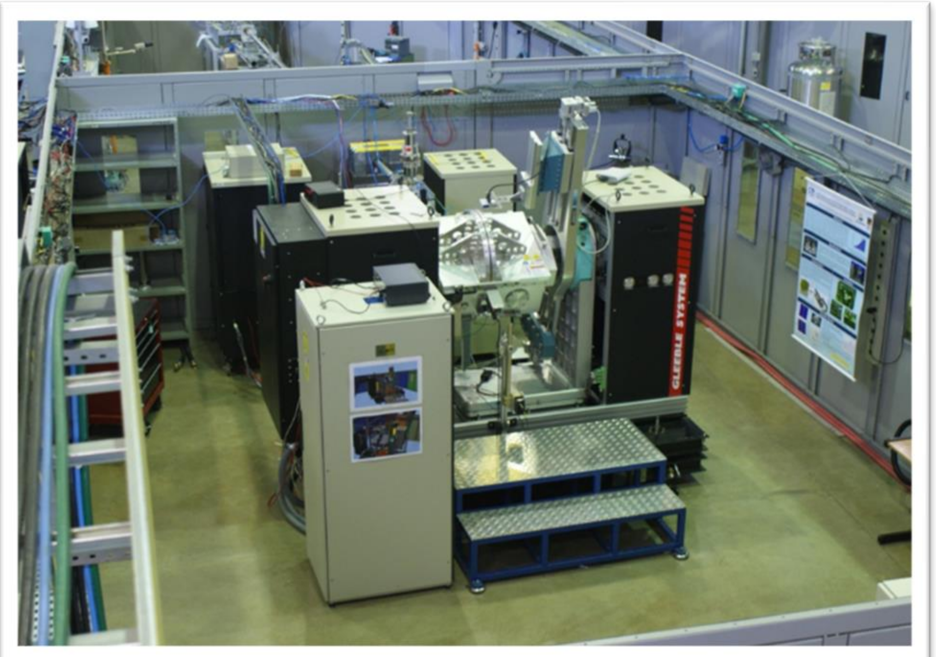
https://doi.org/10.1016/j.apmt.2022.101378

In situ mechanical testing

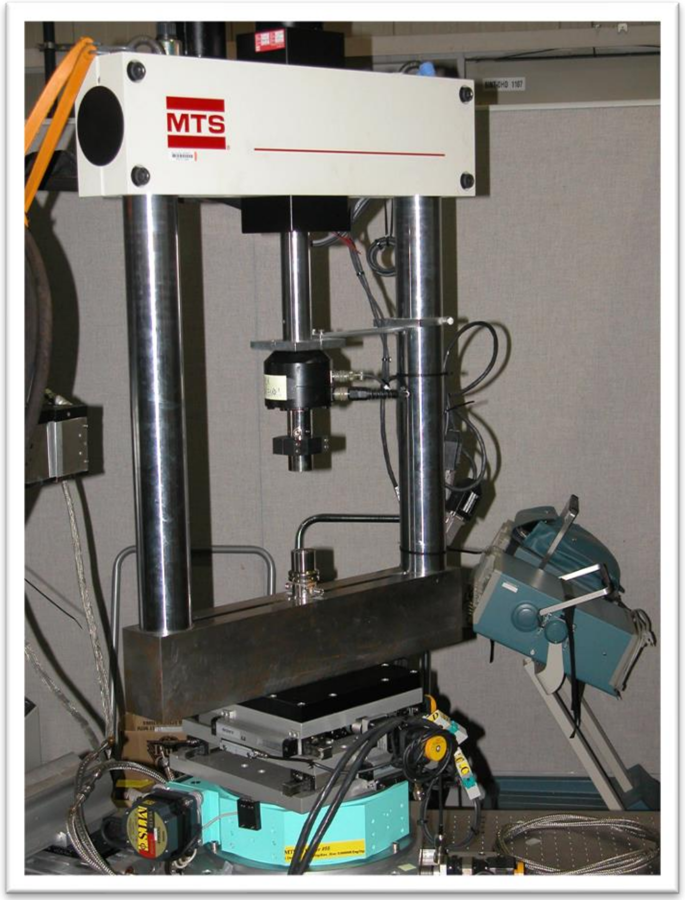
Diamond Deben 20kN



Gleeble 3S50 - Brazil

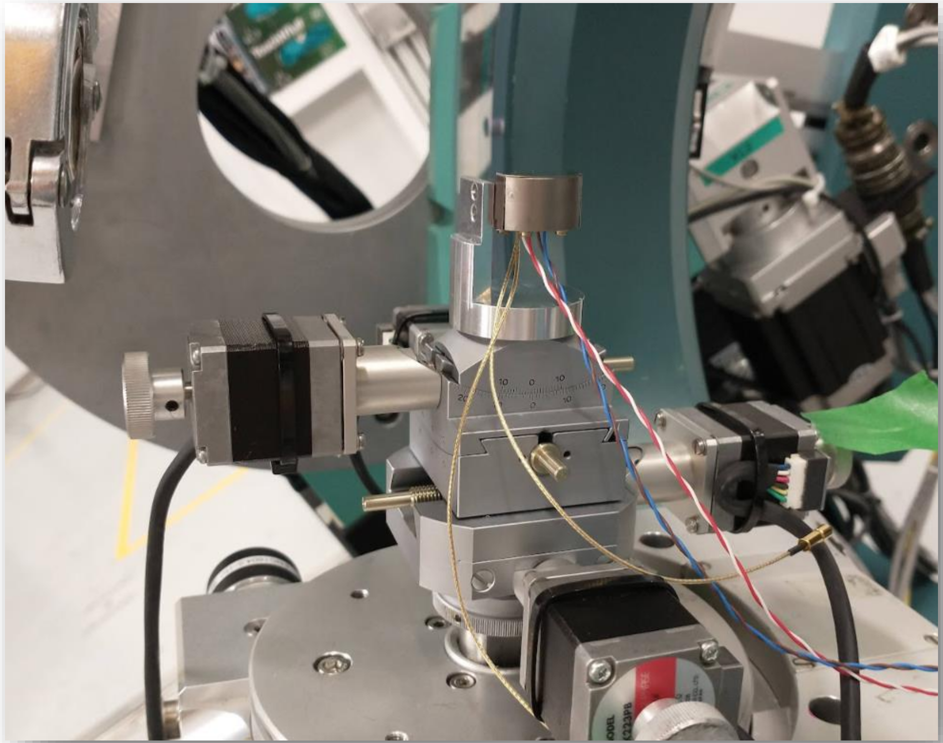


APS MTS 15kN



CLS MTS 10kN

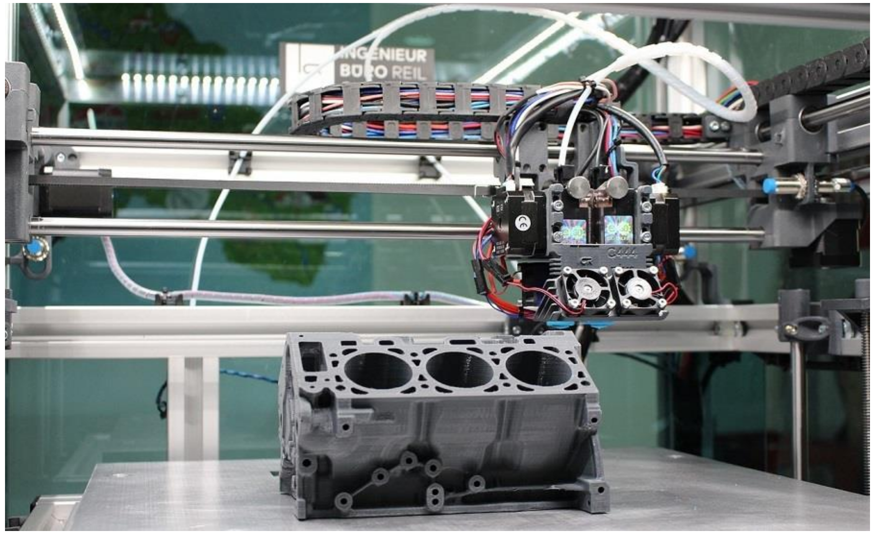
Razorbill strain cell



https://razorbillinstruments.com/uniaxial-strain-cell/

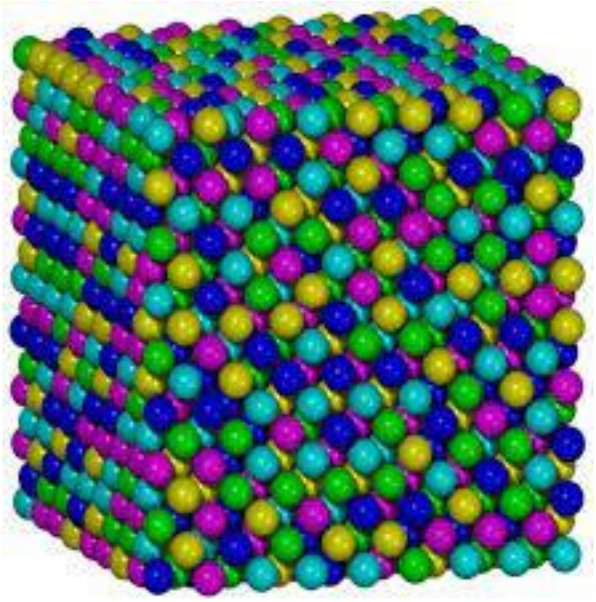
In-situ mechanical testing of additive manufactured high entropy alloys

AM – Additive Manufacturing - An emerging technology that manufactures three-dimensional (3D) objects directly from digital models through an additive process, typically by deposition of successive layers of polymers, ceramics, or metal materials



https://www.qualitymag.com/articles/94881

HEA – High Entropy Alloys – Greatly expanded compositional space for alloy design.



