Understanding precipitation processes in steels through time-resolved high-temperature SAXS/WAXS experiments

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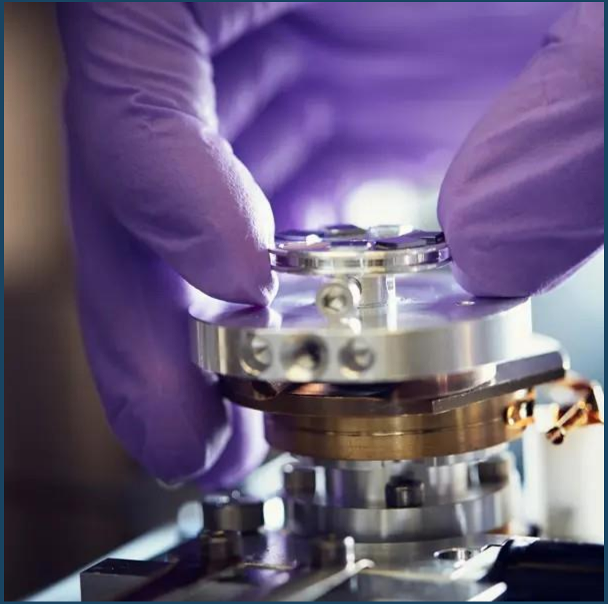
Metal. Mater. Trans. 55A (2024) 4146
doi: 10.1007/s11661-024-07536-z

Chalmers University of Technology
Department of Physics

Division of Microstructure Physics



- Our research focuses on materials and how the microstructure affects their properties.
- Engineering materials in close collaboration with industrial partners.
- A few examples are steels for high temperatures as in thermal power stations, coatings for cutting tools, nickel-base alloys for aeroengines and alloys used in the nuclear industry.
- We use electron microscopy and related techniques, atom probe tomography, X-ray and neutron scattering and diffraction

Chalmers Materials Analysis Laboratory – CMAL

- A research Infrastructure and open to all researchers at Chalmers University of Technology and University of Gothenburg on equal terms.
- The lab offers a broad park of instruments and tools, primarily in the fields of electron microscopy, X-ray diffraction, optical microscopy and atom probe tomography.
- Several powder diffractometers with sample environments for *in situ* tests (up to 1500 °C) and a state-of-the-art single crystal diffractometer.
- A high end, fully automated SAXS/WAXS/GISAXS instrument with *in situ* capabilities -100 to 1000 °C

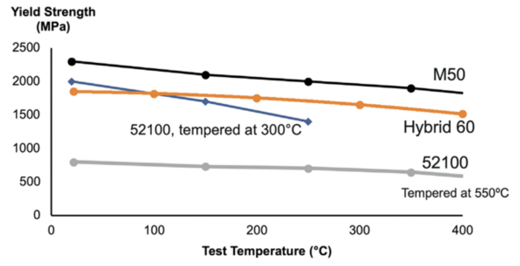
NEUTRON
AND X-RAY SCIENCE
FOR INDUSTRIAL TECHNOLOGY
TRANSITIONS

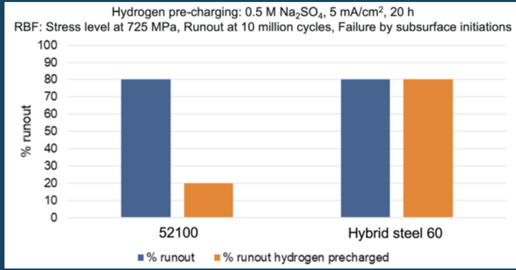
Innovating materials for sustainable development

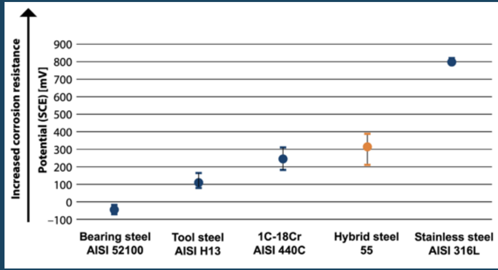
A competence centre for industrial sustainability. Funded by Vinnova, Sweden’s Innovation Agency and 23 partners from universities (KTH, Chalmers LiU), institutes (RISE, Swerim) and companies.

Hybrid steels – A new family of dual-hardening steels from Ovako.

		C	Si	Mn	Cr	Ni	Mo	V	Al
Hybrid Steel 55	Engineering steel	0.18	0.1	0.3	5	6	0.7	0.5	2
Hybrid Steel 60	Bearing Steel	0.28							



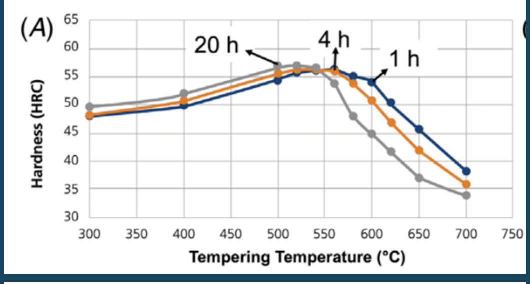




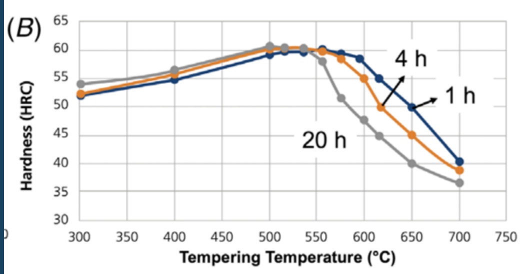
Andersson et al. ASTM STP 1623 (2020) doi: 10.1520/STP162320190163

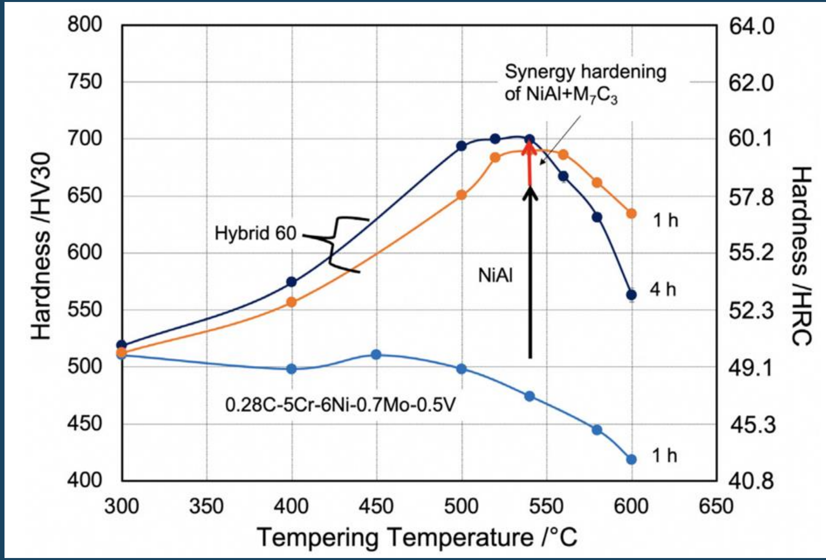
Precipitation hardened by a combination of nanoscale intermetallic NiAl (β) and chromium carbides

Hybrid 55



Hybrid 60





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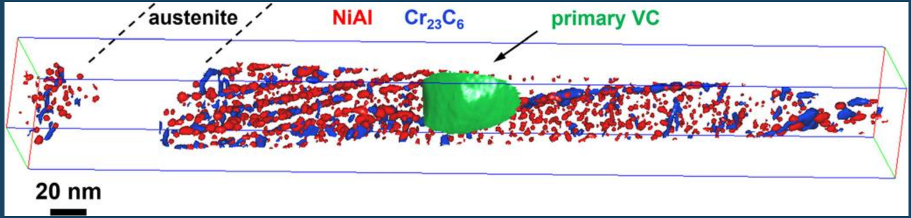
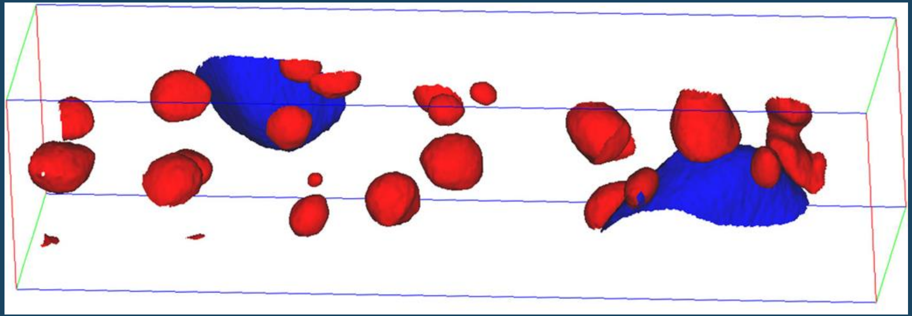
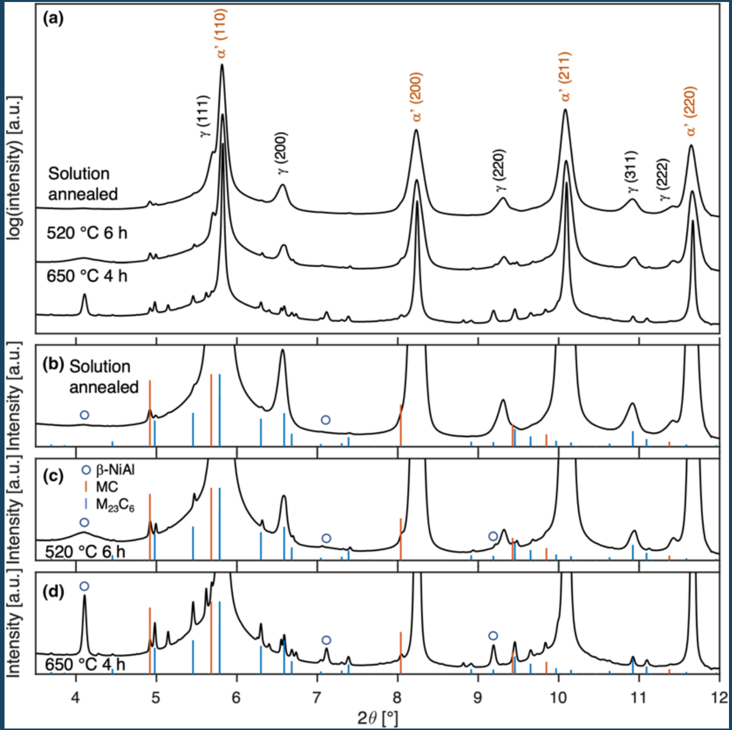
Precipitation hardened by a combination of nanoscale intermetallic NiAl (β) and chromium carbides

