TECHNICAL REPORT

Streamlining
in-situ SAXS/WAXS
heat treatment experiments
at the
PETRA III Swedish Materials Science beamline

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The PETRA III Swedish Materials Science beamline is a high energy X-ray beamline, which was commissioned for research and innovation in materials science and engineering. This beamline is tailored to particularly suit the research interests of the Swedish community.

In-situ/-operando measurements are a key opportunity that the Swedish Materials Science beamline offers. In particular, this beamline's combined SAXS and WAXS (Small- and Wide-Angle X-ray Scattering) instrument setup provides the possibility to capture quantitative information about materials that comprise of structures in a wide range of length scales.

This SAXS/WAXS setup has been refined, resulting in an instrument with outstanding capability. The outstanding SAXS/WAXS capability can provide researchers with new insights into heat treatments because phase information and precipitate information can be captured simultaneously - at temporal resolutions down to 1 second. This enables the kinetics of precipitation and phase transformations to be assessed in detail, *i.e.* microstructural evolution can be quantitatively tracked.

This report therefore aims to enable more Swedish researchers to make the most of the heat treatment research opportunities that the combined SAXS/WAXS instrument setup offers.

Using the heat treatment of martensitic steels that contain precipitates as an example, this report presents a description of how to streamline the research process - from preparing beamtime proposals at your home lab to analysing the beamtime data. Process descriptions are brought to life using information from the research case, with the case also exemplifying details of each stage of the research process.

This report starts with an introduction to the case as well as the PETRA III Swedish Materials Science beamline, and its combined SAXS/WAXS instrument setup. The streamlined research process, and its various stages, are presented and exemplified. In these descriptions, references are also provided so that researchers can go further and delve deeper into details.

Contents

1. Introduction and research background

Heat treatment is an important aspect of steel production processes because the performance of a steel is determined by its microstructure, where that microstructure is determined by the heat treatment parameters.

The heat treatment of martensitic steels includes an austenitisation stage, where the steel is heated to obtain the high-temperature austenite phase, followed by rapid cooling to form martensite, and a tempering step through which the as-quenched brittle martensite is held at an intermediate temperature to enhance ductility. This tempering process softens the martensite matrix. To compensate for the matrix softening, secondary precipitation phases are therefore often stimulated to harden the steel.

The need to design the next generation of high-performance steels is now stimulating research efforts for gaining an improved scientific understanding of the evolution of microstructures during heat treatment. This motivates undertaking simultaneous SAXS/WAXS measurements during *in-situ* heat treatment.

Our research case arose from this motivation. The case used to exemplify the streamlined research process also demonstrates the new knowledge that was gained from simultaneous SAXS/WAXS measurements. The research case concerns carbide precipitation in martensite during tempering of a high-performance martensitic steel, where the research goal was to understand the recovery of martensite and the precipitation kinetics to tailor the properties of this type of martensitic steel. The nominal chemical composition of the steel is Fe$-$0.17C$-$0.5Si$-$0.8Mn$-$1.4Cr$-$0.8Mo$-$0.85V$-$0.7Ni (wt.%). Samples were solution treated at 1100 ˚C for 1 h, and quenched in water to form martensite, before they were prepared for SAXS/WAXS measurements during *in-situ* tempering.

Conducting simultaneous SAXS/WAXS measurements during *in-situ* tempering treatment offers a way to quantitatively track microstructural evolution. The WAXS signal enables the monitoring of secondary phase formation and dissolution, providing their phase fractions, and monitors the martensite recovery. Meanwhile, the SAXS signal allows for the extraction of precipitate evolution in terms of the average size of the precipitates. Moreover, the volume fraction of precipitates can also be extracted from the SAXS signal, under the proviso that additional information such as the chemical composition and crystallographic structure of the precipitates (crystallography can be directly analyzed from the WAXS signal) is available. However, when two precipitate populations are present with similar precipitate sizes, SAXS data alone may not distinguish their scattering contributions. To distinguish scattering contributions in such cases, the SAXS/WAXS research needs to be supplemented with additional data.

With the aim of supporting researchers to approach *in-situ* SAXS/WAXS measurements on precipitation kinetics and microstructural evolution during heat treatment more easily, this report provides an overview of the research process $-$ from planning to result.

2. The facility and experimental setup

The Swedish Materials Science (SMS) beamline at the PETRA III synchrotron in Hamburg is a cutting-edge facility dedicated for advancing materials science research using high energy X-rays. The SMS beamline has two branches, P21.1 and P21.2, each of which were tailored to accommodate various instrument setups.

The P21.2 branch is designed for a combination of SAXS, WAXS and imaging measurements of bulk materials and surfaces. The energy of the X-rays can be set in the range of 40−150 keV. (This beamline is designed to complement low energy X-ray sources (≤ 38 keV) such as the MAX IV Laboratory, Lund, Sweden.)

The particularly high energy X-rays at the SMS beamline provide several advantages when conducting materials science experiments. High energy X-rays have a high penetration power, enabling non-destructive probing of bulk materials with several mm, even cm, thickness (depending on the material).

High energy can also help to reduce the influence of air scattering on the measurements - reducing measurement noise.

High energy X-rays also enable the study of large-scale (mm-scale) samples in transmission geometry, where the scattering is concentrated in the forward direction with minimal polarisation effects on the signals.

Reference [1] provides more information about the SMS beamline. A previous CeXS report [2] also provides information about the variety of sample environments that are available for research experiments at the SMS beamline.

2.1. Small- and wide-angle X-ray scattering (SAXS/WAXS)

In steel research, Wide-Angle X-ray Scattering (WAXS) signals can be used to monitor the formation and dissolution of secondary phases; and, Small-Angle X-ray Scattering (SAXS) signals can be used to monitor particles, such as precipitates, in the range of 1 - 100 nm. The instrument setups for SAXS and WAXS measurements are illustrated in Figure 1 and the details of these instrument setups and measurement possibilities are described below.
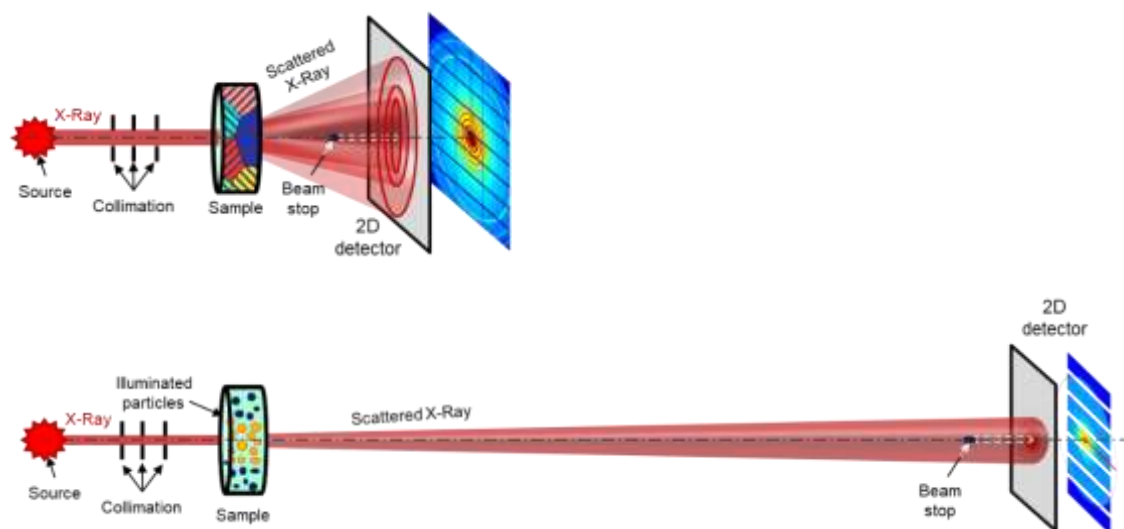
Figure 1. Schematic illustrations of WAXS (top) and SAXS (bottom) instrument setups.