Looking for new materials with improved properties

https://www.dierk-raabe.com/high-entropy-alloys-overview/

In-situ mechanical testing of additive manufactured high entropy alloys

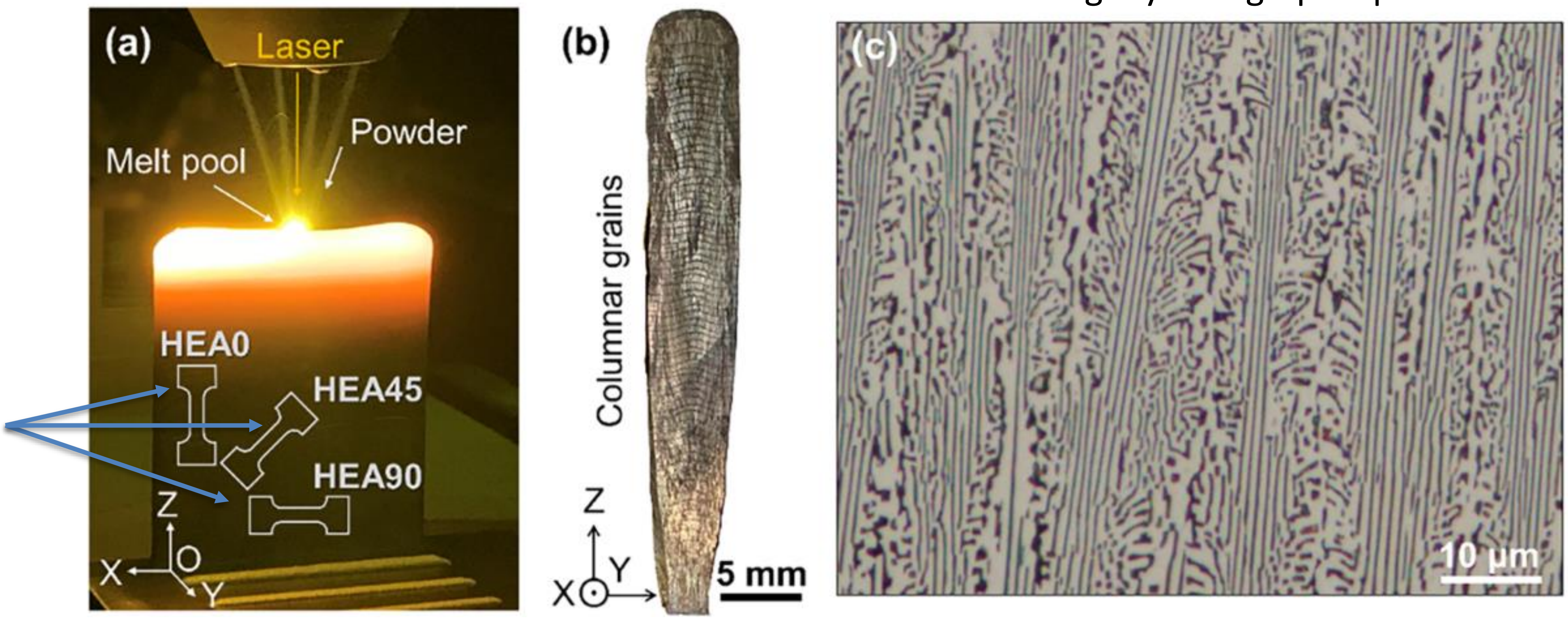
Acta Materialia 271 (2024) 119885

Anisotropic co-deformation behavior of nanolamellar structures in additively manufactured eutectic high entropy alloys

Haoxiu Chen et al.

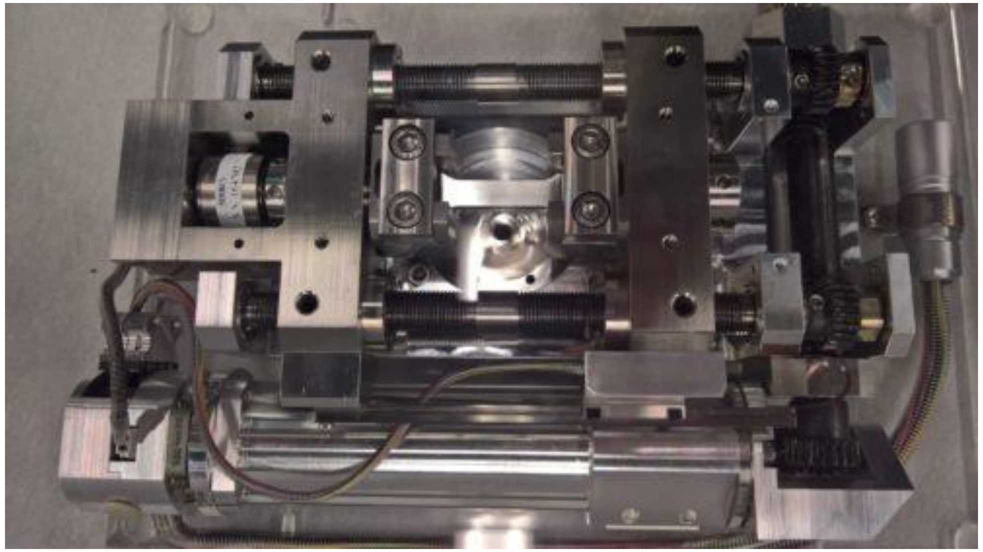
AlCoCrFeNi
Nanolamellar structure
Alternating crystallographic phases

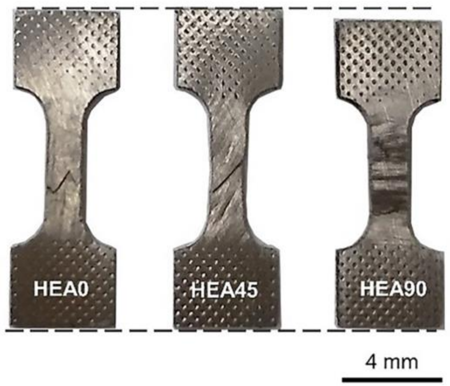
3 test specimens cut at different angles