520 °C 6 h



650 °C 4 h





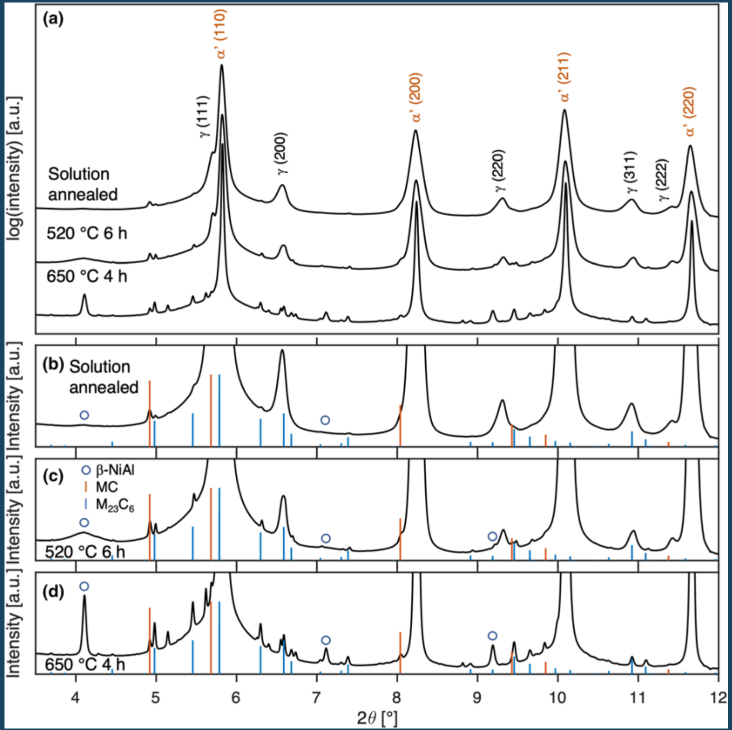
Jakob et al. Metall. Mater. Trans. 55A (2024) 870 doi: 10.1007/s11661-023-07291-7

The questions

- Can we track the precipitation process in real-time, throughout the full heat treatment?
- In which order do the phases (carbides and intermetallic particles appear)?
- What are the kinetics of the precipitation process(es)?

Methods

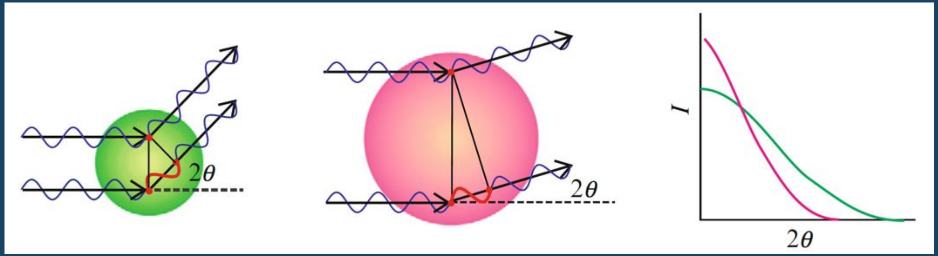
- Simultaneous small-angle scattering (SAXS) and wide-angle scattering (WAXS) during heat treatment at P21.2 at PETRA III
- SAXS for size and volume fraction
- WAXS for phase identification



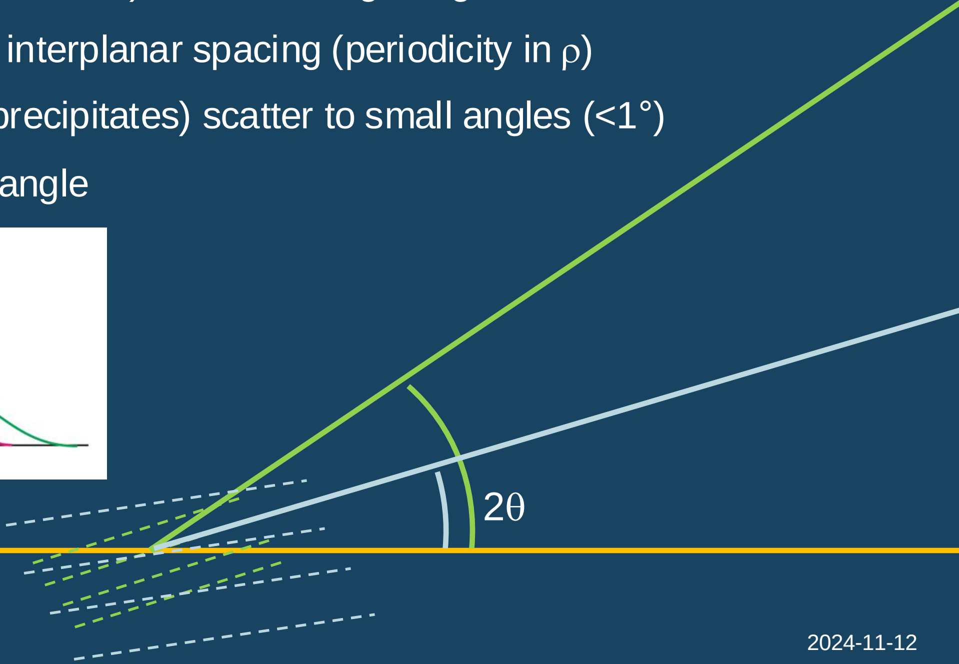
Jakob et al. Metall. Mater. Trans. 55A (2024) 870 doi: 10.1007/s11661-023-07291-7

Small-angle X-ray scattering resolves “large” structures

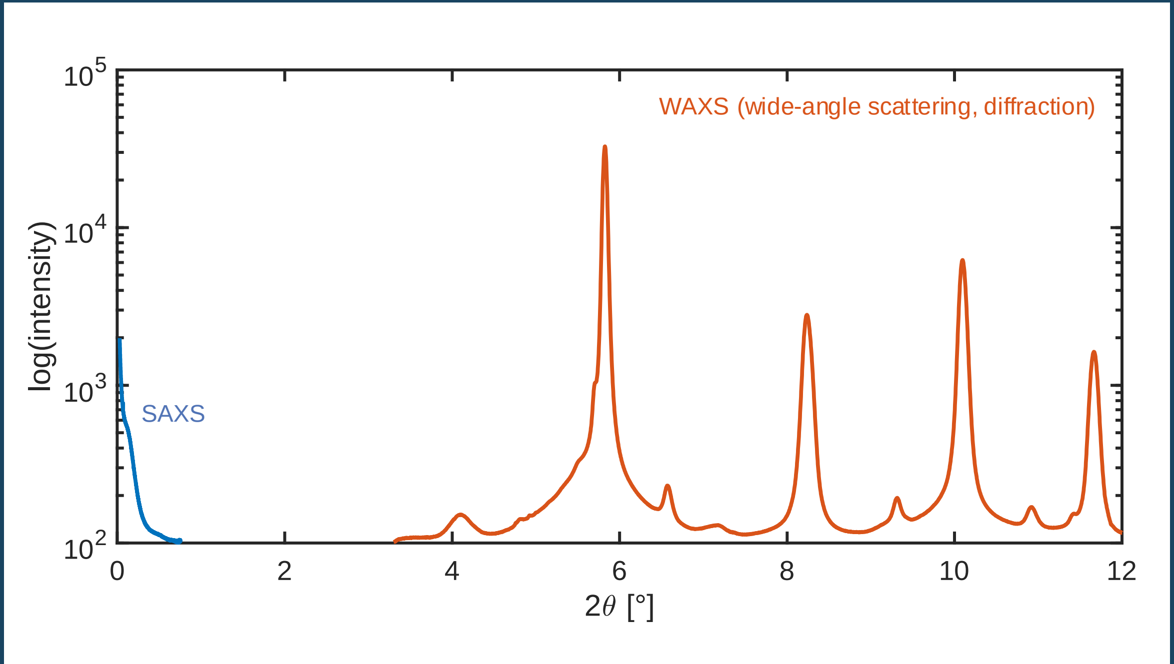
- X-ray scattering measures variations in electron density ρ
- Lattice planes (periodic variations in ρ on the order of Å) scatter to large angles
- The scattering angle decreases with increasing interplanar spacing (periodicity in ρ)
- Variations at longer length-scales nm-μm (e.g. precipitates) scatter to small angles (<1°)
- The larger the object the smaller the scattering angle