When X-rays have high energies, the generated diffraction peaks have low angles, allowing for an easier collection of complete diffraction rings on area detectors. This enables the simultaneous acquisition of a broad range of reciprocal space, directly related to the lattice planes in real space. For the analysis of steels, we can therefore use Wide-Angle X-ray Scattering (WAXS) signals to monitor the formation and dissolution of secondary phases, which is illustrated in Figure 1's top diagram.

Analysis of WAXS signals enables precise measurement of the inter-atomic spacing within crystalline phases present in the material, where those crystalline phases can be both the matrix and precipitates. However, the precipitates are often of much smaller volume fraction and size, which leads to reduced intensity and increased broadening of the diffraction peaks. Precipitates' diffraction peaks are therefore more difficult to analyse than the matrix. Nevertheless, despite this difficulty, *in-situ* WAXS experiments yield valuable information, including:

- Evolution of lattice parameter, calculated from the peak position changes during the thermal cycles.

- Monitoring of phase fractions with thermal cycles, offering insights into phase transformation (which is more precise for the majority phases).

- Estimation of crystalline defect density evolution, such as dislocation density, from the peak broadening evolution with the scattering vector.

- Measurement of lattice strain through shifts in peak position with azimuthal angle.

In our steel research case, SAXS is a powerful tool to measure precipitates. This measurement possibility arises because the precipitates are significantly larger than the wavelength of the X-rays. Therefore, the precipitates scatter an X-ray signal at low q-values (or small angles). That is, in SAXS measurements the precipitates themselves scatter the X-rays – not their crystalline lattice (the crystalline lattice of the precipitates can be detected in WAXS as described above). It is worth noting that even non-crystalline phases and porosities can be measured by SAXS in certain cases.

From the position of this scattering, an average size of the precipitates can be retrieved, while the scattered intensity is related to both the volume fraction of precipitates and their contrast with the matrix.

In metal systems, retrieving the size distribution of precipitates can be challenging at high q-values because of the scattering signal from the precipitates is relatively low compared to higher signal scattered by the solid solution (matrix). To overcome this challenge, it is common practice to fix the size distribution of the precipitates to a pre-defined shape, such as lognormal distribution with a specified dispersion value (here 20%). This approach is supported in cases where the size dispersion values can be estimated well from laboratory microscopy techniques.

Thus, typical outcomes from *in-situ* SAXS experiments include:

- Tracing the evolution of precipitate average size with thermal cycles.

- Monitoring changes in precipitate volume fraction with thermal cycles, provided the composition and crystallographic structure of the precipitate phase are known.

2.2. Furnace sample environment

To conduct experiments using the SAXS/WAXS instrument for a specific *in-situ/-operando* experiment requires a sample environment that subjects the metals to the heat treatment process parameters that are under investigation. The Swedish Materials Science beamline supports a variety of furnaces [2].

In the studied case, a Linkam TS1500 furnace was used. A photograph of this furnace is shown in Figure 2 and more information about the furnace is available from the manufacturer [3]. This furnace allows thermal heat treatment in the temperature range from room temperature up to 1500 °C, with a heating/cooling rate ranging from 0.1 to 200 °C/min with temperature fluctuations of less than 1 °C.

The furnace supports the use of gas (*e.g.* Ar) or vacuum environments to protect the samples from oxidation. In practice, a protective gas atmosphere is preferred. The maximum sample size that the furnace can accommodate is around 7 mm in diameter and 6 mm in thickness. Note. To avoid the risk of damaging the furnace, sample sizes should have a safety margin that takes into account the thermal expansion of the sample during the experiment.

Figure 2. The Linkam TS1500 furnace sample environment [3].

2.3. SAXS/WAXS with the furnace setup

Figure 3 shows the Linkam TS1500 furnace sample environment in a simultaneous SAXS/WAXS instrument setup at the SMS beamline. The bottom photograph shows the entire experimental setup, and depicts the path of high energy X-ray beam in red. The beam travels from right to left. Photographs at the top show details at various points along the X-ray beam path.

At the right, after some optics, the X-rays encounter the sample material that is loaded in the Linkam TS1500 furnace. Some of the high energy X-rays are transmitted directly through the sample. Some of the X-rays interact with the sample and are scattered.

The X-rays that are scattered at wide angles are collected by a grid of four VAREX detectors (XRD-4343CT-F22-C-060), which are located a short distance behind the furnace.

X-rays scattered with small angles travel through a ~15 m long vacuum tube (to reduce air scattering), after which the SAXS signal is collected by a Pilatus 2M detector.

Each VAREX detector has an array size of 2880 × 2880 pixels with pixel size of 150 μm × 150 μm. The typical collection time for the VAREX detector ranges from 0.1 to 8 s. The Pilatus 2M detector has an array size of 1475 × 1679 pixels with pixel size of 172 μm × 172 μm. The typical collection time for the Pilatus detector ranges from 2 ms to 10 s.
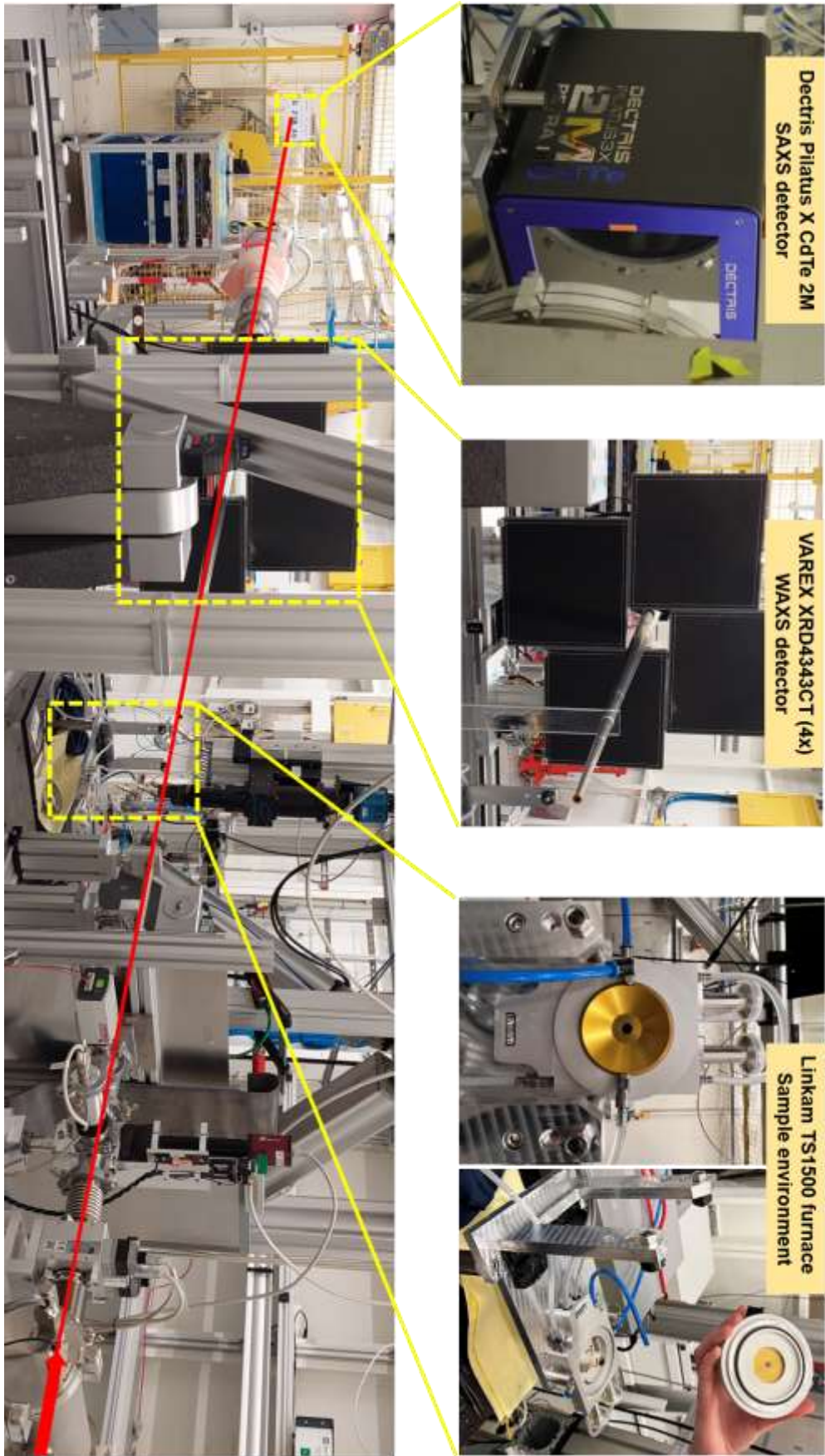
Figure 3. The experimental setup for simultaneous SAXS and WAXS measurements using a furnace sample environment at the PETRA III Swedish Materials Science beamline.