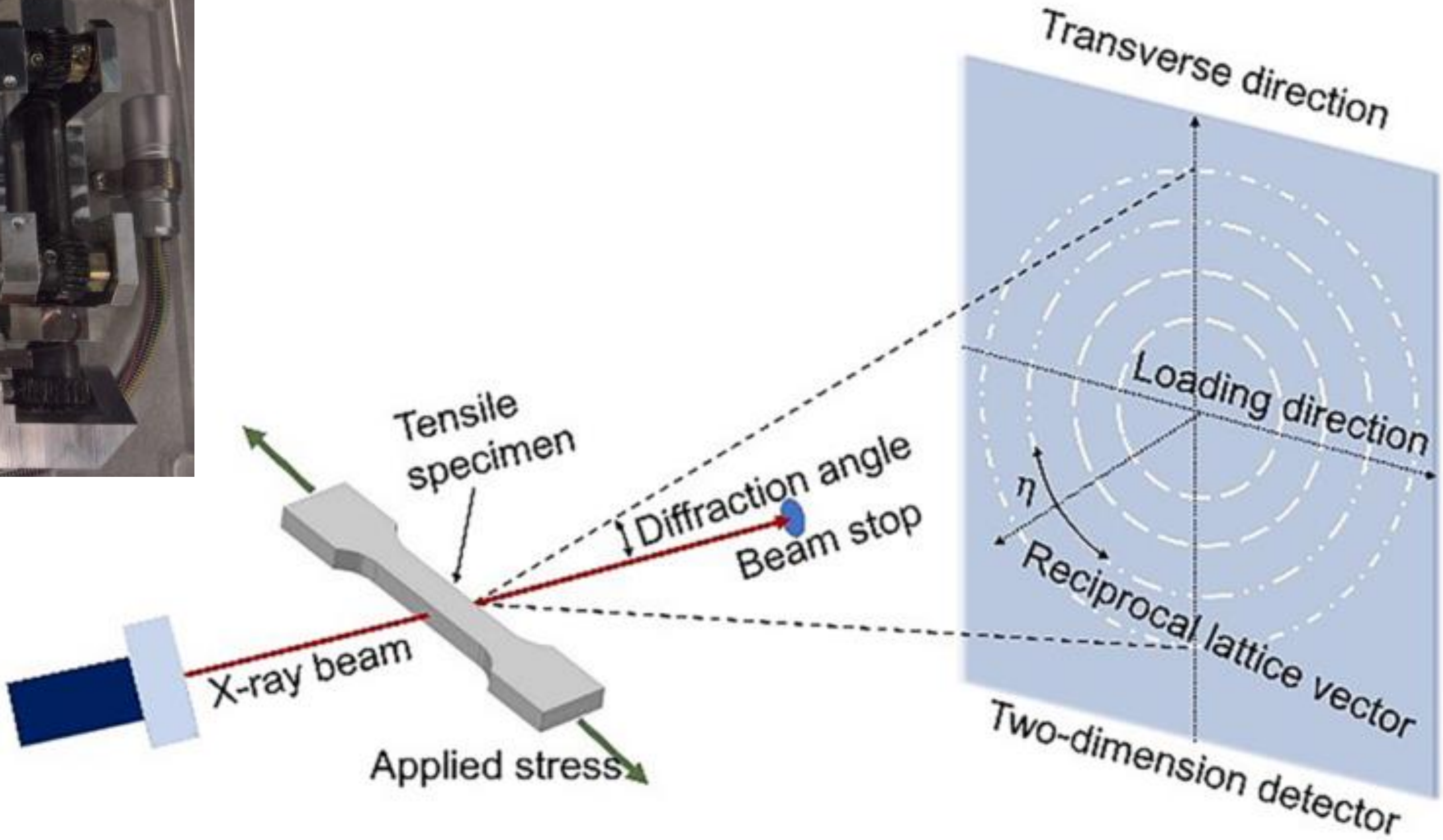


In-situ mechanical testing of additive manufactured high entropy alloys

Acta Materialia 271 (2024) 119885







In-situ mechanical testing of additive manufactured high entropy alloys

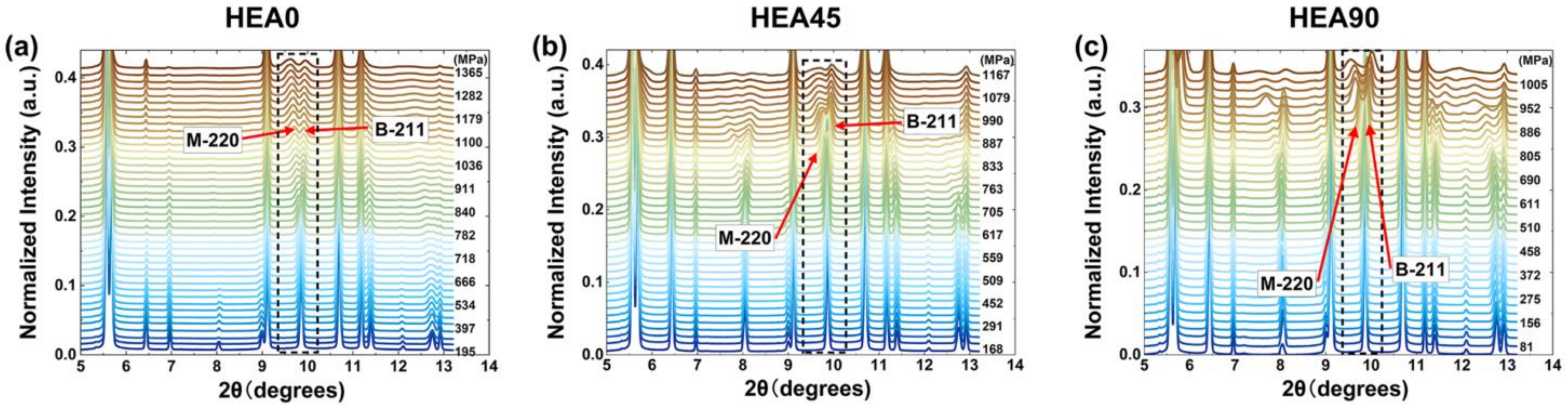
Acta Materialia 271 (2024) 119885

Evolution of the diffraction patterns with the applied load.

- Phase transformations
- Martensite phase formation

They can draw conclusions about:

- Strengthening mechanisms, work hardening and fracture behavior
- Sample along the lamellar direction had the highest tensile strength and ductility



Catalysis

Catalysts play an important part in many chemical processes.

More than 85% of chemicals come from catalytic reactions.

Catalysts:

- increase the rate of reaction
- are not consumed by the reaction
- are only needed in very small amounts

In-situ and operando catalytic experiments include

- Temperature and pressure control
- Structural characterization of intermediate compounds
- Gases in/out, flow control, analysis of gases out of the catalytic reaction

In a refinery, catalysts speed up chemical reactions, converting crude oil into petroleum products, ensuring that oil is refined quickly resulting in higher productivity and lower energy consumption.

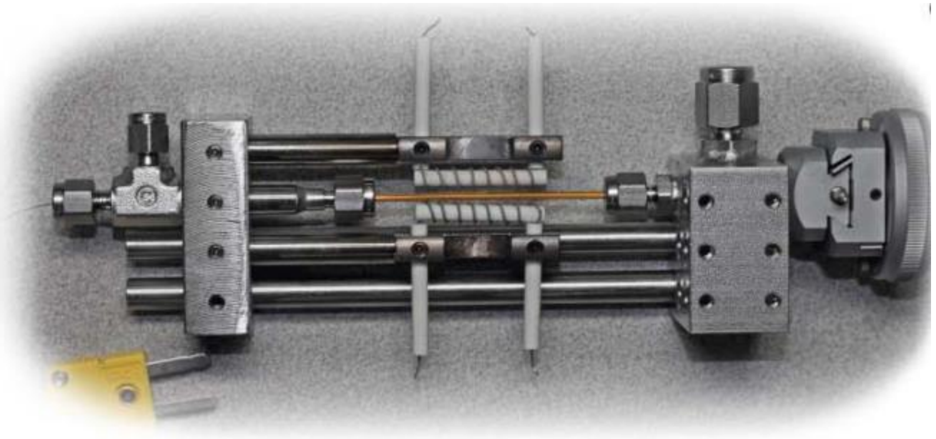
https://appliedcatalysts.com/navigating-the-refinery-catalyst-market-trends-challenges-opportunities/