Pabit et al. Methods in Enzymology 469 (2009) 301
doi: 10.1016/S0076-6879(09)69019-4



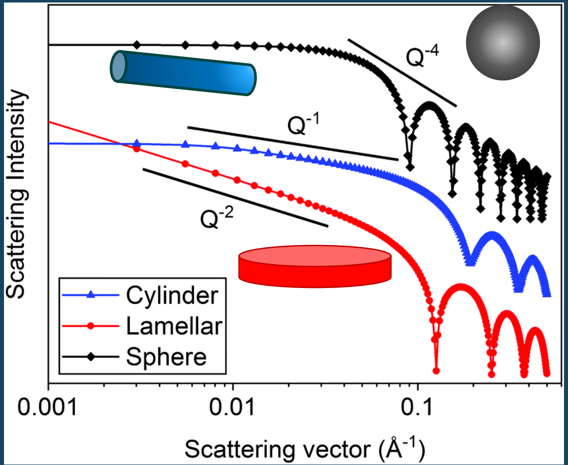
How small angles?



What information can we get from SAXS?

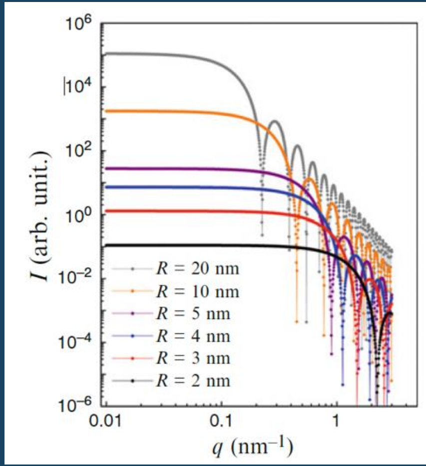
- The shape of the SAXS curve depends on shape and size (distribution)
- The intensity depends on volume fraction and chemistry

Shape



McDowall et al. Soft Matter 18 (2022) 1577
doi:10.1039/D1SM01707A

Size



Londoño et al. in Hanbook of Materials Characterization (2018)
doi: 10.1007/978-3-319-92955-2_2

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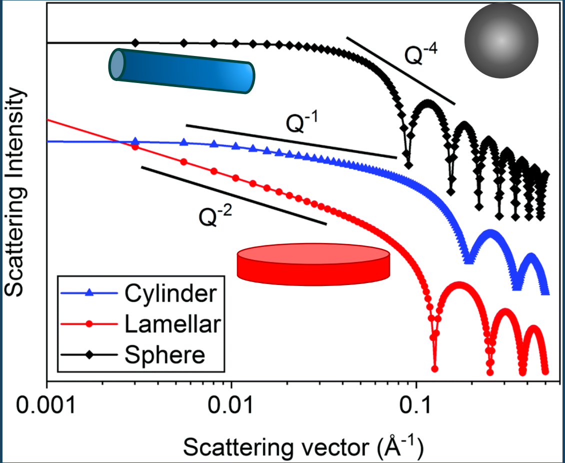

McDowall et al. Soft Matter 18 (2022) 1577
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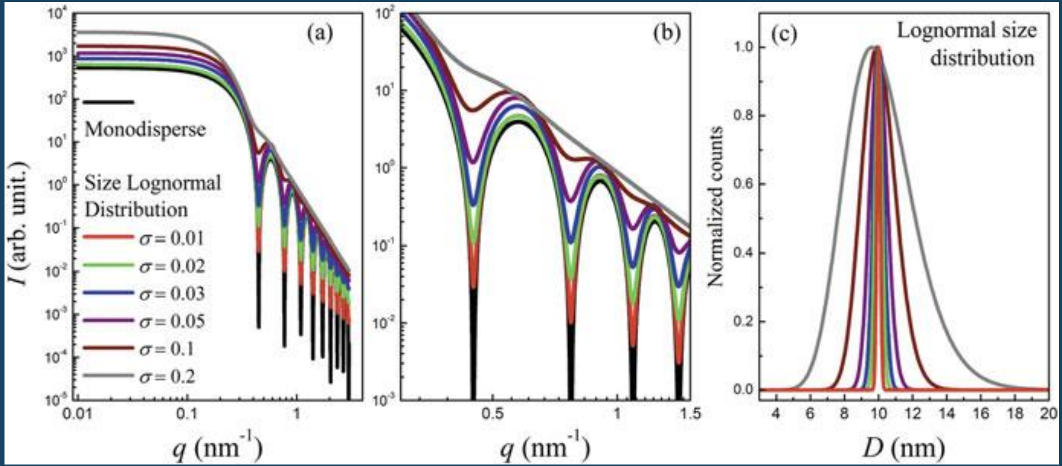
Size distribution



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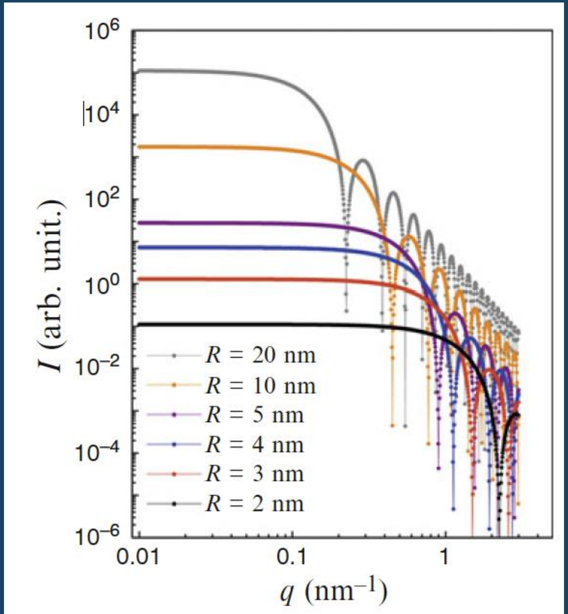
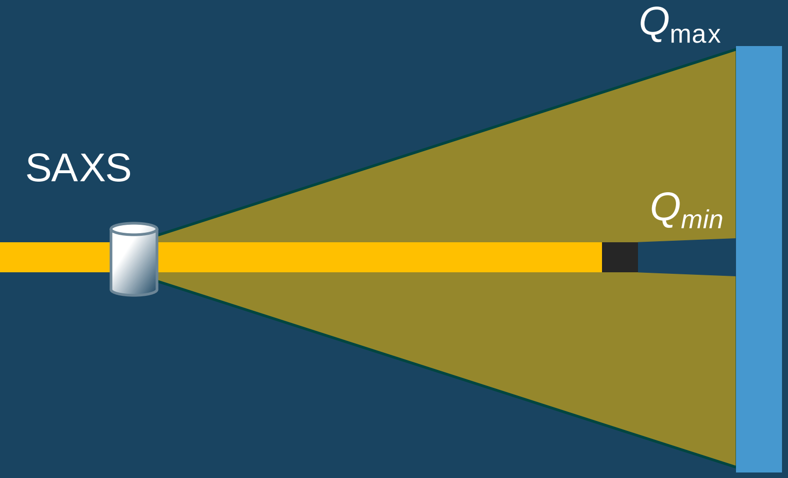
Analysing SAXS data

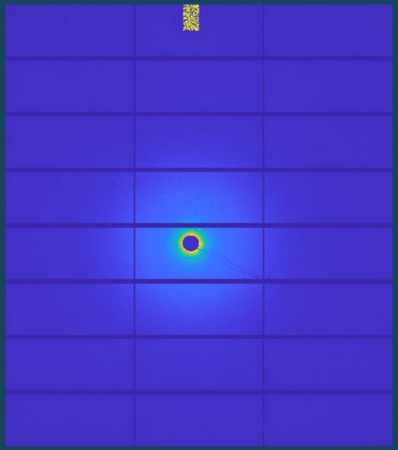


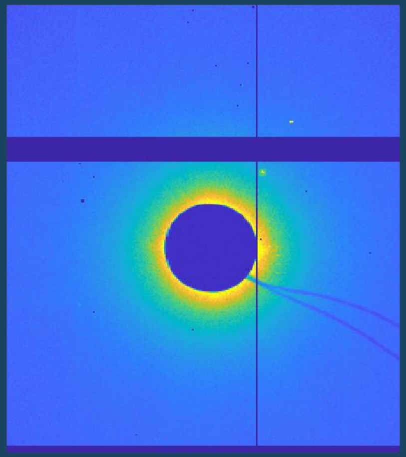
Londoño et al. in Hanbook of Materials Characterization (2018)
doi: 10.1007/978-3-319-92955-2_2

- Small angle scattering is not as intuitive as diffraction
- Fitting of SAXS data can yield quantitative information
  - Particle shape
  - Size distribution
  - Volume fraction
  - Chemistry
- **But it is complicated and requires accurate models and complementary information**
- In many cases sufficient information can be obtained by simplified analyses (as in our case)