3. Streamlined research approach and its various stages

This section describes the research process using a furnace sample environment to study the case of carbide precipitation during tempering of martensite. The stages are beamtime proposal preparation, experiment preparation and beamtimes followed by data analysis

3.1. Beamtime proposals for gaining access to the SMS beamline

Researchers have options for gaining access to the SMS beamline. When results need to be kept confidential, it is necessary to pay for beam time. When results can be published, then researchers have the option to prepare a scientific proposal for using the SMS beamline - without being charged an access fee.

For the latter scientific proposals, the PETRA III beamtime application portal, DOOR, typically has submission deadlines of 1st March and 1st September. If the project leaders are affiliated to Swedish universities, research institutes and companies, selecting the 'Sweden's Privileged Access' enhances the chance of the beamtime proposal getting granted. For more information see cexs.kth.se/.

The proposal's scientific merits and feasibility are evaluated before a decision is taken to grant beam time access. Users therefore ought to actively motivate that there is a strong science case and that there is a feasible case for obtaining publishable research results. Thus, to ensure the scientific importance and feasibility criteria are demonstrated to the evaluators, some preparation work and pre-study activities are advised. It is similarly advised to collaborate with someone who has expertise in SAXS/WAXS experiments in the beamtime proposal as well as to have some discussions with the beamline scientists. Sometimes the beamtime scientists may offer to conduct a feasibility test prior to submitting the proposal.

In the beamtime proposal, a concise description of the scientific background and motivations, the research team's skills in synchrotron X-ray measurements on related topics, experimental plan, expected results and impact ought to be provided as well as provide important references including own references, *etc*. Under the experimental plan, a justification of the requested beamline and beamtime is expected, along with a description of samples and safety related issues as well as technical information about the experimental setup and sample environment. Data analysis approaches may also be important to describe if these are crucial to obtaining research results.

In the case example, when preparing the beamtime proposal we drew upon previous work using computational thermodynamics and kinetics as well as experiments using WAXS and atom probe tomography. This work is now published by Zhou et al (2023) [4]. The key results that we presented to motivate the beamtime proposal's science case are summarised in Figure. 4. These results were TC-Prisma simulations which suggested that metastable cementite firstly forms before dissolving in favor of precipitation of the stable MC carbide during 600 ˚C tempering. Synchrotron WAXS/X-ray diffraction (XRD) results showed the appearance of MC phase peaks after 600 ˚C tempering for 2 h. Atom probe tomography found that there was a high number density of V- and Mo-rich carbides, mostly around the martensite boundaries [4]. Thus, from this data in the beamtime proposal, the science case was evident: *in situ* beamline measurements would provide new and useful *quantitative* information about kinetics of this metal system during the heat treatment process.
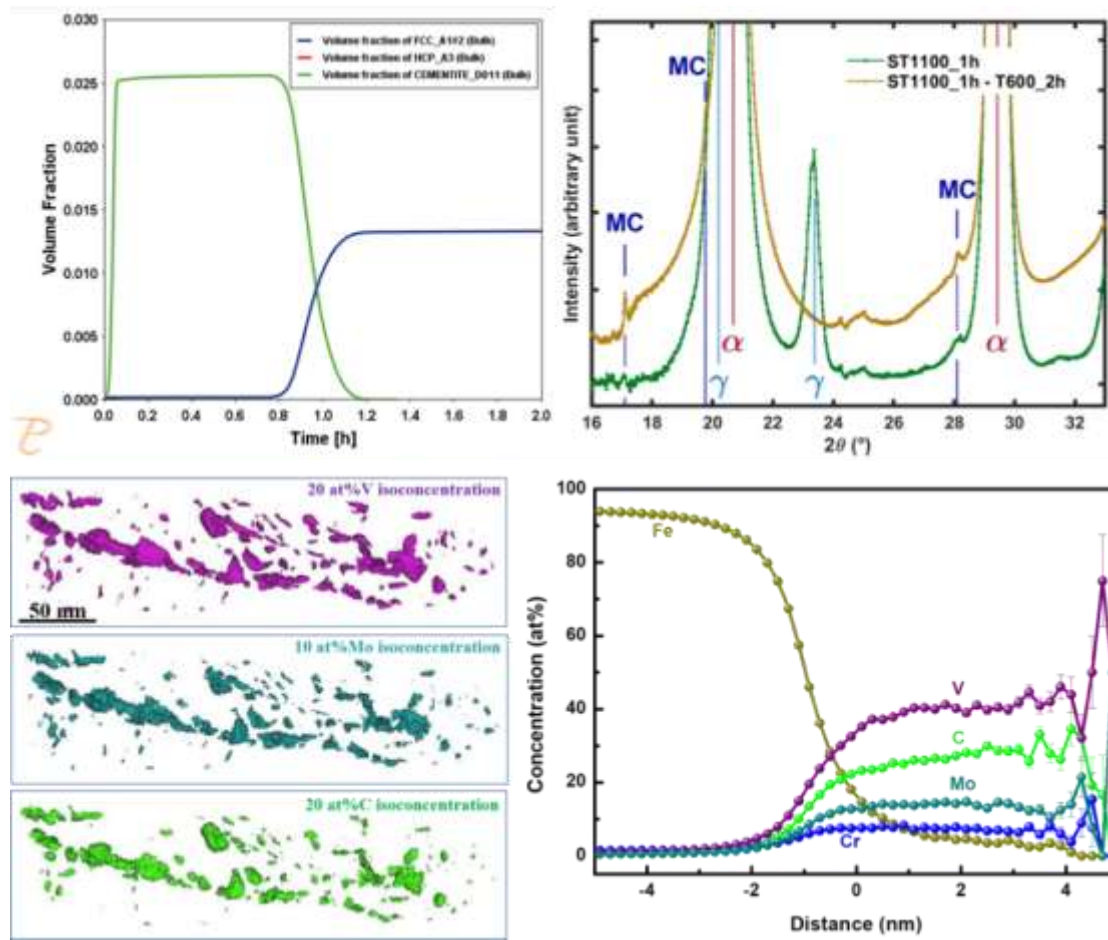
Figure 4. TC-Prisma simulation of carbide precipitation kinetics at 600 ℃ isothermal treatment (upper left), synchrotron WAXS measurement of the as-quenched and peak-hardened (600 ℃ tempering for 2 h) samples (upper right), atom probe tomography results of V- and Mo-rich carbides in the peak-hardened sample (bottom left), and the quantification of the average chemical composition of the carbides (bottom right) [4].

