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Laboratory setup for rapid *in situ* powder X-ray diffraction elucidating Ni particle formation in supercritical methanol

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ABSTRACT

The design and function of a custom-made Soller slit for a laboratory 2D area detector is presented through a series of demonstration images and an *in situ* experiment following the formation of nickel particles in supercritical methanol. The *in situ* experiment is performed in a capillary sample environment, modified for a laboratory scale Rigaku Smartlab diffractometer, and with a temperature range of 300–1050 K. The formation of nickel particles was followed successfully using laboratory *in situ* X-ray powder diffraction with a time resolution in the order of 27 s. Observations from the area detector images showed the appearance of three distinct phases during the reaction: $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$, NiO, and Ni. The images were linearly integrated and analyzed using Rietveld refinement. A reaction mechanism is proposed based on an evaluation of the weight fractions and scattering factors as a function of reaction time.

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INTRODUCTION

The field of X-ray diffraction is entering a new era with the introduction of the next generation synchrotrons and light sources, like MAX-IV in Sweden and upgrade programs of existing sources, including X-ray Free Electron Lasers (FEL), e.g., the European XFEL in Germany, SwissFEL in Switzerland, and SACLA in Japan. The high brilliance and short-pulsed beams allow for faster and more advanced experiments. This calls for new and innovative sample environments for *in situ* (including *operando*) experiments, in order to follow never-before-seen reactions, transitions, and mechanisms. *In situ* X-ray diffraction experiments are already widely used in a broad selection of fields, especially in inorganic chemistry where the stronger scattering elements allow for faster data acquisition. Examples include *operando* studies of battery cells,^{1,2} decomposition of hydrogen storage materials,³ mechanochemical reactions,^{4,5} and crystallization in solvothermal reactions.^{6–8} The recently performed *in situ* experiments have hugely improved our understanding of crystallization processes and operations of advanced functional materials.^{9–13} Dedicated instruments are being built at the new synchrotrons and neutron sources, e.g., DanMAX at MAX-IV

and HEIMDAL at ESS. Both instruments strive to have the ability to investigate real materials, under realistic conditions in real time.^{14,15}

The high intensity and narrow beams provided by modern synchrotrons have made it possible to collect diffraction data with a very high time resolution, without sacrificing significant data quality. However, *in situ* experiments generally tend to be complicated to perform and are rarely successful in the first try,⁷ making trial experiments in the home laboratory particularly useful as preparation for synchrotron beamtime. It is thus relevant to improve the time resolution of laboratory scale diffractometers in order to increase the scientific yield of synchrotron *in situ* experiments. Some experiments may also be sufficiently slow that they can be performed at a laboratory source, where the added speed of the synchrotron does not add further to the understanding of the system.

One approach to improving the time resolution of laboratory scale powder diffractometers is by increasing the incoming beam size to a broad line shaped beam, thus illuminating more powder and increasing the intensity of the diffracted beam. This can be further improved by using an area detector to observe a larger part of the Debye-Scherrer rings. However, simply increasing the width of the

incoming beam leads to a significant overlap of the Debye-Scherrer rings, as each infinitesimally small segment of the illuminated sample gives rise to individual diffraction rings. The solution to the overlapping rings was introduced by Soller in 1924,¹⁶ as what is now known as Soller slits. The Soller slits consist of two sets of several closely spaced absorber plates, placed on the incident and receiving side, respectively. The slits are placed such that the absorber plates are parallel to the goniometer plane, i.e., the diffraction plane. The incident slit shapes the line beam into many thin parallel beams, which are diffracted from the sample and pass through the receiving slit before detection. Only X-rays that are diffracted in the Soller slit plane pass on to the detector, thus reducing ring overlap significantly. In Soller's original setup an ionization chamber was moved in a circle around the sample; this setup was very similar to detectors used at laboratory instruments today. However, modern 2D area detectors offer new possibilities. When combined with the Soller slits, the area detector also provides spatial information on the scattering from the sample, due to the parallel nature of the collimated

X-rays. This is particularly useful for *in situ* experiments, where the spatial information can elucidate heterogeneous changes throughout the sample.

Presented here is a detailed description of a novel laboratory setup useful for *in situ* experiments. The setup consists of a diffractometer (Rigaku SmartLab) equipped with an area detector combined with a custom made Large Area Soller Slit (LASS). The components of the setup are described along with examples of the images produced by the area detector with and without the LASS. Finally, a demonstration experiment is presented, investigating *in situ* the formation of elemental Ni particles from a supercritical solvothermal synthesis.