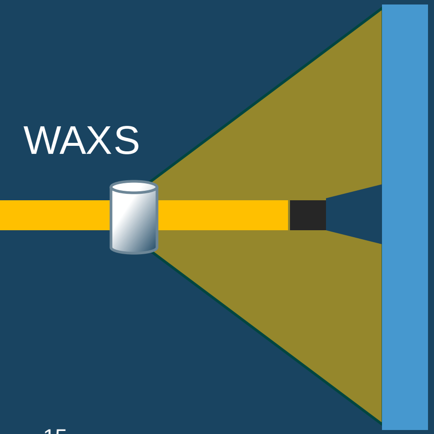
SAXS

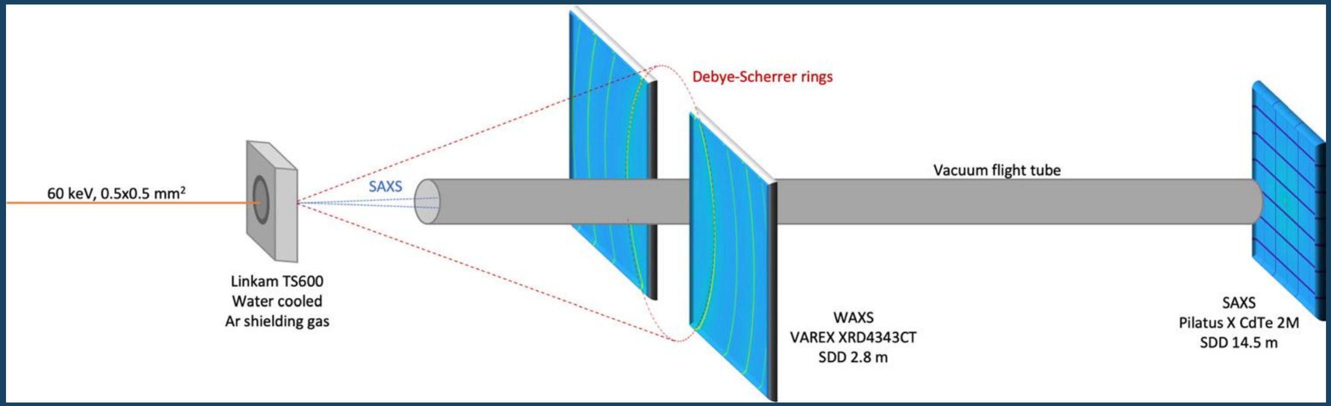

Q_{max}
Q_{min}

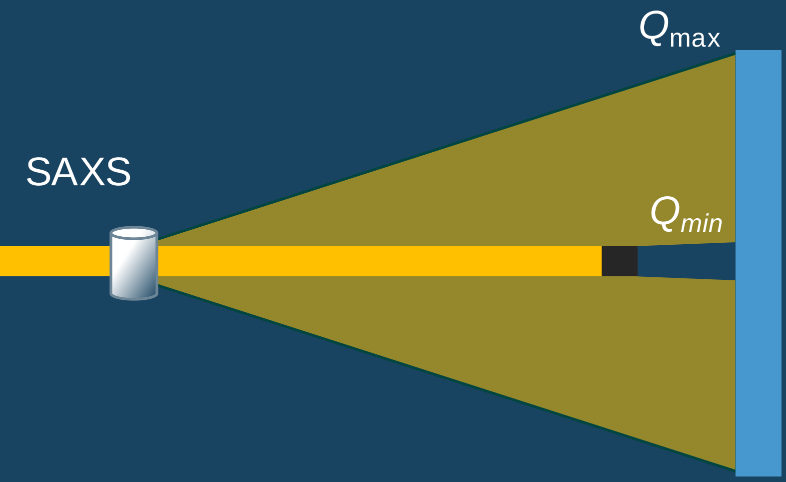




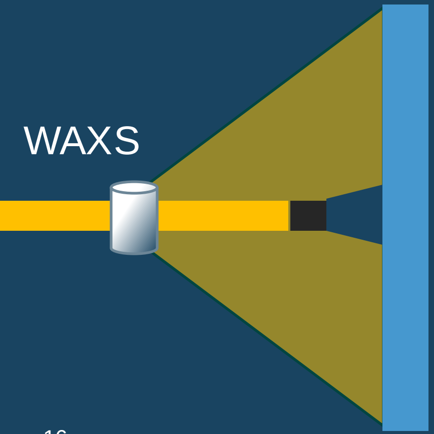
WAXS

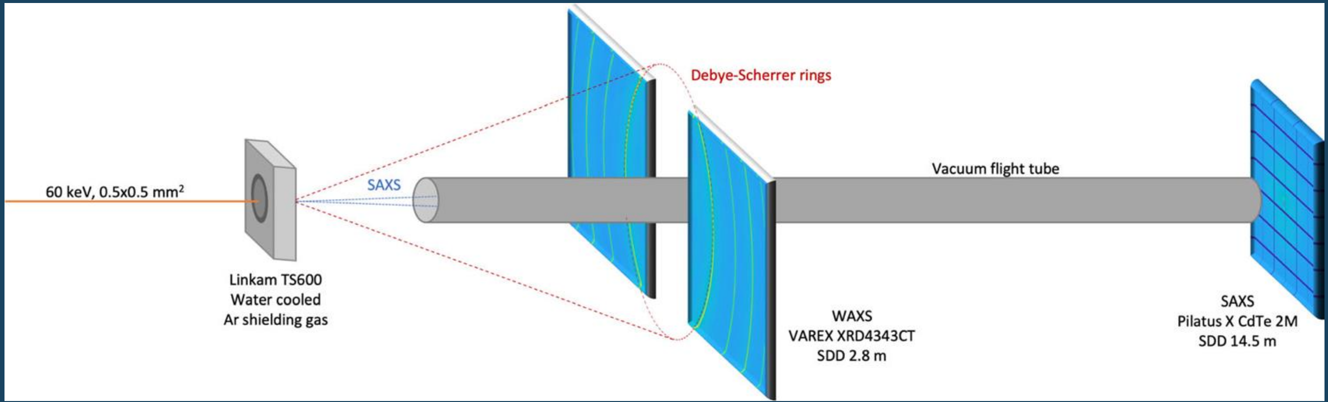



Debye-Scherrer rings
Vacuum flight tube
60 keV, 0.5x0.5 mm²
SAXS
Linkam TS600
Water cooled
Ar shielding gas
WAXS
VAREX XRD4343CT
SDD 2.8 m
SAXS
Pilatus X CdTe 2M
SDD 14.5 m

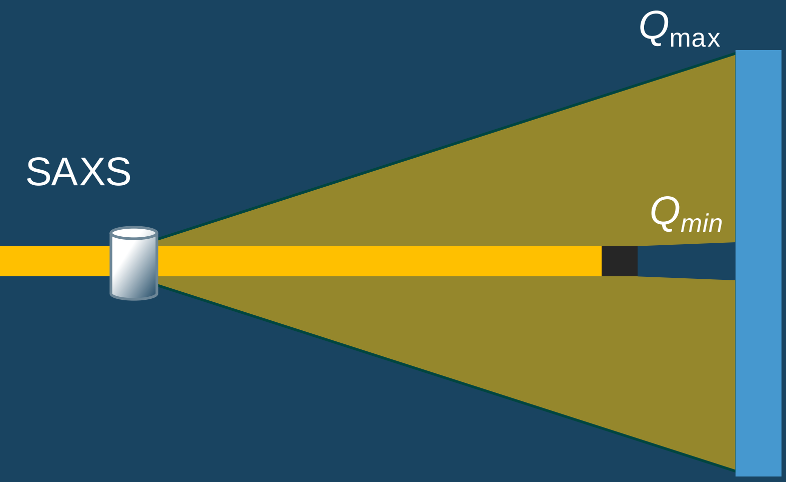


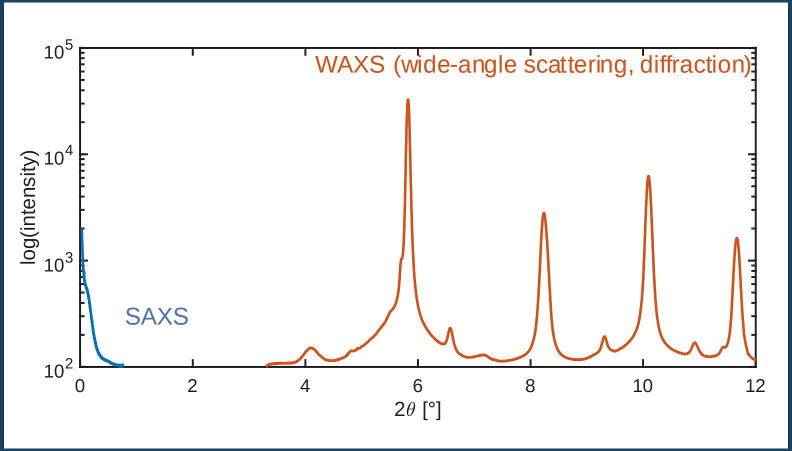
- For SAXS the *Q*-range is extremely important – it defines the size range of objects which can be resolved
- *Q*-range depends on detector size and distance, photon energy, beam stop
- Requirements often in competition with WAXS – a compromise is required