3.2. Beamtime preparations

Once the proposal gets granted and the beamtime date is set, it is good practice to make an early start to prepare for the measurements. The lead time in preparing good samples for examples can take some weeks - depending on the state the material is in, sample geometry and how many samples are planned for the specific case.

The sizes of the samples that need to be prepared is partly determined by the sample environment. The Linkam furnace in the research case allows sample size in maximum of Φ7 mm. The sample thickness is determined from both the sample environment (as it can limit the sample dimensions) and the X-ray energy that is planned to use. For SAXS, the scattering length density difference, *i.e.* the contrast between the matrix and precipitate can be calculated based on their chemistry and structure. The scattering length density difference and the volume fraction of precipitate determine how easily the evolution of precipitation can be captured from the SAXS. Researchers are therefore advised to make calculations of X-ray absorption (through *e.g.* [5]) of the planned samples under certain X-ray energies, which can guide the determination of sample thickness for the measurements.

As a general guideline, a sample thickness of around 2 to 3 times the absorption length (thickness at which the sample have a 37% transmission) of the investigated material, is a reasonable value to conduct SAXS experiments. However, the desired transmission level for a successful SAXS/WAXS measurement is very much dependent on the material (composition, grain size, *etc*.) and the expected results (such as precipitation kinetics by SAXS, phase fraction quantification by WAXS, and density of crystal defects by WAXS), all these factors must be taken into account to find a correct transmission value. A dialogue with the beamline scientists is recommended in this regard.

It should also be noted that to perform successful SAXS measurements, a small grain size compared to the volume probed by the X-ray (depending on the beam size and thickness) is necessary. In the research case, samples with dimensions of about Φ5 mm × 1 mm were used. The samples were prepared by grinding and polishing using silica paper up to grit #1200 for both sides of the samples.

The experimental setup, including X-ray energy, sample to detector distance, *etc*., determines the q-range for the SAXS and the WAXS, thus some calculations are also mandatory to make sure the precipitate size and phases could be captured well in the proper q-range for SAXS and WAXS, depending on the features which need to be observed. The features that need to be observed need to appear within the detected q-range.

The q-range can be calculated from simple formulas given below involving the detector radius R_{det} (which can be the diagonal or smallest side if full rings are needed), the beam stop size R_{BS}, the sample to detector distance D and the X-ray wavelength λ.

$$\theta_{\min} = \arctan\left(\frac{R_{BS}}{D}\right)$$

$$2\theta_{\max} = \arctan\left(\frac{R_{det}}{D}\right)$$

$$q = \frac{4\pi}{\lambda}\sin(\theta)$$

The sample to detector distance D is fixed at the P21.2 beamline due to the flight tube. Thus, only the X-ray energy can be varied to move the observable q-range.

For our research case, the calculated q-range for SAXS was $0.01-0.6$ Å^{-1} with the X-ray energy of 83 keV.

When at your home organisation, it is also advised to prepare your computer system so that you can conduct preliminary data analysis during the beamtime.

3.3. Beamtime measurements

The duration of granted beamtimes varies from case to case but is normally a couple of days. This time includes setting up.

3.3.1 Beamtime setup

The beamtime measurements start with beamline scientists helping with the setting-up of the sample environment and calibration procedures. The calibration procedures can take anything from a few hours to a day.

The calibration procedure is actually crucial to the data analysis process – especially when researchers aim to determine quantitative data about microstructural evolution and kinetics. The calibration procedure, is therefore described more fully in Section 3.4.

After calibration, the researchers at the beamline will get trained how to enter the experimental hutch, change samples, do safety check, write/change macros for the specific measurements, handle bugs, *etc*. After a few times of practicing, the researchers attending the beamtime should be capable of independently conducting the measurements.

3.3.2 Beamtime measurements

In the current research case, three samples were heated up to 550 °C, 600 °C and 650 °C respectively with a heating rate of 100 °C/min and holding for 3 h before cooling to around ambient temperature at a cooling rate of 200 °C/min. Exposure time of 0.1 s for WAXS and 1 s for SAXS were used for the measurements during the whole thermal processes.

3.3.3 On-site data reduction and preliminary data analysis

It is advised to conduct preliminary data analysis during the beamtime in order to ensure that the quality of the captured data is likely to give you the desired results.

Since the data reduction software for SAXS is not available for now at the beamline. The researchers need to use data reduction software such as DPDAK (from DESY) or Dioptas [6] or prepare own codes beforehand to check the recorded 2D SAXS data on-site and tune the plans for the measurements.

Without own SAXS data reduction, what the researchers can see are the 2D data for the SAXS, 2D and 1D data for the WAXS (*Figure 5*), and their evolutions with the thermal cycles.
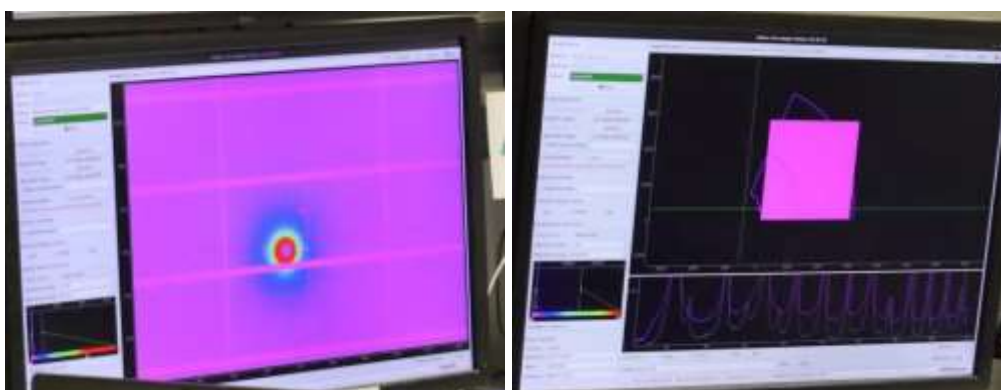
Figure 5. The monitoring of SAXS (left) and WAXS (right) data during thermal treatments.

3.3.4 Data storage

A more comprehensive, and time demanding, data analysis process is typically undertaken after the allocated beamtime period.

Therefore, during the beamtime measurements, data needs to be captured and stored. The data can be gathered using storage device transfer at the beamline

or for later by the Gamma portal using the FTP protocol to download to the researchers' home site.

## 3.4. Comprehensive data analysis

After the beamtime, researchers ought to reserve some time for more comprehensive data analysis. The data assessment procedure involves data reduction, which includes calibration, and various data analysis stages described below.

3.4.1 Data reduction, including calibration

With data reduction, the output was 1D plots from the measured 2D images for both the WAXS and SAXS. For the example case, these plots were obtained using our own code when connecting to the DESY server.