DIFFRACTOMETER SETUP

The diffraction setup presented in Fig. 1 comprises three main parts: The X-ray source and incident optics, the sample environment, and the receiving optics and detector. Several sample

FIG. 1. Schematic of the diffraction setup in transmission mode (Debye-Scherrer geometry).

environment options are available for *in situ* investigations, e.g., XY-table, high-temperature stage, a spinning capillary, or a battery mount developed in-house.¹⁷ Presented here is an in-house developed “*in situ*” capillary environment allowing a range of nonambient sample conditions at elevated temperatures, as presented in Refs. 7, 12, and 18. Previous applications of the capillary environment have primarily been for synchrotron-based experiments; however, here we present a novel modification for laboratory diffractometer use. In the laboratory modification, temperatures up to 1050 K can be reached and several gas flows are available, enabling *in situ* experiments such as reduction of metal oxides using reducing gas, calcination and annealing, and even solvothermal synthesis.¹⁹

For the demonstration described here, two similar systems have been used; both are equipped with an X-ray source consisting of a rotating anode target. Setup (I) A Co anode equipped with Cross Beam Optics (CBO)²⁰ providing a parallel beam, which in reflection mode was used to collect images from a standard 660B NIST LaB₆.²¹ The beam passes a commercially available incident Soller slit, which reduces the horizontal divergence, and through two beam-shaping slits, before reaching the sample environment. The diffraction patterns were collected with (a) a point beam using a microarea slit and a 0.5 mm incident slit, (b) a line beam using an incident slit of 10 mm, and (c) using a 10 mm incident slit in combination with the in-house build Large Area Soller Slit (LASS).

Setup (II) uses a rotating Cu anode target, a curved Johnson Ge(111) monochromator selecting only Cu K α_1 and an elliptical focusing mirror (CBO-E, not illustrated in Fig. 1) resulting in a convergent beam, which is subsequently shaped by beam slits before reaching the sample. The convergent X-rays are scattered from the sample and pass through the LASS to remove horizontal divergence. Incident slits of 15 mm (horizontal) and 0.6 mm (vertical) were used to shape the beam. The detector was placed with the center at $2\theta_{center} = 48.0^\circ$ and at a distance of $L_{SD} = 135.5$ mm. The exposure time for each frame was 20 s, with a few seconds of readout time, giving a time resolution in the order of 27 s.

The LASS consists of 20 equidistant 100 μm thick tungsten blades, with a slit spacing of 1.5 mm and a depth of 30 mm, corresponding to a 5° collimation. Behind the LASS, the scattered intensity is measured by a Rigaku HyPix-3000 semiconductor area detector. The center of the detector is positioned at a fixed angle with respect to the incident beam, with a sample-to-detector distance of 135.5 mm. The active area of the detector is a flat rectangle with dimensions 77.5 by 38.5 mm, divided in pixels of 100 μm by 100 μm , giving 298 375 pixels.

Due to the flat nature of the detector, the relation between the scattering angle 2θ and the pixel position x is not linear but are related according to

$$2\theta(x) = \frac{180^\circ}{\pi} \tan^{-1} \left(\frac{x + C}{L_{SD}} \right) + 2\theta_{center} \quad (1)$$

with x being the vertical distance from the corresponding pixel to the center of the detector, L_{SD} being the sample-to-detector distance, C being a detector displacement correction, and $2\theta_{center}$ being the fixed detector angle. The conversion from the pixel position to 2θ angle is performed in a Python script written specifically for the setup. The script also filters out dead pixels using a simple smoothing function and masks out the dark edges of the images. The script uses linear

integration to convert the images into 2θ diffractograms to make them more accessible for analysis software like FullProf,²² TOPAS,²³ or GSAS.²⁴

DETECTOR AND LARGE AREA SOLLER SLIT (LASS)

Figures 2(a)–2(c) illustrates the images collected in reflection mode from the LaB₆ standard sample, demonstrating three distinct situations. The first image is the Debye-Scherrer cone segments produced when the powder is illuminated by a thin point-shaped beam. The segments have minimal tail broadening from ring overlap and the intensities can comparatively easily be integrated azimuthally. The point beam and the even ring segments come at the cost of intensity and powder statistics.