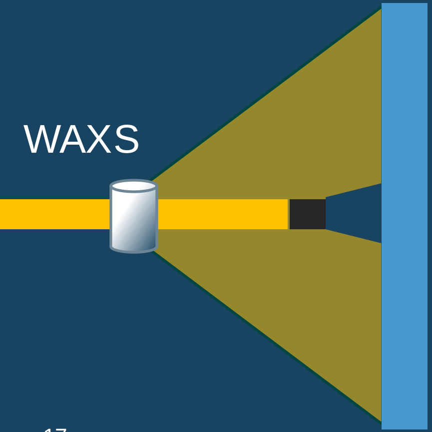


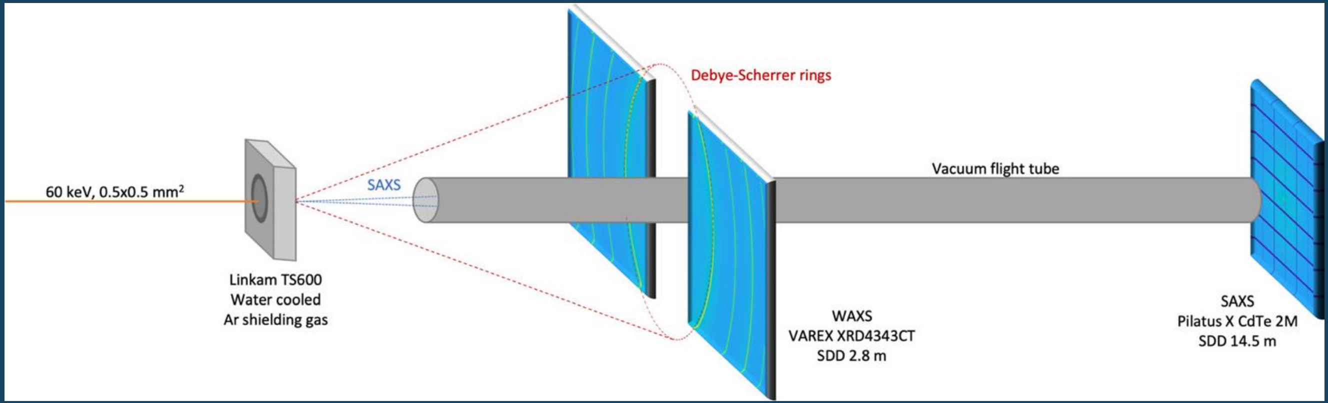
SAXS


Q_{max}
Q_{min}

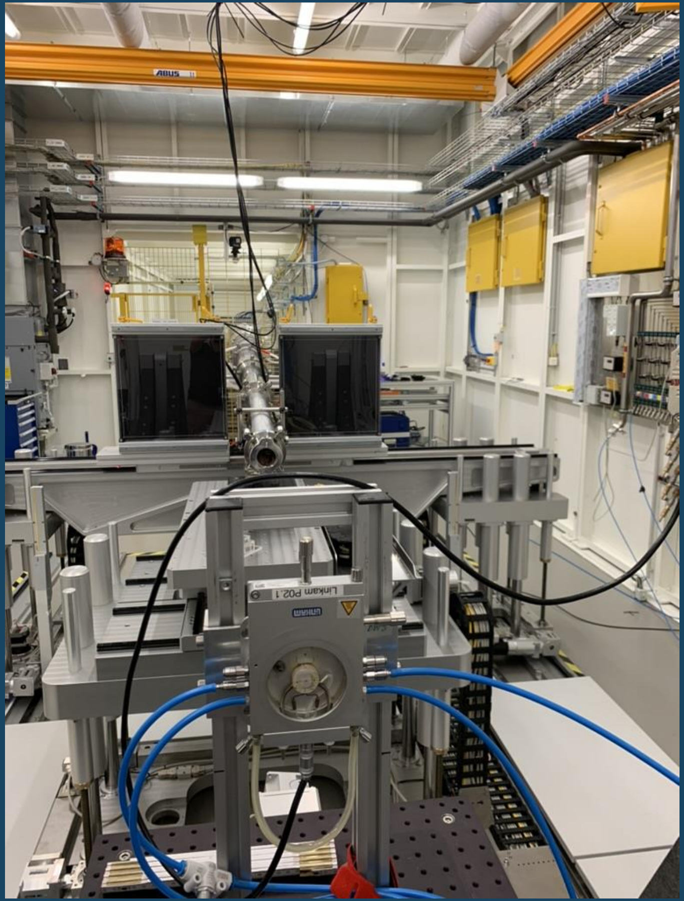

WAXS (wide-angle scattering, diffraction)
SAXS
log(intensity)
10^5
10^4
10^3
10^2
0
2
4
6
8
10
12
2θ [°]

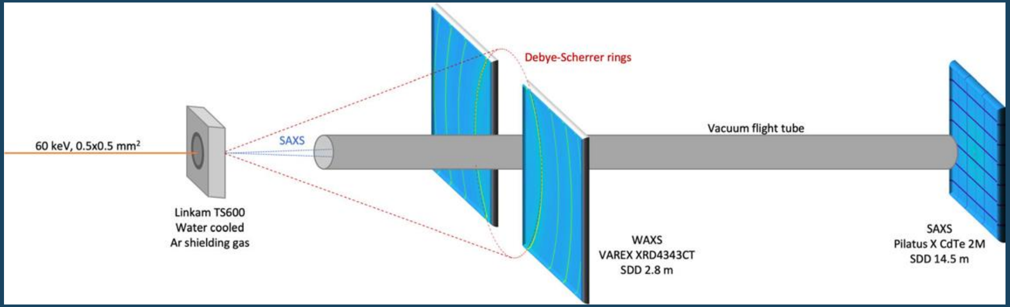
WAXS

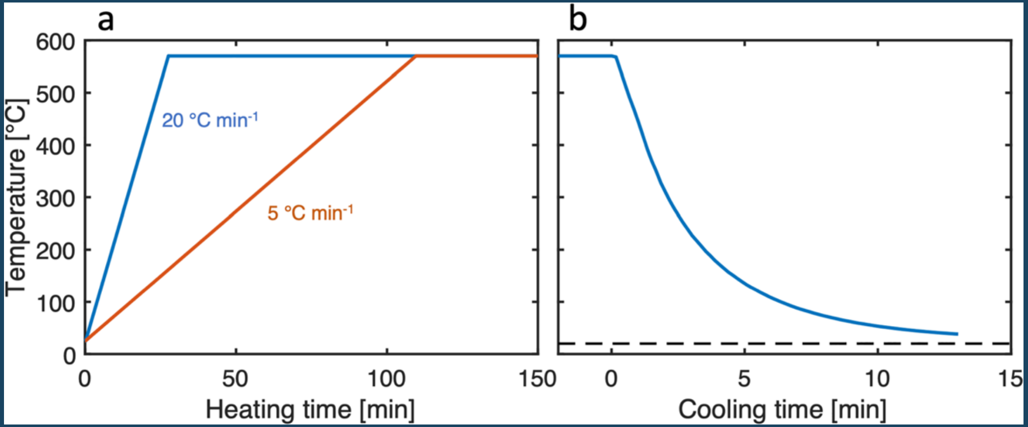


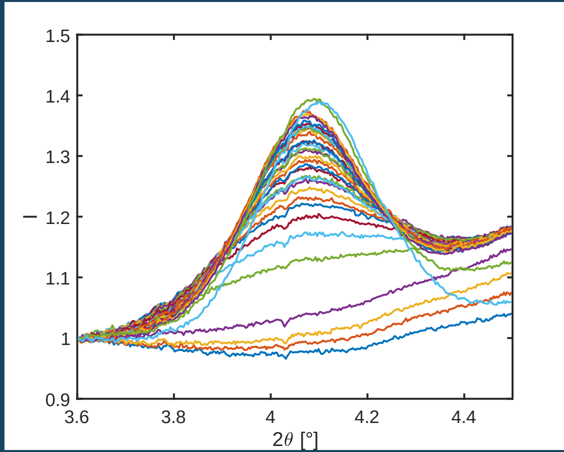

Debye-Scherrer rings
60 keV, 0.5x0.5 mm²
SAXS
Vacuum flight tube
Linkam TS600
Water cooled
Ar shielding gas
WAXS
VAREX XRD4343CT
SDD 2.8 m
SAXS
Pilatus X CdTe 2M
SDD 14.5 m

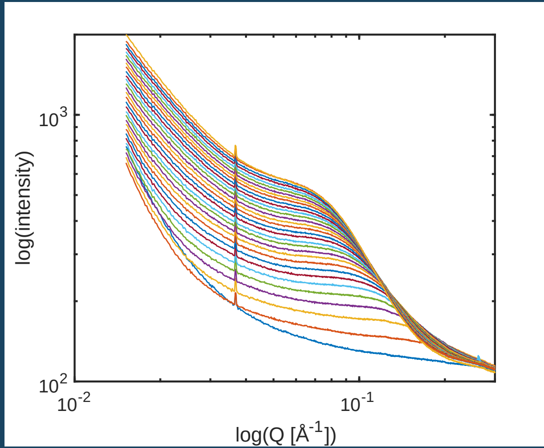
Ageing of Hybrid 55 and Hybrid 60 at 545 °C (7 h) and 570 °C (4 h)