For both the SAXS and the WAXS the detector geometry (position in space) must be retrieved to perform the azimuthal integration. This geometry was retrieved thanks to the measurement of a standard sample (see Section 3.3 Beamtime measurements), giving rise to multiple well known diffraction rings when they are irradiated by X-rays.

In the example case, the calibration samples were silver behenate (AgBeh) and lanthanum hexaboride (LaB_6) for SAXS and WAXS, respectively. The diffraction patterns from those two materials are displayed in Fig. 6.
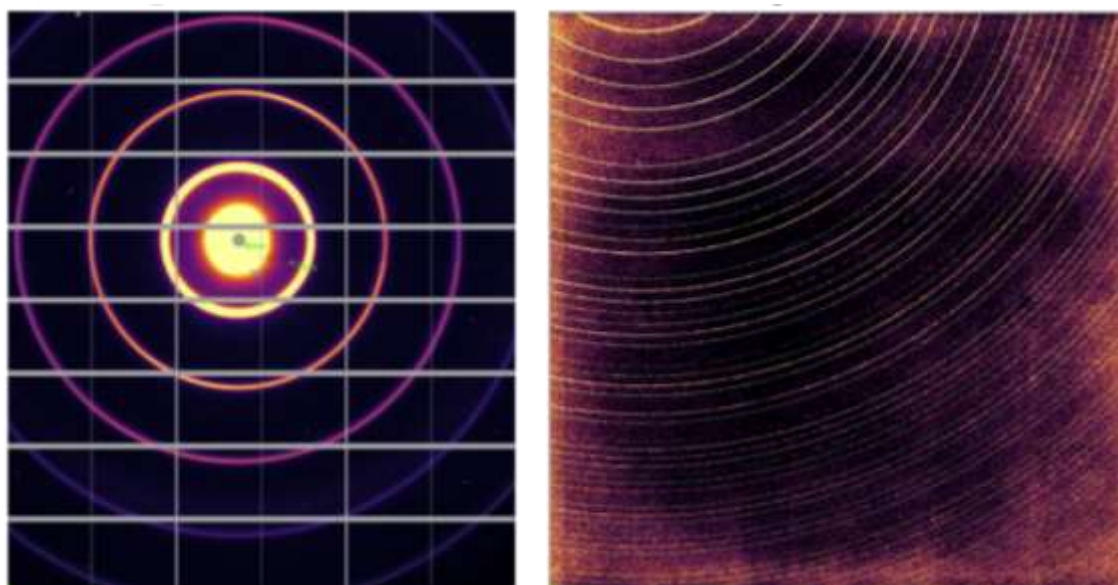
Figure 6. Diffraction patterns on the (left) AgBeh for SAXS geometry calibration, and (right) LaB_6 for WAXS geometry calibration (displayed on one detector).

Once the geometry has been retrieved, azimuthal integration is possible. Then, no additional steps for the WAXS signal are required.

For the SAXS, background subtraction must be performed to retrieve the signal from the sample only. The background of SAXS arises from all potential sources of scattering, reflection, *etc.* – that is, everything else in the measurement system other than the sample. For instance, air can scatter the X-ray beam, even though the air interaction is minimized by the SAXS vacuum flight tube. The Kapton (or

other X-ray transparent materials) windows present on the SAXS flight tube or on the sample environment might give rise to a background as well. To subtract this background, a measurement without sample, but with the same sample environment/holder (in this case the empty furnace) must be captured. As the signal from the background is weak, it is important to set a long counting time for this measurement.

In the example case, we used a 2 min counting time. This counting time was acquired in 120 frames of 1 sec duration (not 1 frame). Counting several times, each with short counting time, is preferred compared to counting one time for a long counting time. The reason for this is that in the latter case, a lot of cosmic rays will be included in the measurement (this is true if the detector is a hybrid pixel technology, like for the Pilatus). Once captured, the background signal must be normalized by the incident flux of X-ray and the solid angle of the detector (or preferably each pixel of the detector, which is then performed during the azimuthal integration). The X-ray incident intensity is estimated thanks to an upstream monitor (ionizing chamber, diode on the beam stop measuring the direct beam, diode measuring kapton fluorescence, *etc*.). In this case, this monitor does not integrate the flux during the measurement but is instead refreshed periodically. Thus, the X-ray intensity from the upstream monitor must be multiplied by the counting time to have the best estimation of the incoming X-ray intensity. The measurement from the sample must be normalised by the incident flux, the solid angle, and the sample transmission and thickness, before being subtracted from the background.

If a quantitative measurement of the SAXS intensity is intended to extract volume fraction of precipitates for instance, then a SAXS intensity normalization is needed. This was performed in the example case thanks to a glassy-C standard from NIST. The materials give rise to a scattering of known shape and intensity (in absolute unit), which can be used to scale the measurements into absolute unit. More details about SAXS intensity calibration can be found elsewhere [7-10]. For more information about SAXS theory in general, the reader is referred to the literature [11-14].

Figure 7 shows the results after data reduction for the measured three samples that were isothermally treated at 550 °C, 600 °C and 650 °C respectively up to 3 h. The SAXS results show precipitation during isothermal holding, and the precipitates' rate of growth increases with the increase in temperature. The WAXS results show the high-intensity peaks that are signals the Fe-BCC matrix, and some changes in the low-intensity peaks that are due to the retained austenite and precipitate phases, during the isothermal holding process.