In the second image, a broad beam is used to illuminate the powder, and a significant ring-overlap is observed. This leads to broad tails on the ring segments but gives an increased intensity in the center of the diffraction segments. The broad tails make azimuthal integration difficult and give peaks that are asymmetrically broadened toward higher angles. A linear integration would likewise cause profoundly asymmetric peaks at low angles due to a combination of ring overlap and axial divergence, as illustrated in Fig. 2(d).

The last image is produced using the LASS. Ring overlap is significantly reduced and the diffracted intensity is observed as horizontal lines across the detector. The slit blades cast a shadow on the detector, which is seen as equidistant vertical lines. The Soller slit also removes scattered X-rays that are outside the width of the incident beam, making the sides of the image completely dark. The linear intensity lines are easily integrated and introduce only a small asymmetry, compared to the open geometry case, and they provide a significant increase in intensity compared to the point beam case. Furthermore, by illuminating more samples, the powder statistic is improved, especially for setups that do not allow a rotating sample holder.

The resulting peak-shapes for the three setup options are summarized in Fig. 2(d), which illustrates the linearly summed (110) peak for each of the three detector images. The point beam image has been azimuthally integrated, while the uncollimated and LASS collimated images have been linearly integrated, and the intensities are normalized with respect to the maximum linearly summed intensities: 24.9(3) cps, 1148(2) cps, and 76.0(5) cps, respectively. From the figure, it is evident that the sharpest peak is obtained from the LASS collimated image, which has a FWHM of $0.144(6)^\circ$ as compared to $0.218(2)^\circ$ and $0.281(9)^\circ$ for the point beam and uncollimated images, respectively. The point beam image has a slightly higher peak resolution of about 0.023° per pixel as compared to 0.039° per pixel for the collimated image. Furthermore, the higher count rate of the collimated image compared to the point beam image results in a better signal-to-noise ratio for the collimated image. The uncollimated image has the highest count rate and thus the best signal-to-noise ratio, but at the expense of a significantly higher background and a very asymmetric peak shape.

The area detector in combination with the Large Area Soller Slit gives rise to another useful feature, namely, a spatial resolution. Due to the parallel nature of the beam, each diffraction segment observed between the vertical slit shadows correspond to a small segment of the sample. This is an extremely useful feature, as it can be

FIG. 2. Illustration of X-ray powder diffraction from a LaB_6 sample collected with the HyPix3000 area detector in three distinct cases: (a) Using a point beam without the LASS, (b) using a 10 mm broad beam without the LASS, and (c) using a 10 mm broad beam collimated with the LASS. The intensity of the colors have been scaled with respect to each other, as indicated in the top right corner and are represented by the linear colormap Cividis.²⁵ (d) Comparison of the linearly summed (110) peak for the three cases, normalized with respect to the largest linearly summed intensity [$I_{\text{max}} = 24.9(3)$ cps, 1148(2) cps, and 76.0(5) cps, respectively]. The X-ray source is $\text{Co K}\alpha$.

used to track inhomogeneous changes *in situ*, e.g., arising from a temperature gradient or a reaction propagating from one side of a capillary to the other, without having to scan over the sample. The spatial resolution is demonstrated in Fig. 3, where a one euro coin has been exposed in reflection geometry using parallel beam $\text{Co K}\alpha$ radiation. Part of the coin was illuminated in a thin line, as indicated in the figure, hitting both the inner and outer segments of the

coin. The inner segment consists of a 75% copper and 25% nickel alloy, while the outer segment consists of a 75% copper, 20% zinc, and 5% nickel alloy.²⁶ The transition between inner and outer alloys are seen as peak displacements in the diffraction image, as expected from Vegard's law, due to the larger atomic radius of Zn compared to copper. The observed overlap is due to both beam divergence and the curvature of the segment interface.

DEMONSTRATION EXPERIMENT

Purpose

The purpose of the experiment is to investigate the supercritical solvothermal synthesis of nickel particles by using the laboratory scale *in situ* setup described. In general, it is useful to study the formation of metal nanoparticles to understand and control growth. Here, nickel is chosen because of the low absorption and high scattering power for the $\text{Cu K}\alpha$ radiation. Nickel nanoparticles have gained interest due to their catalytic properties as well as their magnetic properties,^{28,29} making their nucleation and growth mechanism a relevant research subject.