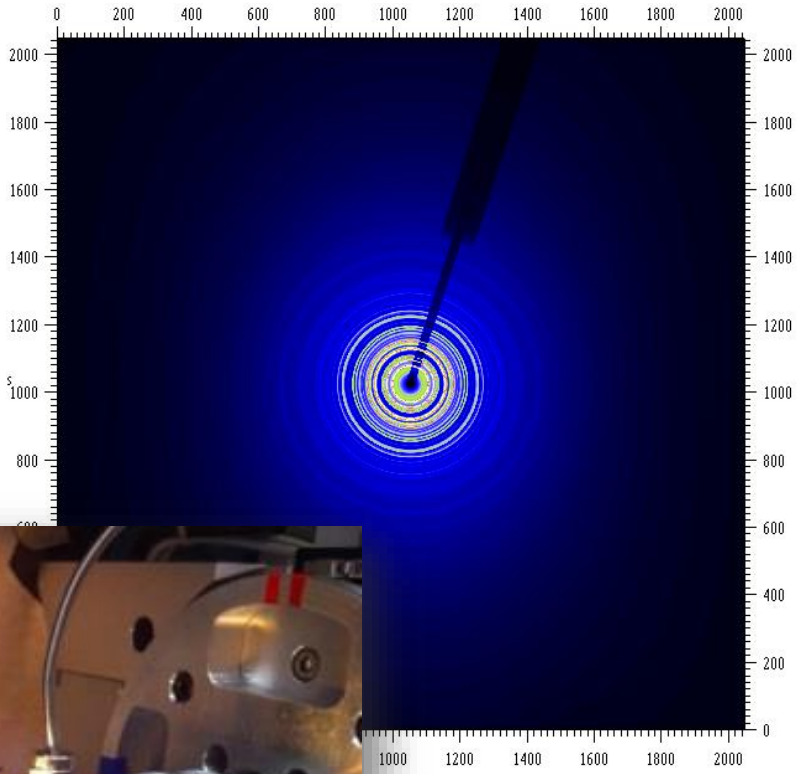
In-situ catalytic experiments

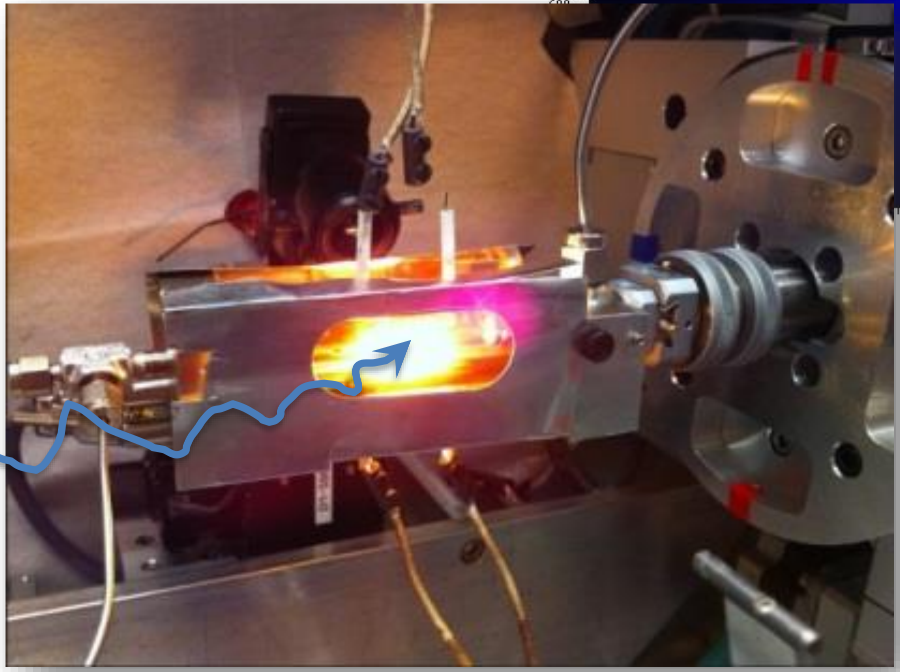
Controlled temperature and atmosphere

A versatile sample-environment cell for non-ambient X-ray scattering experiments

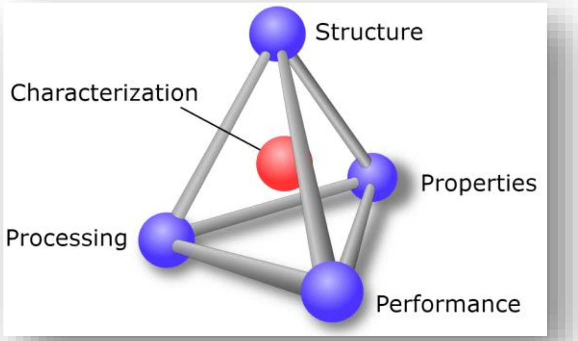
J. Appl. Cryst. (2008). **41**, 822–824







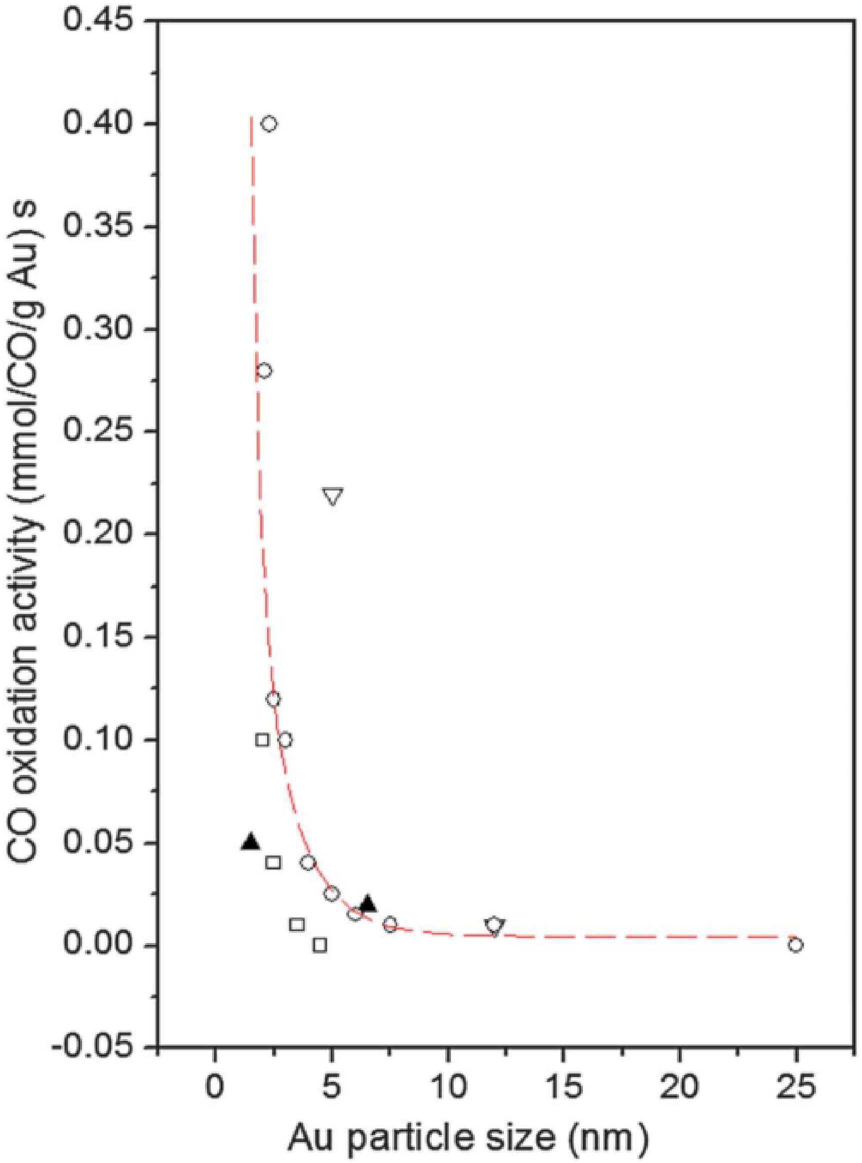
Structure - property relationship



Many times, catalytic activity is enhanced by braking the material into nanoparticles.

Nanoparticles have a high surface area, which can increase catalytic activity.

Catalytic activity of gold nanoparticles vs size →

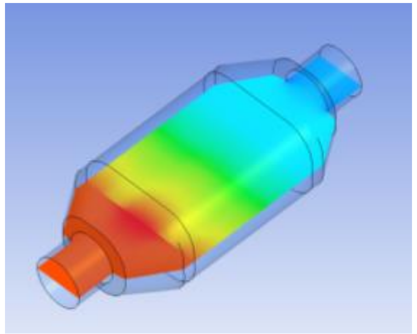


Petkov, V., et al. (2014). "A distinct atomic structure-catalytic activity relationship in 3-10 nm supported Au particles." Nanoscale **6**(1): 532-538

In-situ catalysis

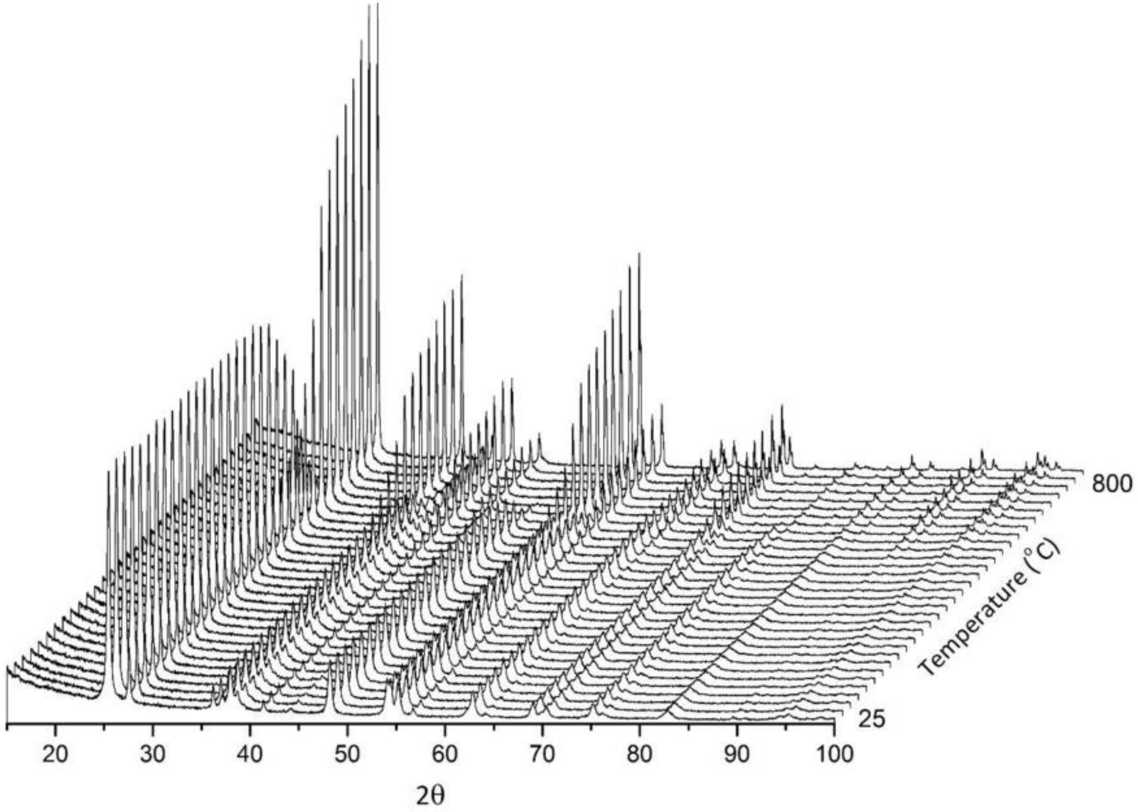
Commercial catalyst Aurolite® (1% Au-P25)