Figure 8 illustrates the evolution of the Fe-FCC phase (retained austenite) for the measurements at 600 °C, visible on the WAXS detector. It is displaying the dissolution of the retained austenite during tempering. The evolution of the small diffraction peaks coming from secondary phases (such as carbide precipitates) is also displayed in Figure 8, showing the growth of MC carbides and other precipitates.
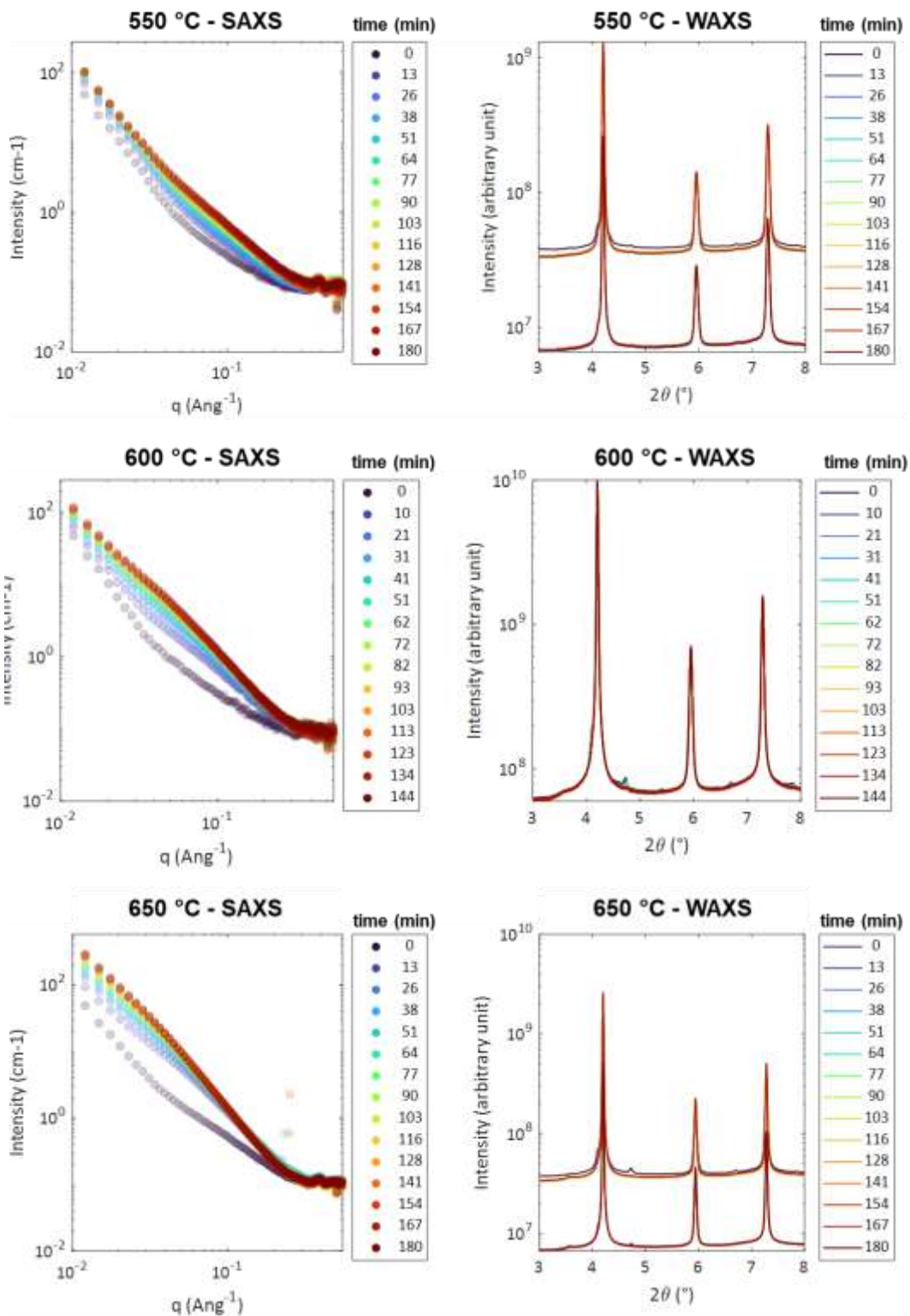
Figure 7. The 1D SAXS (left) and WAXS (right) results after data reduction for the three samples during isothermal holding at 550 °C, 600 °C and 650 °C respectively for 3 h.
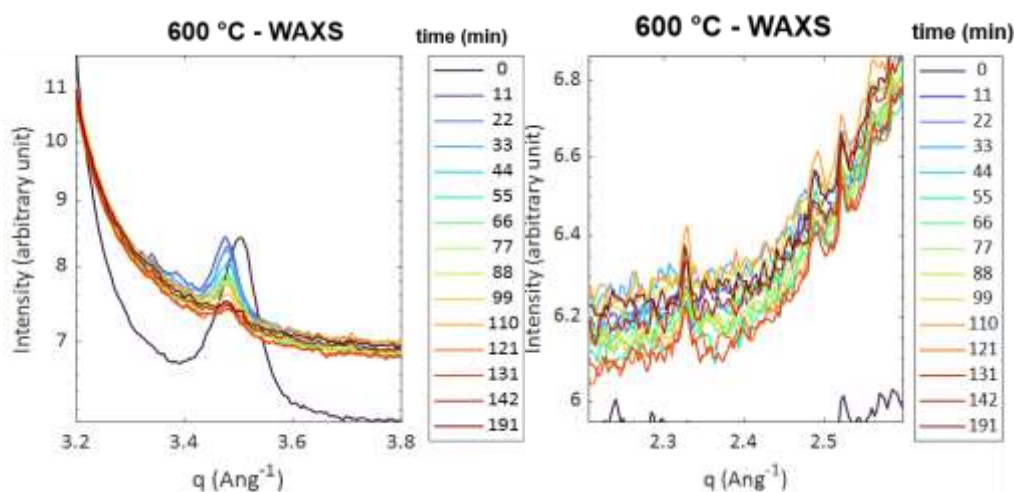
Figure 8. Evolution of the Fe-FCC peak (left) and the secondary phase peaks (right) during the heating up to 600 °C, followed by 3 h holding.

3.5.2 Data analysis

With further data analysis on the reduced SAXS data shown in Figure 7, Figure 9 shows the evolution of precipitate mean radius, and the the squared contrast multiplied by volume fraction of precipitates during *in-situ* thermal treatments of the three samples that were heated up to 550 °C, 600 °C and 650 °C respectively, 3 h holding and cooling. These were analysed using our own code, with methodology described in Ref. [15]. It shows that the mean radius increases from around 1.6 nm to 2.3 nm and to 3.1 nm after 3 h holding when the isothermal temperature increases from 550 °C, to 600 °C and to 650 °C.

From SAXS measurements, the volume fraction cannot directly be retrieved as it is correlated to the contrast (difference between the electron density from the matrix and the precipitates, "as seen" by the X-ray, multiplied by the scattering factor of the matrix/precipitates elements). The volume fraction can only be estimated after making a hypothesis on the chemistry and crystallographic structure of the precipitates, allowing to calculate the contrast. Some input from other characterisation techniques such as atom probe tomography (APT) and transmission electron microscope (TEM) can be valuable to estimate the precipitates chemistry and structure. In addition, microscopy technique can observe the shape of the precipitates, and potentially their dispersion in size, which is invaluable for the SAXS data analysis as well. However, these inputs, especially on the chemical composition of the precipitates should be considered with great care, as in many cases, the chemical composition of precipitates is expected to evolve significantly during nucleation, growth and coarsening, and these evolutions are extremely difficult to catch by destructive techniques such as APT and TEM. Moreover, APT - particularly well suited for chemical composition analysis - suffers from a number of reconstruction artifacts, especially for small size precipitates, which can significantly bias the measured composition [16]. In addition, APT and TEM, in comparison to SAXS, allow the observation of a very small number of precipitates, typically in the order of tens or hundreds compared to billions for SAXS. This should also be considered during the analysis, as the composition may vary depending on the location of the precipitates. The crystallographic structure of the precipitates however can be precisely measured by the WAXS measurements, which is performed simultaneously to the SAXS measurements. This is an invaluable input for the