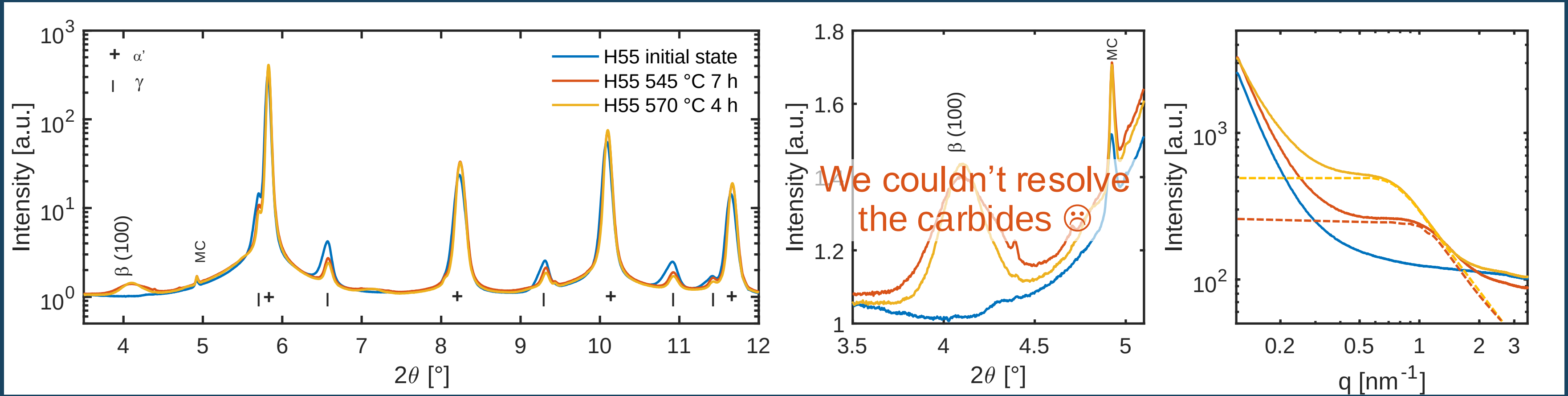












We couldn't resolve the carbides ☹

Data analysis

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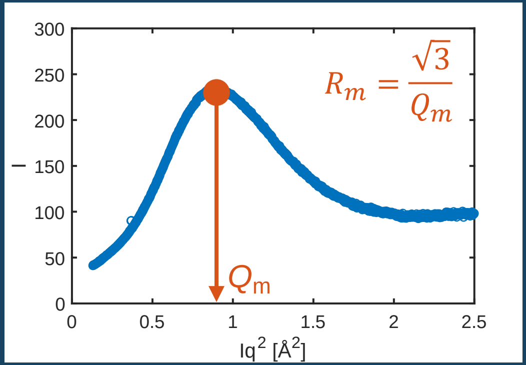
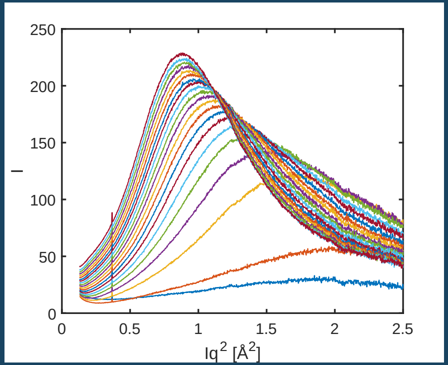
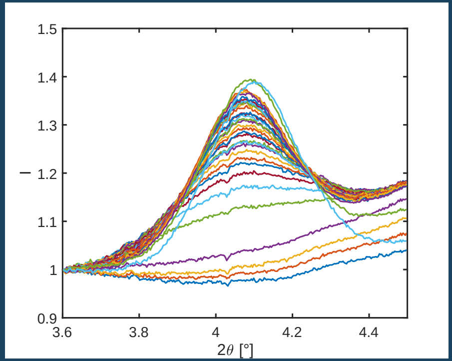
- The *Q*-range in the SAXS data was not enough to allow model fitting
  - The volume of NiAl fraction could **NOT** be approximately determined from SAXS
  - The mean size was extracted from the ”Kratky plot”
  - $R \approx R_m$ **ASSUMING TYPICAL SIZE DISTRIBUTIONS**
- Volume fraction was determined from the relative intensity of the (100) NiAl and (200) α’ peaks
  - **ASSUME** $(Ni_{0.4}Fe_{0.1})(Al_{0.4}Fe_{0.1})$
  - Approximate DW factors

$$V_\beta = \left(I_\beta^{100} / R_\beta^{100} \right) / \left(I_\beta^{100} / R_\beta^{100} + I_{\alpha'}^{200} / R_{\alpha'}^{200} \right)$$

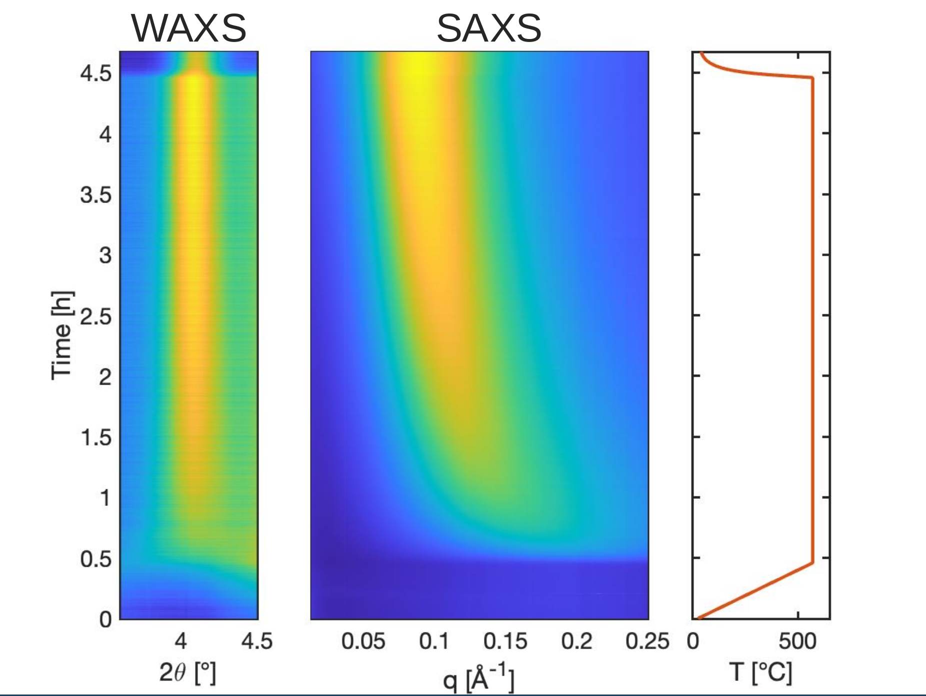
$$R_p^{hkl} = v^{-2} F_{hkl}^2 mLPe^{-2W}$$