Catalytic converter

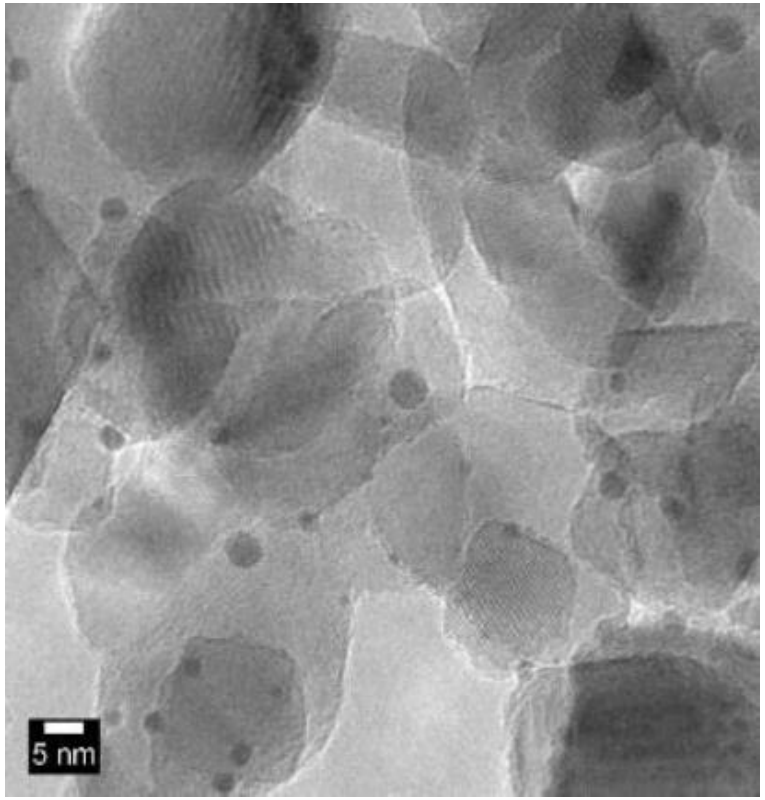


Exhaust emission control
Toxic gases in
catalyzed to
less toxic gases out

Operation at elevated
Temperatures!



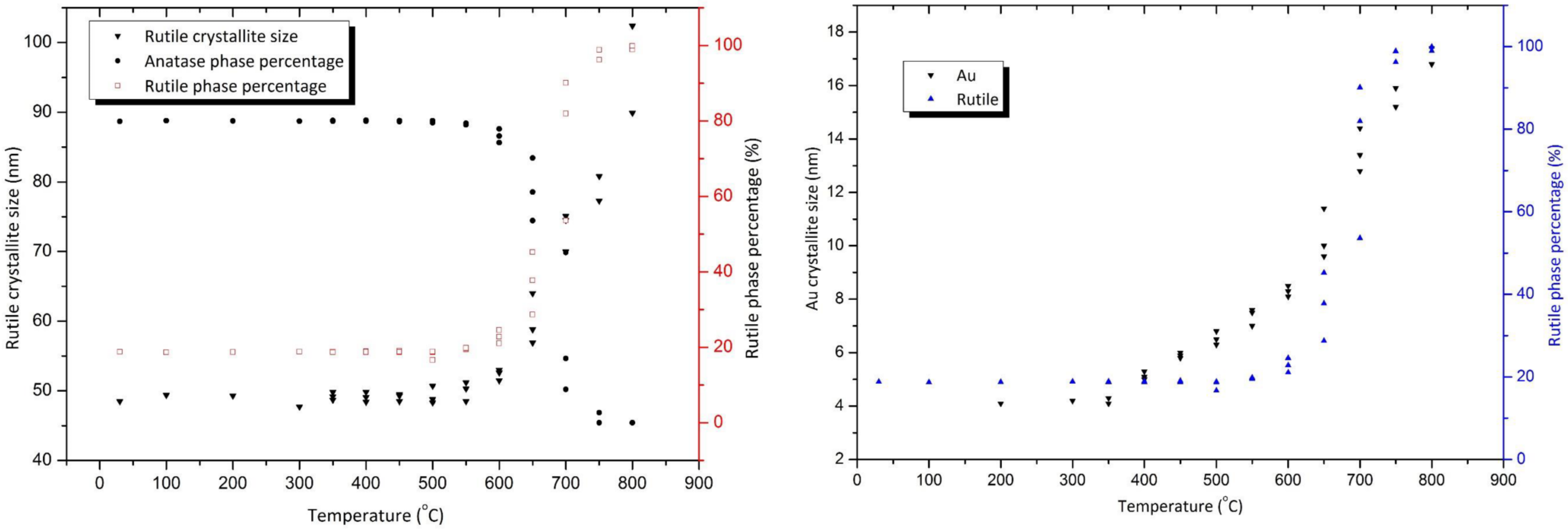
Phase change from anatase to the
thermodynamically stable rutile phase



TEM of commercial Au-TiO_2
catalysts after calcination at 300°C.

In-situ catalysis

Commercial catalyst Aurolite® (1% Au-P25)