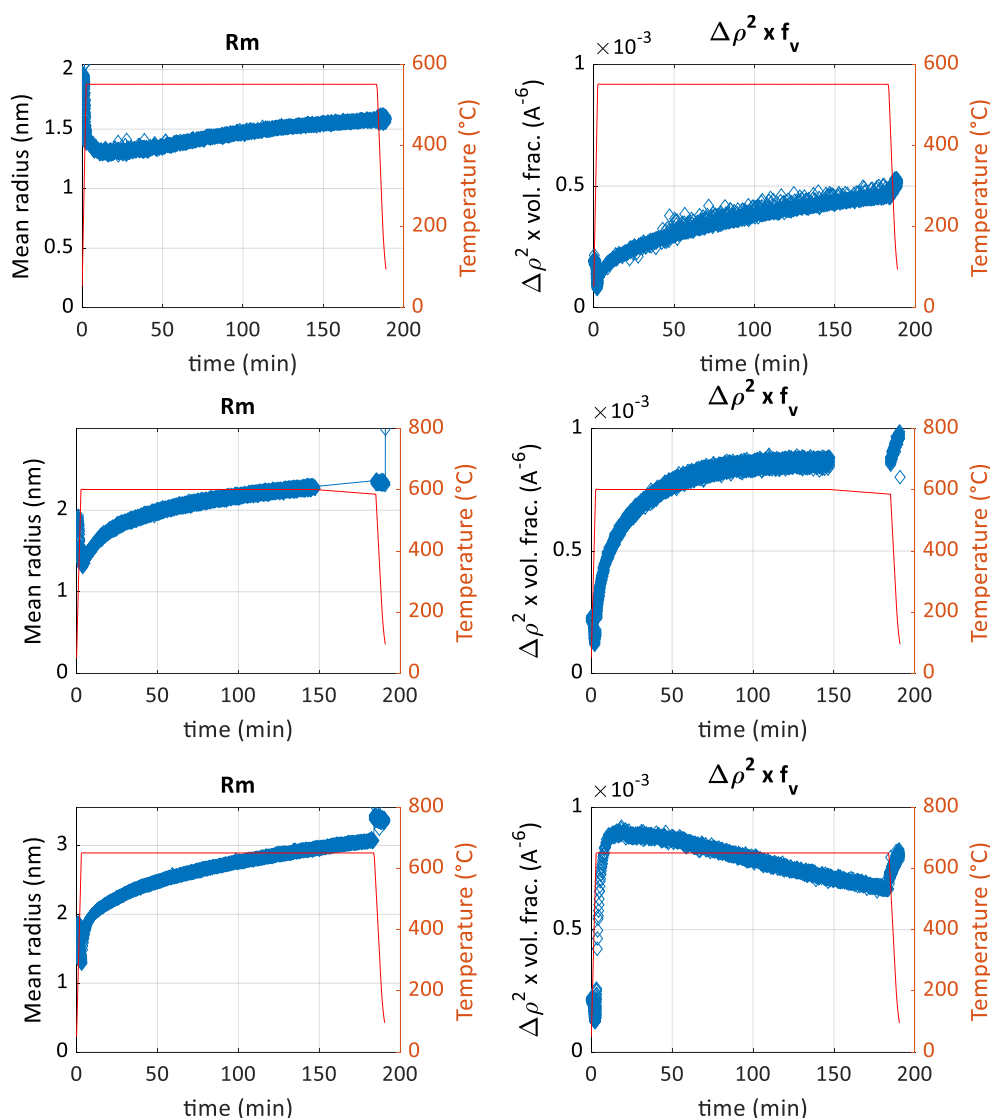SAXS data analysis, and a great advantage of the simultaneous SAXS/WAXS setup.

Figure 9. The SAXS results on the mean radius and the squared scattering length density difference multiplied by volume fraction of precipitates during in-situ thermal treatments of the three samples that were heated up to 550 °C, 600 °C and 650 °C respectively, 3 h holding and cooling.

Figure 10 displays the evolution of the apparent volume fraction of precipitates considering two hypotheses for the chemistry of the precipitates: first pure VC precipitates, second MC precipitates with a composition of 42V−30C−14Mo−8Cr−6Fe (at. %) measured by APT at the end of the thermal treatment. These results highlight the importance of the chemical composition on the retrieved volume fraction of precipitates. On the 650 °C curve, the decrease of apparent volume fraction could be linked with a partial dissolution of MC (driven by the chemical driving force and higher solubility limits of MC solutes in the matrix at higher temperature), or by a change in the chemistry of the precipitates (like an enrichment or depletion in Mo, Fe or Cr for instance).
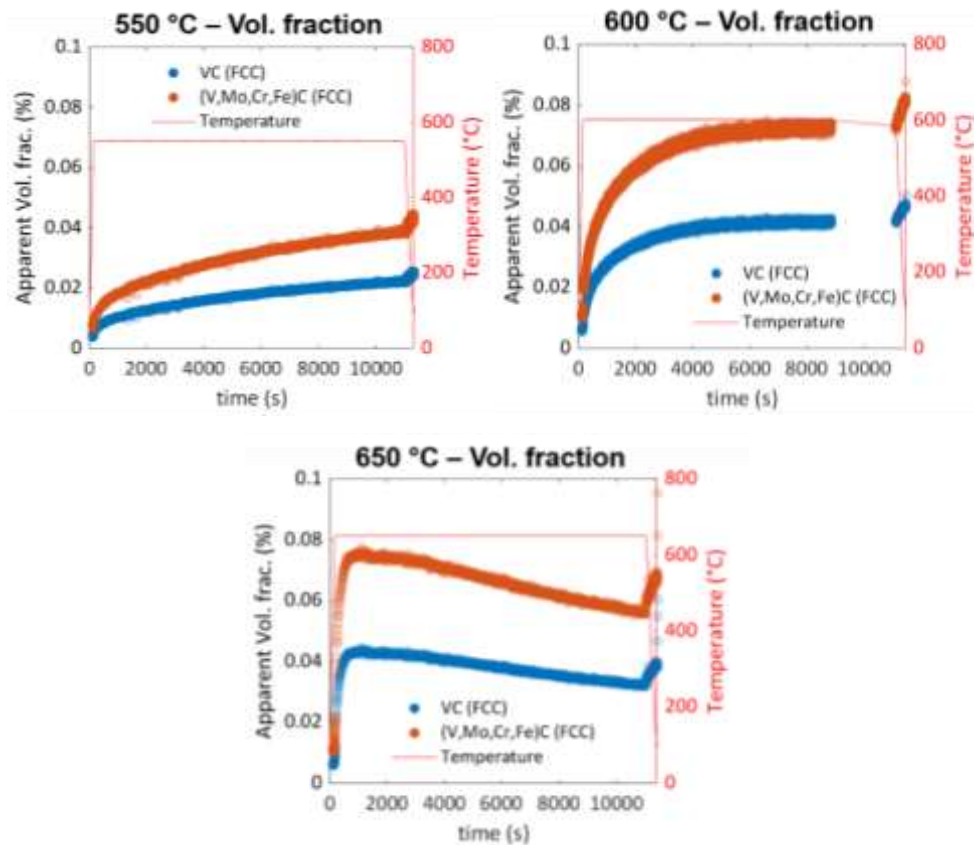
Figure 10. Curves showing the evolution of the apparent volume fractions of precipitates with the hypothesis of VC and $(V_{42}Mo_{14}Cr_8Fe_6)C_{30}$.

With further data analysis on the reduced WAXS data shown in Figure 7, one could get the lattice parameter and peak broadening after peak fitting as exemplified in Figure 11.
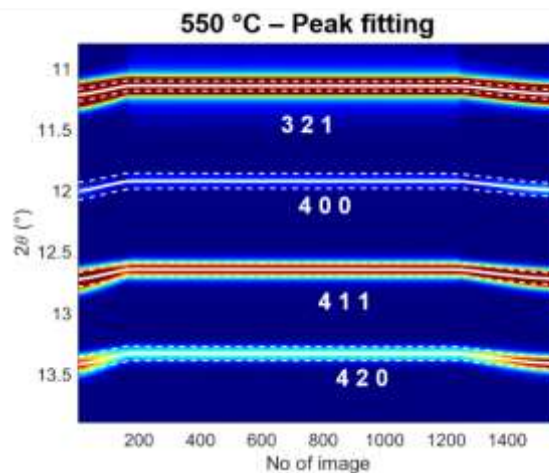

Figure 11. Evolution of some of the diffraction peaks (Fe-BCC) during the thermal treatment at 550 °C showing the results from the peak fitting position (solid line) and Full Width Half Maximum (dashed lines).