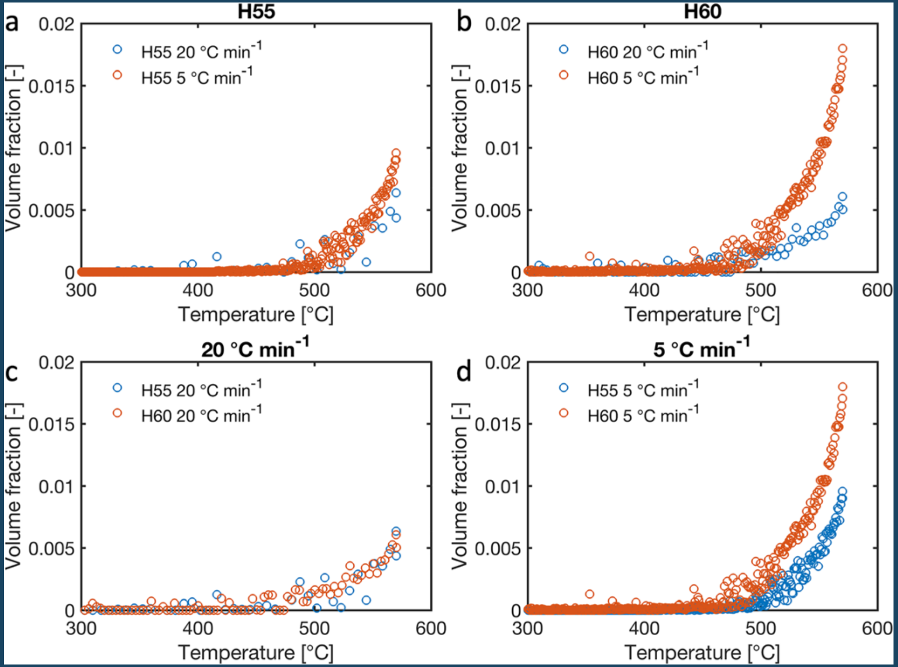


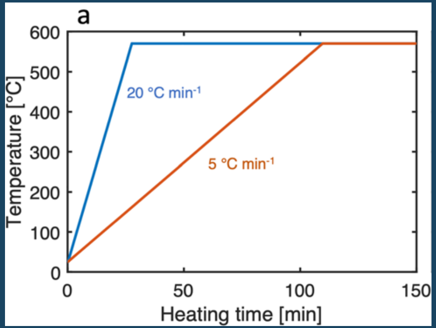


Time-resolved data with 10 s temporal resolution throughout the ageing

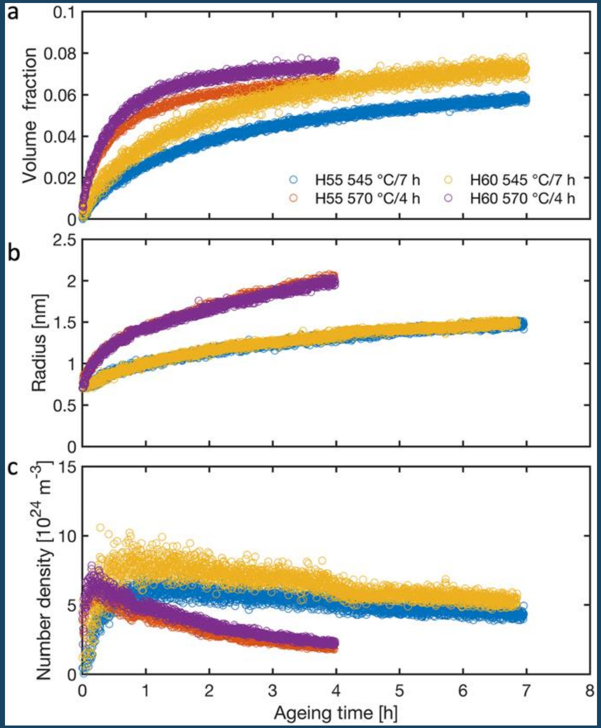


Precipitation starts already during heating





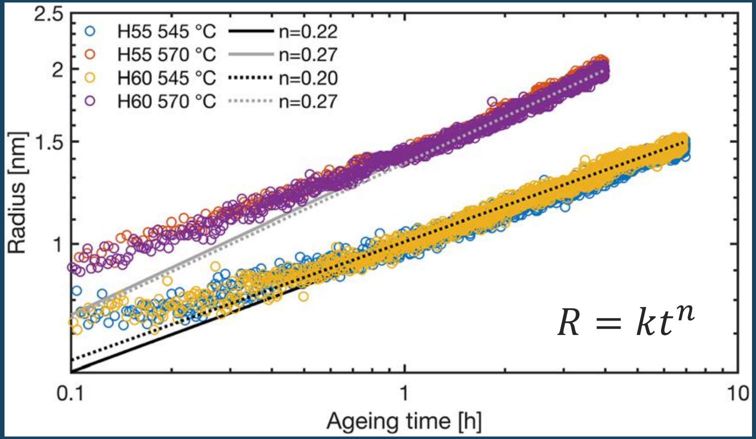
Precipitation kinetics



Bulk diffusion: *n*=0.33

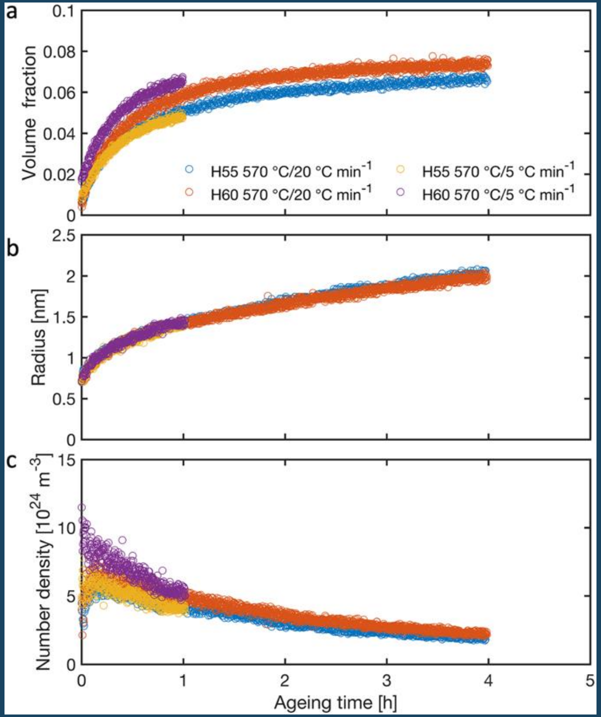
Dislocations/low angle boundaries: *n=0.25*