Experimental

A 2.0 M solution of Ni^{2+} was prepared by dissolving $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Technical grade >98% purity Sigma-Aldrich) in methanol (Baker Analyzed LC-MS Reagent). The precursor solution was injected into a ~30 mm long fused silica capillary with an inner diameter of 0.70 mm and an outer diameter of 0.85 mm and sealed using Swagelok fittings and pressurized to 110 bars using a high-performance liquid chromatography (HPLC) pump with a methanol supply. The capillary was mounted in the Rigaku SmartLab diffractometer using a custom build capillary shoe and heated with a Hi

FIG. 3. Demonstration of the spatial resolution obtained with the LASS using a standard one euro coin. The approximate X-ray footprint is illustrated by the red line. The white arrows indicate the (111) and (200) reflection indices of the inner and outer alloys. The X-ray source is $\text{Co K}\alpha$. Euro coin image is taken from Ref. 27.

Heater SAH 1 A F T 400 W heat gun from Miyawaka Corporation, Japan, placed immediately below the capillary. The nozzle of the heater has been custom made with a 20 mm broad rectangular profile that allows for more homogeneous heating of the full length of the capillary. The diffractometer used incident slits of 15 mm (width) and 0.6 mm (height), and the detector was placed with the center at $2\theta_{\text{center}} = 48.0^\circ$ at a distance of $L_{\text{SD}} = 135.5$ mm. The exposure time for each frame was 20 s, with a few seconds of readout time and opening and closing the shutter, giving a time resolution in the order of 27 s. Three *in situ* experiments were performed at set temperatures of 350 °C, 400 °C, and 450 °C for 42 min, 37 min, and 13 min, respectively. It is acknowledged that the sample temperature is slightly lower than the set temperature of the heater. All reactions were carried out at a pressure of 110 bars, above the critical point of methanol (240 °C, 80.9 bars).³⁰

Results

The formation of nickel particles from dissolved nickel(II) nitrate hexahydrate goes through at least two intermediate phases, with a strong dependence on the reaction temperature. This is evident from the selected detector images for the three experiments, illustrated in Figs. 4(a), 4(c), and 4(e). In Fig. 4(a) at $t = 0$ min, no Bragg peaks are visible, as is expected for a solution. Shortly after heating begins, five peaks start emerging; two sharp peaks at 33° and 59° and three broad peaks at 36° , 43° , and 60° as is visible at $t = 1.9$ min. At the end of the experiment, at $t = 41.6$ min, three distinct peaks are visible at 37° , 43° , and 62° and five weak peaks are visible at 33° , 36° , 44° , 52° , and 59° . It is also noticeable that the weak peaks appear to be predominantly in the right half of the detector image, indicating that the nucleation has not taken place

FIG. 4. Selected detector images (a), (c), and (e) and time-resolved diffraction patterns (b) and (d) for the three experiments. All intensities are linearly scaled to an arbitrary interval in order to best illustrate the features. Expected peak positions and relative intensities for the Ni, NiO, and $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ phases are illustrated at the top of (b) and (d), and the X-ray source is $\text{Cu K}\alpha_1$.

uniformly, likely due to an uneven heat distribution in the capillary. The phase development of the experiment can be visualized by plotting the linearly summed intensities as a function of time, as is illustrated in Fig. 4(b). Included in the figure are the expected positions and relative intensities for $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ (PDF 00-022-0752),³¹ NiO (COD ID 4320502),³² and FCC Ni (COD ID 2100637).³³ From this, it is evident that the nickel(II) nitrate hydroxide phase forms at the beginning of the experiment, before the formation of nickel(II) oxide and finally elemental nickel. It is seen that the decrease in intensity of the $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ peaks coincide with the increase in intensity for the NiO peaks, suggesting that the NiO is formed through an intermediate. The high peak resolution provided by the LASS enables a distinction of the variation in peak widths for the $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ phase, which confirms a layered Ni/OH structure as is often observed for nickel hydroxides.³⁴

At 400 °C, the same mechanism is observed [Figs. 4(c) and 4(d)]; the $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ peaks are briefly visible at the heating onset, but now the NiO peaks quickly appear at the expense of the $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ peaks. After a few minutes of heating, the Ni peaks at 44° and 52° increase tremendously, outshining the remaining peaks. Again, the increase in the Ni peaks coincides with a decrease in the NiO peaks, suggesting another phase transformation. At 450 °C, the Ni formation happens even faster, with only a brief hint of the intermediate peaks visible in Fig. 4(e). The time-resolved diffraction pattern has been omitted, as the phase formation happens faster than the time resolution.

Apart from evaluating the diffraction data directly, the LASS collimated images are also suitable for analysis by for instance

Rietveld refinement as is illustrated for four selected images in Fig. 5. Here, an early and a late integrated pattern are plotted for the two experiments at 350 °C and 400 °C, along with the refined Rietveld model of the NiO and Ni phases. The $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ phase has been excluded from the Rietveld model (gray open symbol), as the structure, to the best of our knowledge, has not been solved yet.