The fitted cell parameters from the peak positions of the first 13 diffraction peaks of Fe-BCC are displayed in Figure 12. The decrease of the cell parameter during

the isothermal treatments is a sign that substitutional elements with large atoms and interstitial elements diffuse out of the matrix, through precipitation. The error bar (shaded area) represents both the error on the fitting procedure and the dispersion of the cell parameter observed depending on the fitted diffraction peak, related to a slight shift from a perfect BCC cell (which can relate to the solute element present in the crystal lattice), or residual stress.
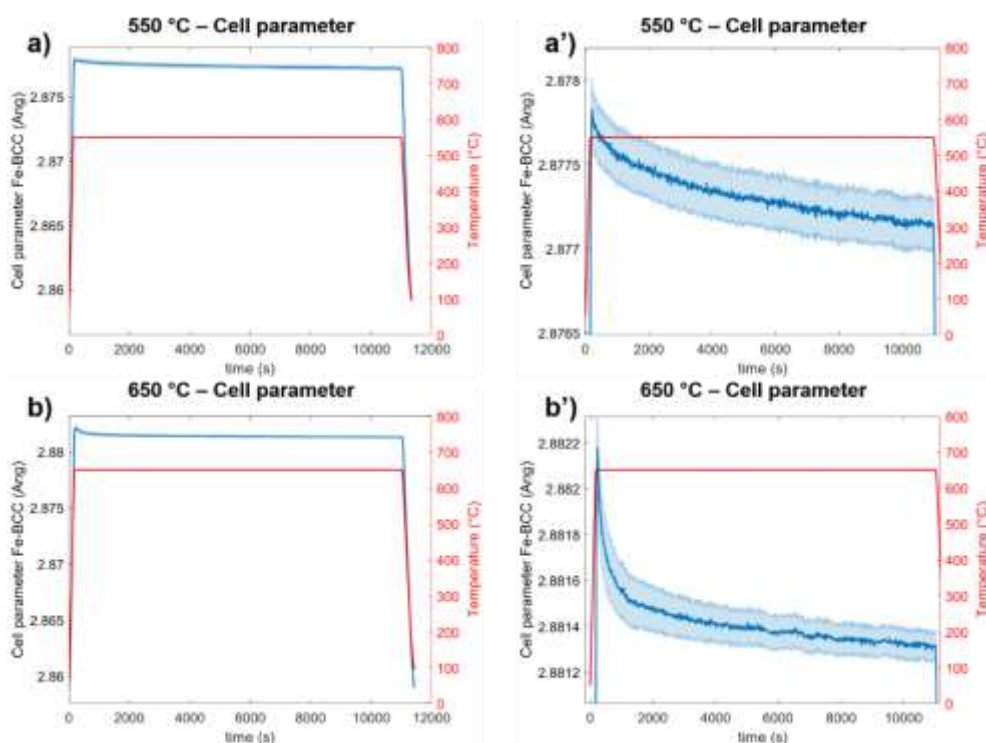

Figure 12. Evolution of the cell parameter of Fe-BCC with the thermal treatment showing (a, b) thermal dilatation and (a', b') a decrease during the isothermal holding.

The evolution of the Full Width Half Maximum (FWHM) peak broadening of the first 7 Fe-BCC diffraction peaks (only 7 peaks are represented for visibility purpose) is shown in Fig. 13. The decrease of the peak broadening is related to the decrese in lattice defects, *e.g.* dislocations. The quantitaive data of dislocation density can be further analyzed from the peak broadening using the modified Williamson-Hall and Warren-Averbach method as used in Ref. [17].
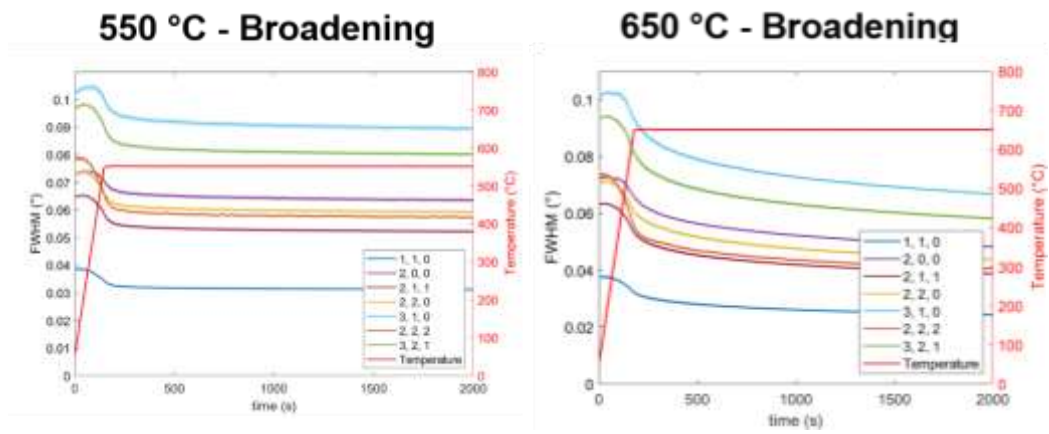
Figure 13. Evolution of the full width half maximum (peak broadening) of the Fe-BCC diffraction peaks over the thermal treatments.

4. Summary and conclusions

At the Swedish materials science beamline, simultaneous SAXS/WAXS measurements during thermal treatments captures data about both the matrix phases and the precipitate phases, with results being fully representative of bulk behaviour.

A streamlined research process to capture data about both the matrix and precipitate has key stages, and activities, which are summarised as follows:

Stage 1. Preparing beamtime proposals, where key success factors in being awarded a beamtime, are:

- That there is a clearly motivated science case for using the beamline *e.g.* a presentation of prior lab scale studies and modelling indicate the significance of precipitates and the importance of quantifying the kinetics during heat treatment processes.

- That the feasibility of achieving research results is demonstrated *e.g.* via a description of the instrument setup parameters for the particular experiment or data analysis processes.

Stage 2. Beamtime preparations, where key activities are:

- To prepare good samples, that are also suitable for the sample environment.

- To detail, for the particular sample material and sample dimensions, the experimental setup (*e.g.* required X-ray energy, detector positions) – so you are confident that you can capture measurements from features that are located deep within the material.

Stage 3. Beamtime measurements, where key activities are:

- Beamtime set up, including calibration of the particular experimental configuration that you are using (for use in Stage 4. Data reduction).

- Beamtime measurements.

- On site, preliminary data analysis *e.g.* prepare your own scripts to ensure that the captured data has sufficient quality to enable the target results to be obtained.

- Storage of measurement data.

Stage 4. Comprehensive data analysis, where it is important to recognise that allocating sufficient time to this task is vital to obtaining data. (Data reduction also requires that a good calibration of the experimental setup has been obtained during the beamtime.) The results that can be obtained are as follows.

- The crystallographic information of precipitate phases obtained from WAXS can be directly used for the SAXS data analysis (for the analysis of volume fraction of precipitates).

- From the WAXS data, the peak position and peak broadening can be directly related to the cell parameters and lattice defects. The evolution of the unit cell parameter can be further correlated with the change in the matrix composition, while the peak broadening can be used for the quantification of dislocation density using *e.g.* the modified Williamson-Hall and Warren-Averbach method.

- From the SAXS data, one can obtain the mean radius of the precipitates. In many cases, complementary techniques such as APT and TEM are needed since precipitate chemistry and crystal structure information is required to quantify the precipitate volume fraction. Hypotheses on the precipitate shape and dispersion are needed, and complementary characterization techniques such as TEM can be invaluable to decide on those hypotheses.

Such results are not possible by destructive techniques such as APT and TEM.

Accordingly, the PETRA III Swedish Materials Science beamline's combined SAXS/WAXS instrument setup offers a powerful research tool for *in situ* assessments of steels as they are undergoing heat treatments.

5. Acknowledgements

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