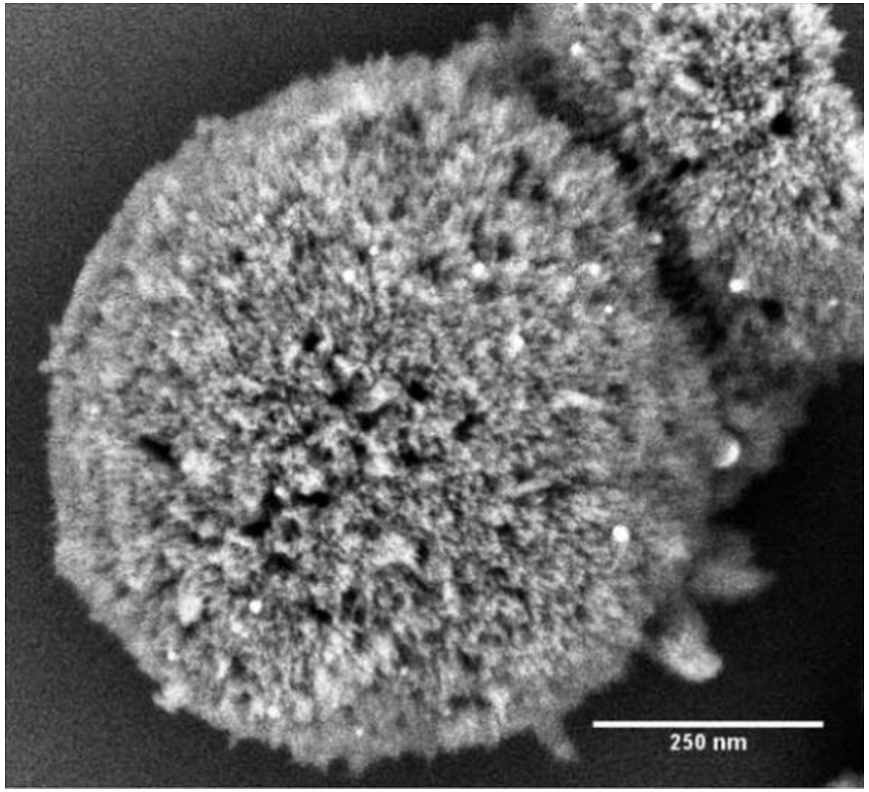


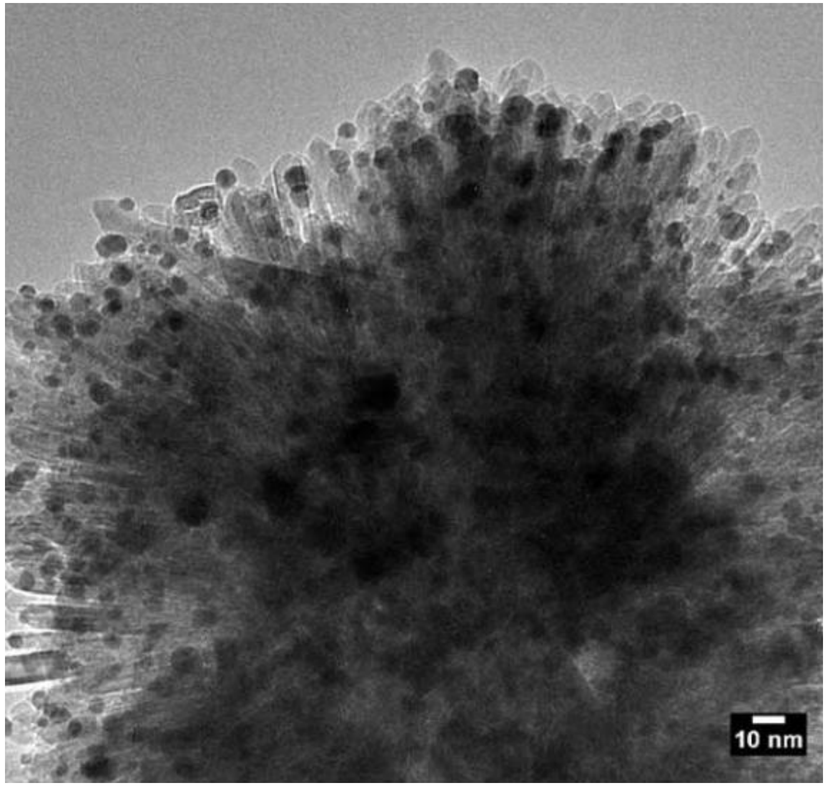
Structural instability of the support is a major factor in Au-nanoparticle growth

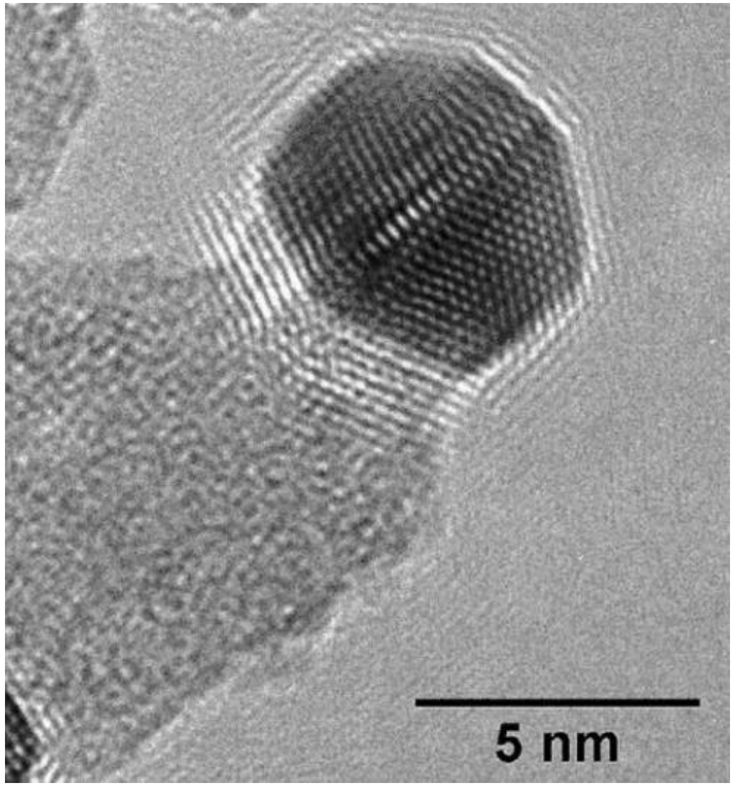
→ catalytic activity decreases

Achieving nano-gold stability through rational design† D. Barret et al.