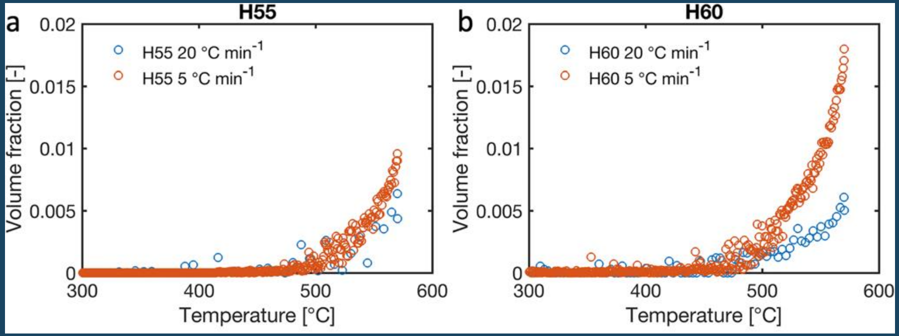
High angle boundaries: *n*=0.2



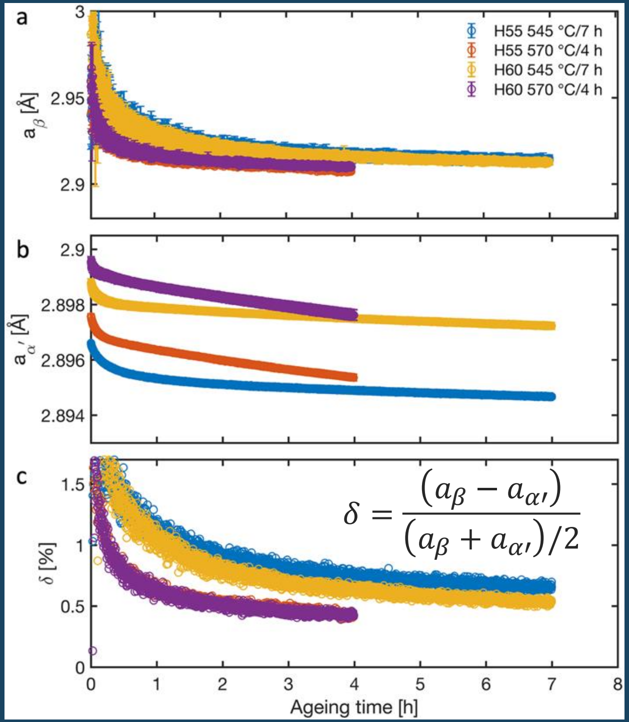
$$R = kt^n$$

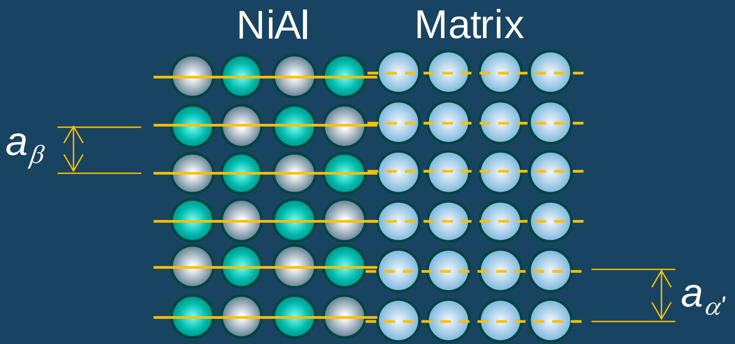
Influence of heating rate

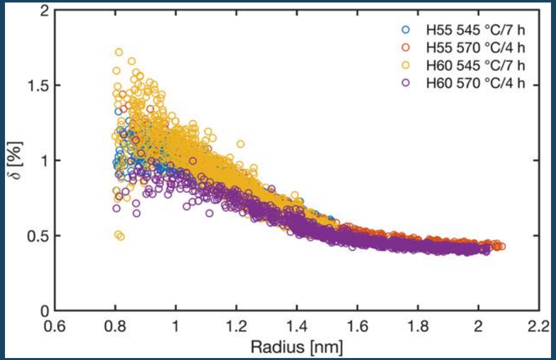




Development of lattice mismatch

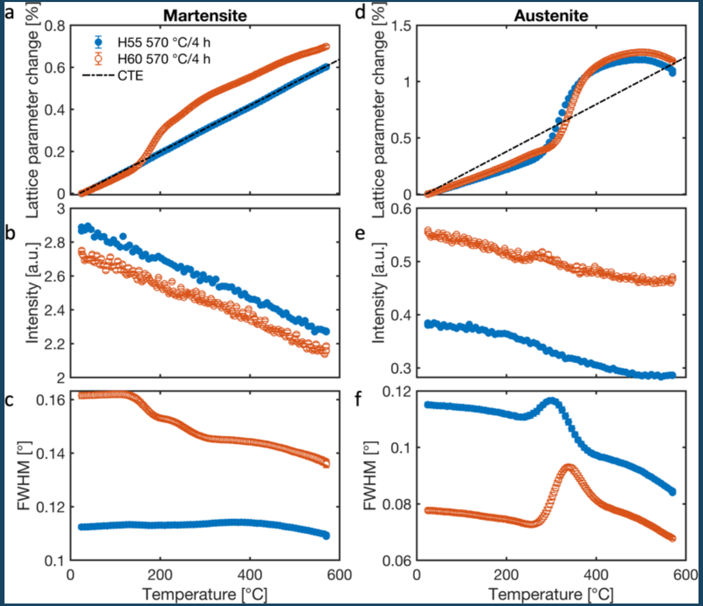


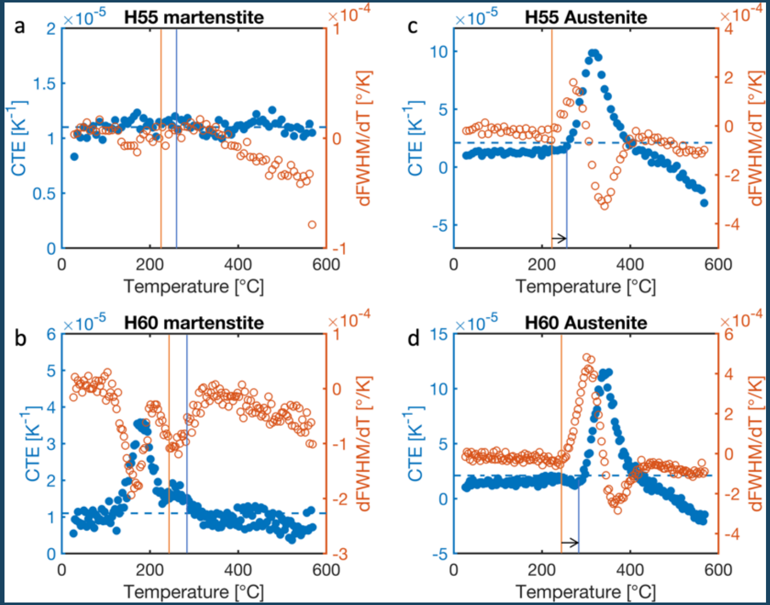




What about the matrix?

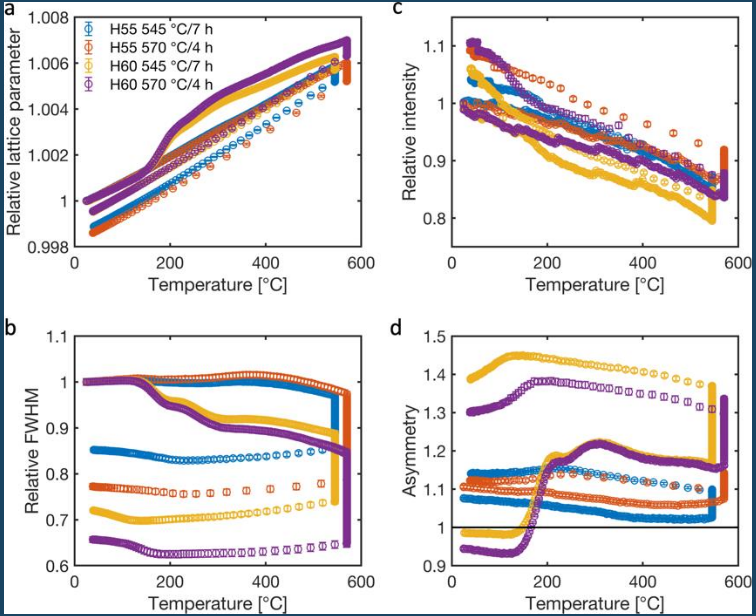
Behaviour during heating

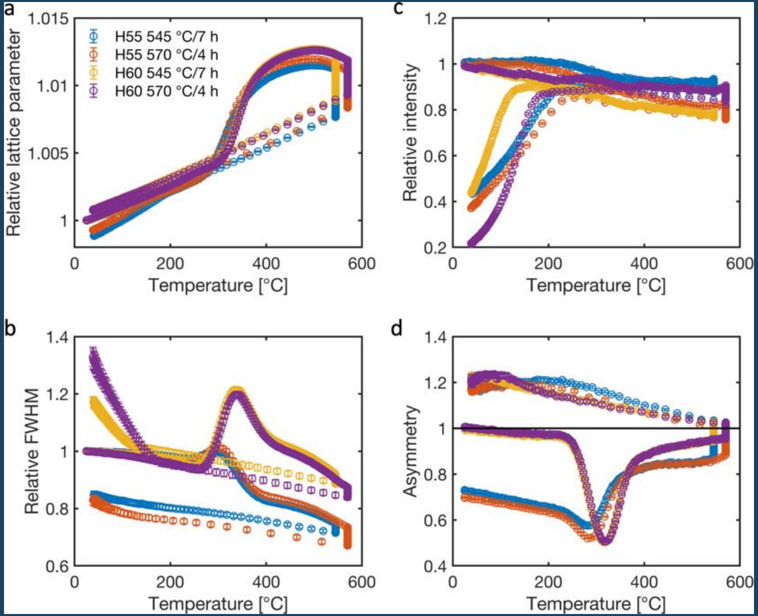




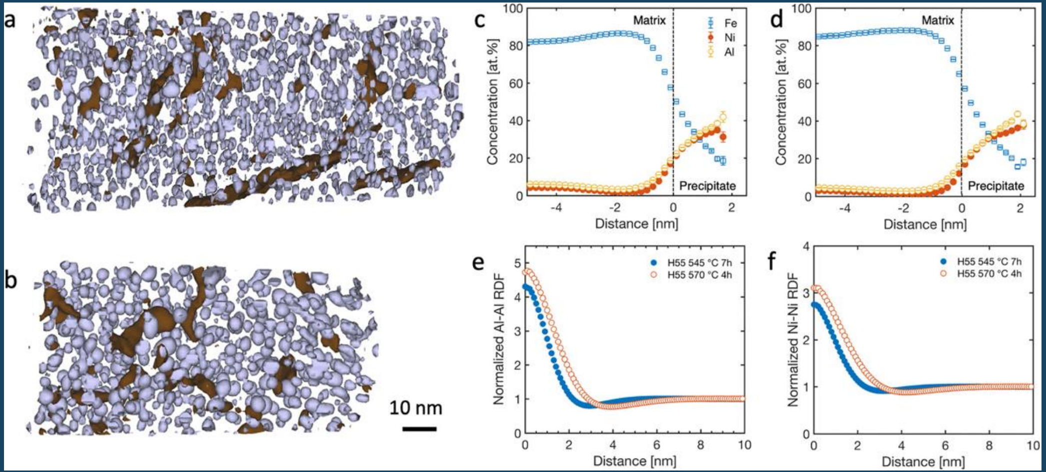
What about the matrix?

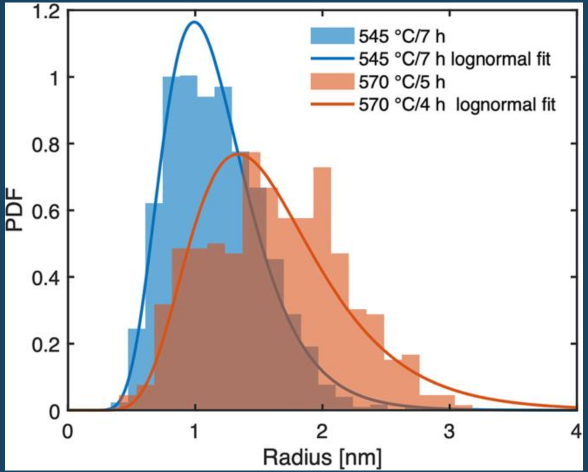
Through-cycle development





Cross-check and validation using atom probe tomography





- Assumed chemistry of NiAl seems valid (good news for volume fraction determination)
- Atom probe analysis after full ageing shows slightly larger particle sizes
- Can be explained a polydispersity slightly larger than assumes

Take-home messages

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Time-resolved in situ investigations provide much **more details** than conventional investigations of pre/post heat treatment – and **removes** sample-to-sample and treatment-to-treatment **variations**

Combined SAXS/WAXS measurements are extremely useful to provide a **complete picture** of the precipitation processes in metallic materials

SAXS analysis is generally **more complex** than diffraction – **complementary data is often necessary**

Talk to the experts at the facilities and in your network and make sure you plan your experiment well!

More reading

Most of the content of this presentation is available here:

Magnus Hörnqvist Colliander, Steve Ooi, Kristina Lindgren, Timo Müller, and Mattias Thuvander: *In Situ Measurements of NiAl Precipitation During Aging of Dual Hardening Hybrid Steels*. Metal. Mater. Trans. 55A (2024) 4146. d*oi:* 10.1007/s11661-024-07536-z

For more information on SAXS for precipitation metallic materials have a look at these:

Alexis Deschamps and Frédéric De Geuser: *Quantitative Characterization of Precipitate Microstructures in Metallic Alloys Using Small-Angle Scattering.* Metall. Mater. Trans. 44A (2013) 77. doi:10.1007/s11661-012-1435-7

Frédéric De Geuser and Alexis Deschamps: *Precipitate characterisation in metallic systems by small-angle X-ray or neutron scattering.* Comptes Rendus Physique 13 (2012) 246. doi:10.1016/j.crhy.2011.12.008

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