From Fig. 5, it can be seen that satisfying Rietveld models can be produced, with a well-described background and a low residual plot. From sequential refinements of all images, the relative weight fraction and scale factor evolution throughout the experiments are determined, as illustrated in Fig. 6.

From the weight fractions in Fig. 6 the same trends are observed as from the selected images in Fig. 4: at 350 °C, the reaction is slow and only small amounts of elemental Ni is observed; at 400 °C, the conversion is faster ending at about 70% Ni after 36.9 min; and at 450 °C, the reaction is significantly faster reaching 70% Ni after 2.5 min and 80% Ni at the end of the experiment. From the 400 °C and 450 °C experiments, it is seen that the majority of the reduction from NiO to Ni takes place shortly after heating is started after which the conversion rate decreases and the weight fraction seems to converge toward 80% Ni.

Evaluating the scale factors, which are (among other effects) proportional to the illuminated volume of the phases, indicates that the formation of Ni depends on the NiO concentration. This is seen in the 350 °C case, where the NiO scale factor steadily increases in the initial 29 min and then remains constant, coinciding with a steady increase in Ni scale factor. This suggests a steady-state where NiO is reduced to Ni at the same rate as new NiO is formed from

FIG. 5. Selected linearly summed intensities and Rietveld refinements for four selected images from the 350 °C and 400 °C experiments. Expected peak positions and relative intensities for the Ni, NiO, and $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ phases are illustrated at the top of the figure. No Rietveld refinement has been performed on the 350 °C $t = 1.4$ min. Data points excluded from the Rietveld models are shown in gray.

FIG. 6. Relative weight fractions and scale factors obtained from sequential Rietveld refinements of the integrated images for the three experiments at 350 °C, 400 °C, and 450 °C. The Ni weight fraction and scale factor for the 350 °C experiment have been set to zero from $t = 4.2$ min to 27.6 min. The weight fractions are calculated relative to the Ni and NiO phase content.

the $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ phase. At 400 °C, the NiO formation rate is beyond the time resolution, but the NiO scale factor at the point of Ni formation is very similar to that of the 350 °C steady state. From there on, the NiO scale factor steadily drops as the Ni scale factor increases, again confirming the reduction from NiO to Ni. At 450 °C, the initial reaction is even faster but confirms that the reaction retards before the full reduction of the NiO. A possible mechanism is as follows: NiO is formed during heating from dissolved $\text{Ni}(\text{NO}_3)_2$ through the $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ intermediate in methanol. The NiO is then reduced to Ni in supercritical methanol, possibly by H_2 formed from a NiO catalyzed oxidation of the methanol. As the NiO is used up, the reaction slows down and halts when the NiO concentration is too low. A very simple representation could be

Here, (MeOH) denotes dissolved in methanol, (l) is in liquid state, (s) is in solid state, (Sc) is in supercritical state, and (g) is in gas state.

Other reaction mechanisms cannot be excluded based on the powder diffraction data.

CONCLUSION

The Large Area Soller Slit (LASS) was presented, combined with a modified capillary sample environment for a temperature range of 300–1050 K build to fit in a laboratory scale Rigaku SmartLab diffractometer. A detailed description of the LASS was given along with a schematic representation of the full laboratory scale *in situ* setup.

The effect of the LASS was demonstrated through three images collected from a LaB₆ NIST standard using different beams; point-shaped, uncollimated, and LASS collimated. The LASS collimated beam produced the sharpest peak with least instrumental broadening, at the expense of intensity, but with a satisfactory signal-to-noise ratio and a low background. The LASS furthermore provides a unique spatial resolution to the area detector images, as was demonstrated from the distinct peak shift observed from an image taken using a standard one euro coin.

The *in situ* capabilities were demonstrated by investing the formation of Ni particles in supercritical methanol. Elemental nickel was successfully synthesized in a capillary setup mounted in a Rigaku SmartLab diffractometer. From *in situ* X-ray powder diffraction, three phases were observed directly from the area detector images, suggesting that Ni is formed through $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ and NiO intermediates. The images were linearly integrated by a

custom-written python script and analyzed using Rietveld refinement. From evaluation of the weight fractions and scattering factors as a function of reaction time, it was possible to propose a simple reaction mechanism for the formation of nickel particles.

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