In-situ catalysis



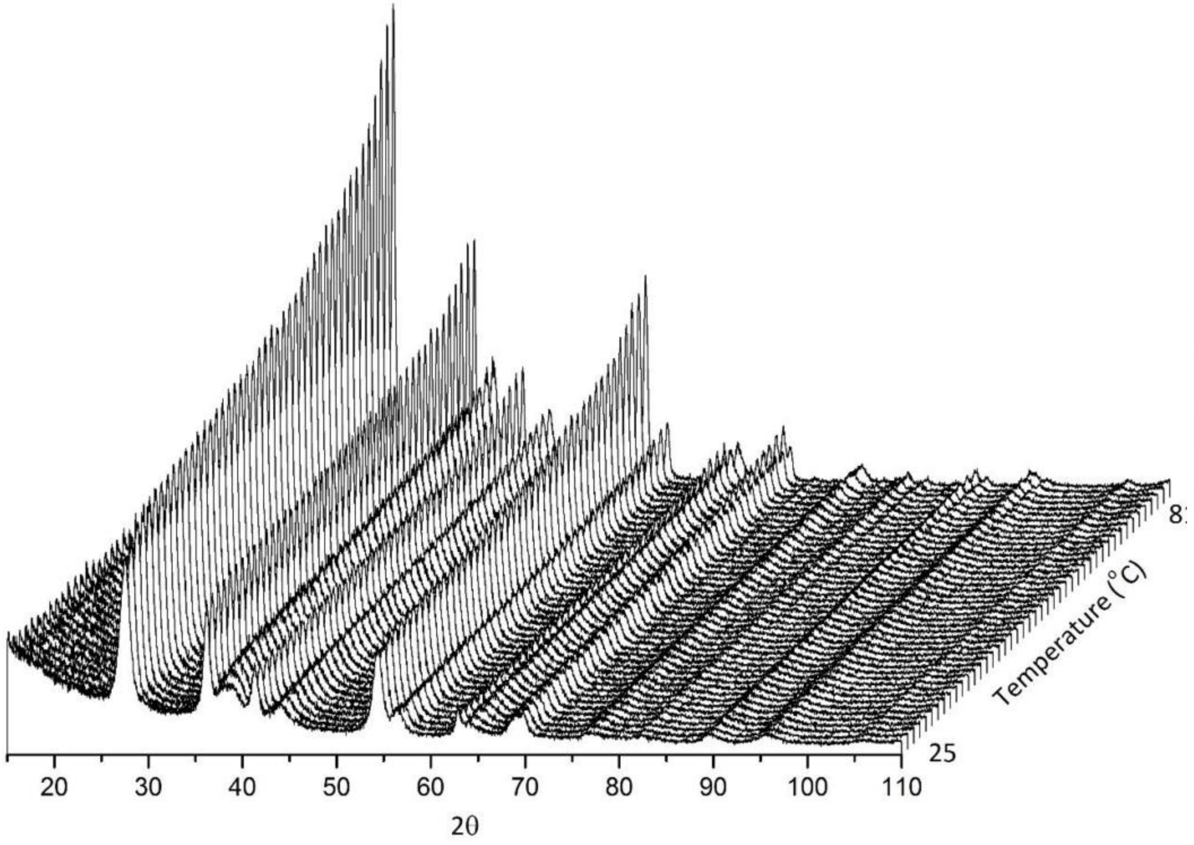


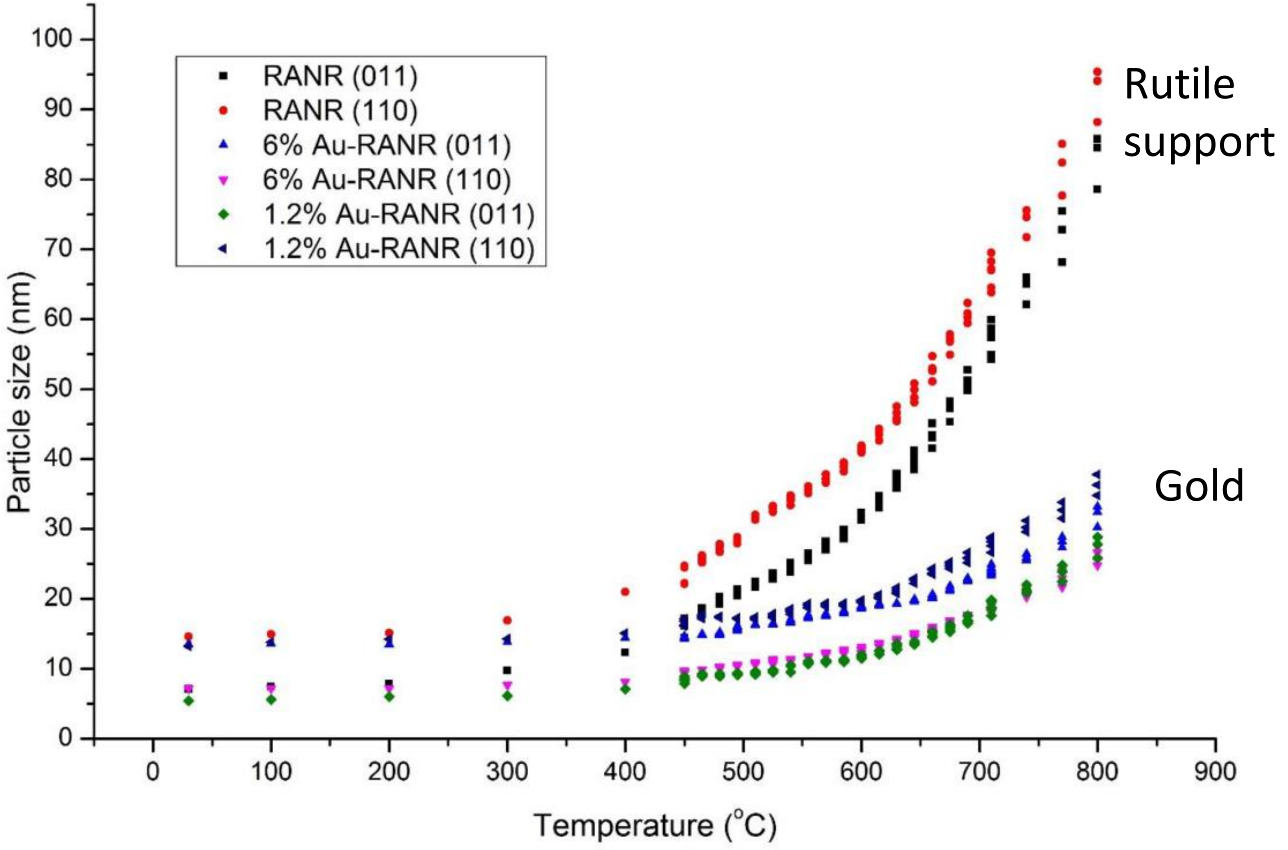


Achieving nano-gold stability through rational design† D. Barret et al.

In-situ catalysis

The presence of Au resulted in a stabilizing effect with regards to the growth of the support structure.





Achieving nano-gold stability through rational design† D. Barret et al.

Aurolite vs RANR

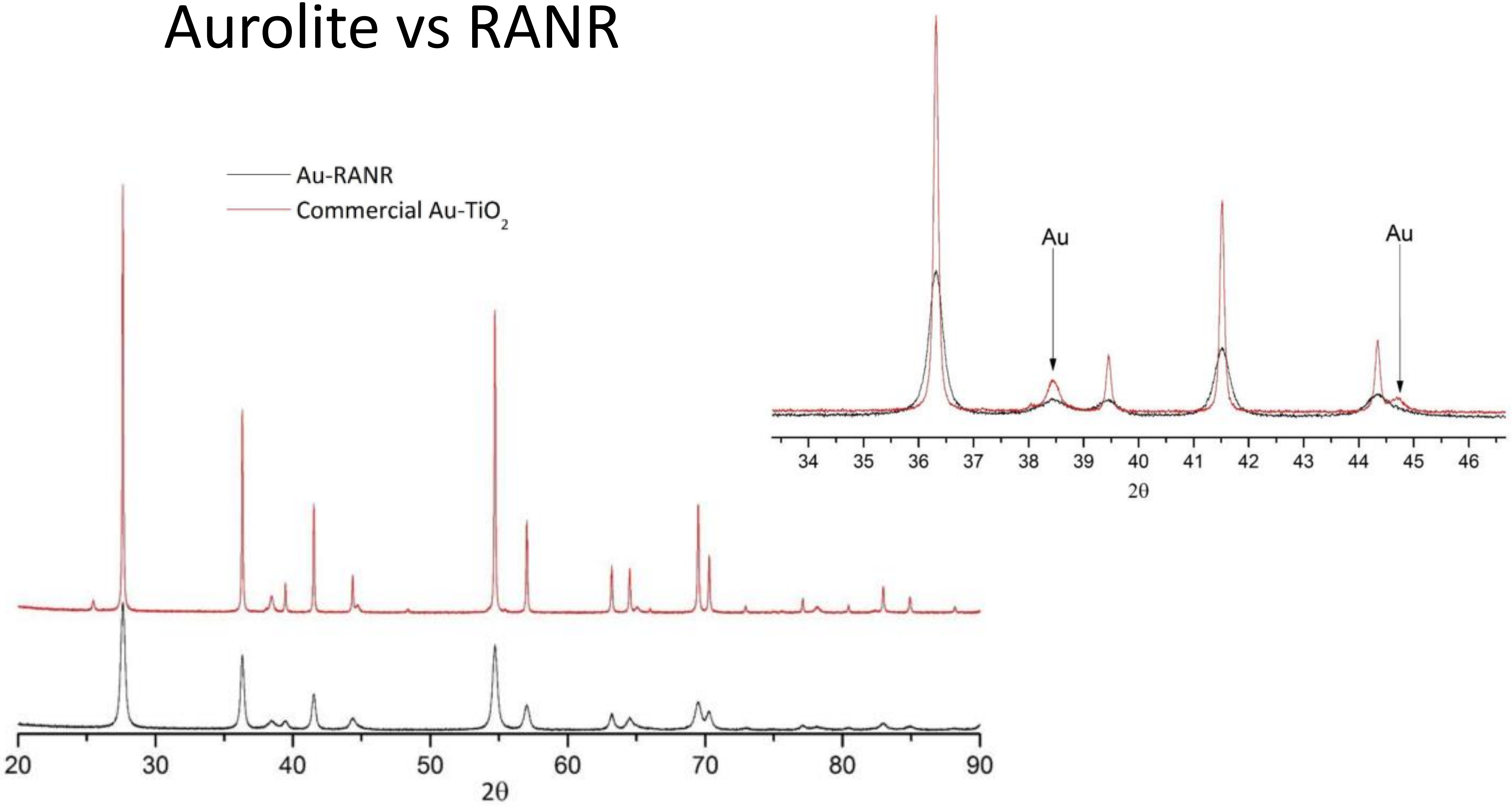


Figure S13: 1% Au loadings on commercial and RANR after the catalytic reaction.

In-situ catalysis

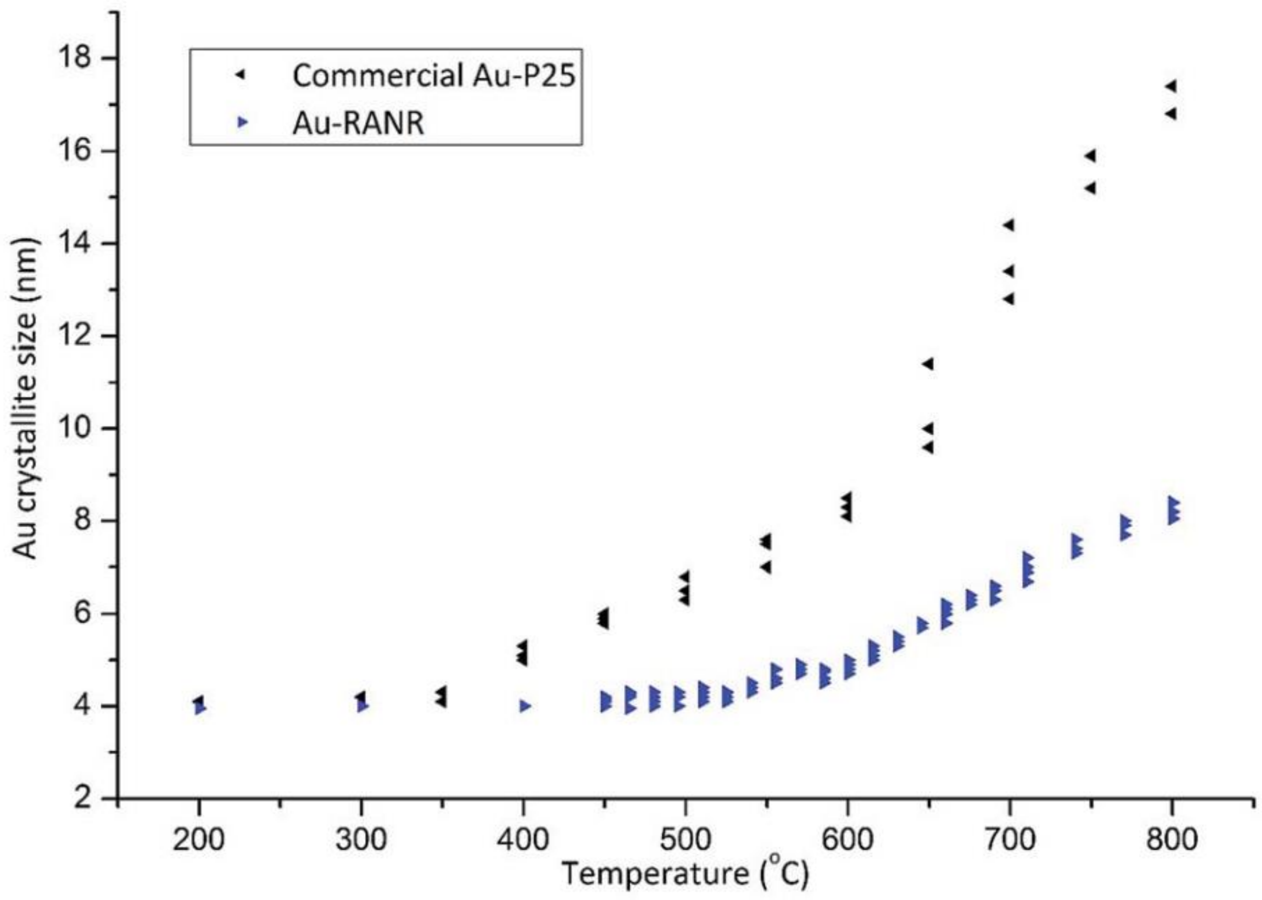


Fig. 3 Au crystallite sizes of the commercial Au–TiO_2 and Au-RANR catalysts determined from Rietveld refinement from *in situ* PXRD.

In-situ catalysis

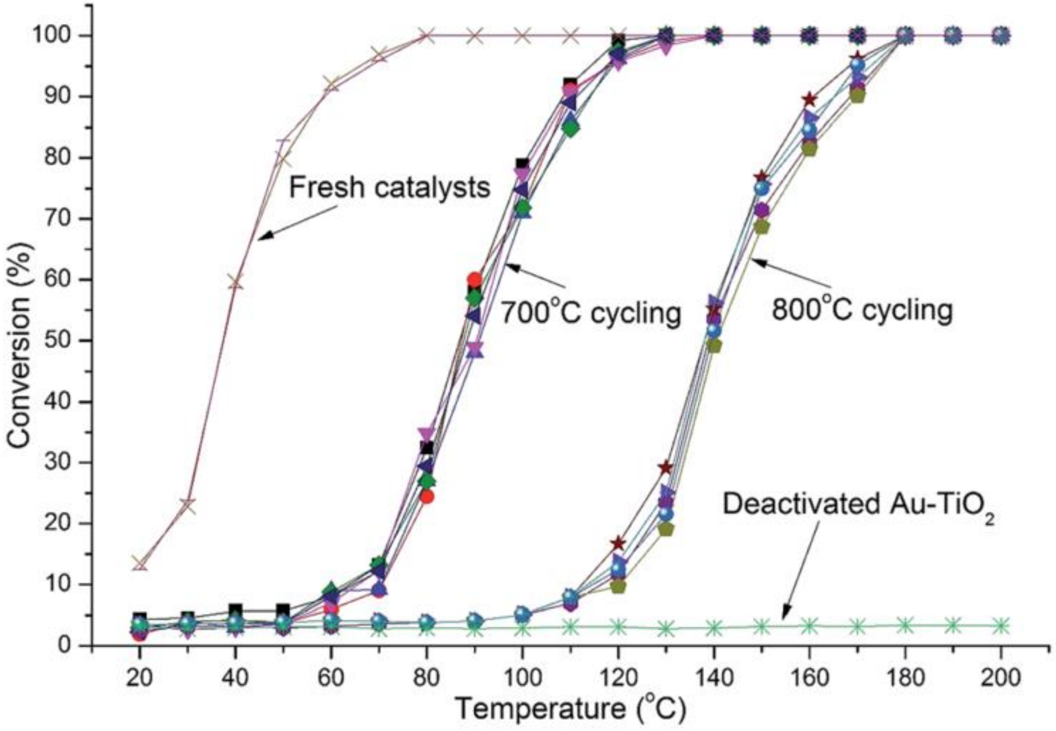
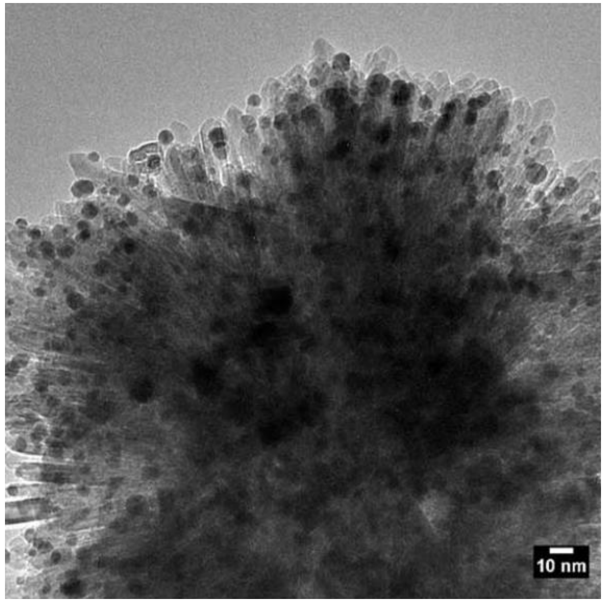


Fig. 4 Light-off curves for catalysts with 1.2% Au-RANR and commercial Au–TiO_2 after multiple 700 and 800 °C heating cycles (10 cycles in total).



- ✓ Thermodynamically stable support material
- ✓ Improved morphology
- ✓ Au nanoparticles sit isolated on the rod tips -> reduced mobility and coalescence
- ✓ Remarkable catalytic stability tested with CO oxidation after multiple heating cycles

Achieving nano-gold stability through rational design† D. Barret et al.

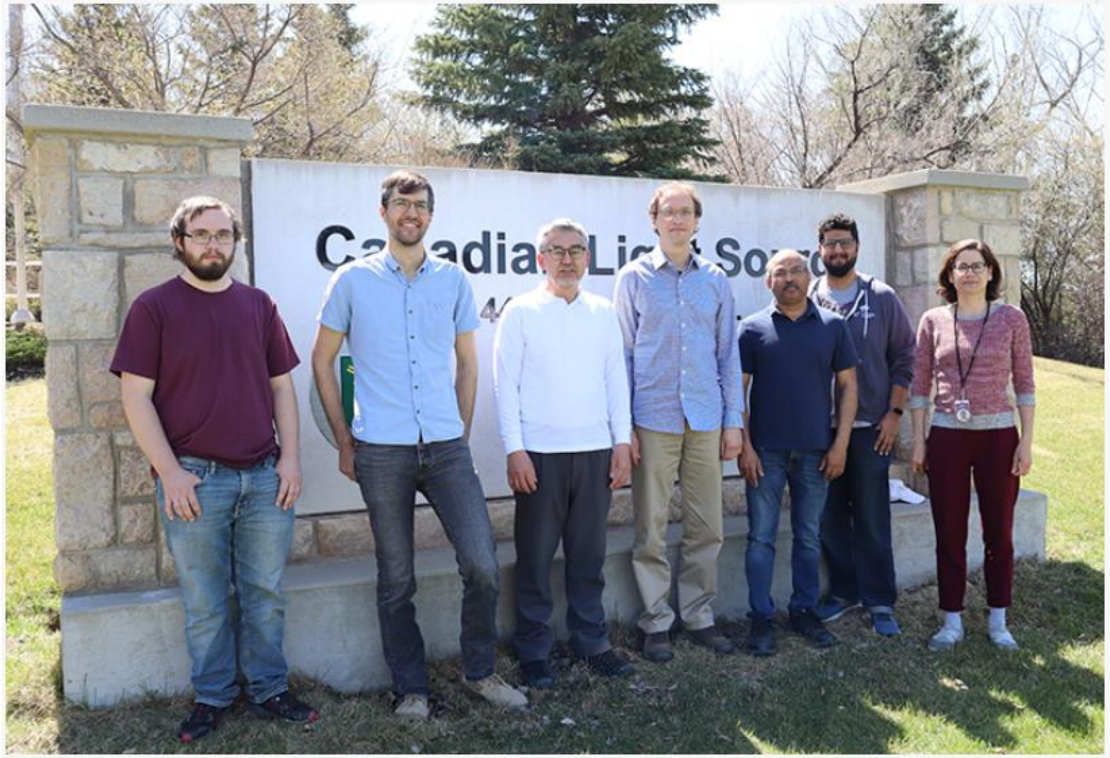
Conclusions

- In-situ experiments allow to study the materials and components under working conditions
- They yield very important information about the processes, facilitating the improvement of the materials and devices
- There are many options, both for in-house diffractometers and synchrotrons
- Synchrotrons are very flexible and well suited for in-situ experiments.

brockhouse.lightsource.ca

Brockhouse Diffraction Sector Beamlines

Home | Beamlines | User Guide | Contact Us | CPDW13



Welcome to the Brockhouse homepage. We provide a wide range of complementary diffraction and scattering techniques to fully characterize your materials.

- High resolution powder diffraction
- Pair distribution function (PDF)
- High energy diffraction for in-situ studies
- Reciprocal space mapping
- Small/wide angle X-ray scattering (SAXS/WAXS)
- High pressure crystallography
- X-ray reflectivity
- Grazing incidence diffraction (GID)
- Anomalous diffraction and magnetic diffraction

All 3 beamlines are now part of the general user program!

beatriz.moreno@lightsource.ca

Acknowledgments