Report on the outcomes of a Short-Term Scientific Mission[1]

Action number: CA20129 "Multiscale Irradiation and Chemistry Driven Processes and Related Technologies"

Grantee name: Marta Jaros

Details of the STSM

Title: Studies of potential new FEBID precursors for nickel complexes containing N- and O-donor ligands.

Start and end date: 26/05/2025 to 15/06/2025

Description of the work carried out during the STSM

Description of the activities carried out during the STSM. Any deviations from the initial working plan shall also be described in this section.

(max 500 words)

Preliminary parameters for FEBID experiments were chosen based on the results for precursor $[Ni_2(^sBuNH_2)_2(\mu\text{-}O_2CC_2F_5)_4]$ obtained at Nicolaus Copernicus University in Toruń. The GIS temperature was 80°C, and the deposition process was conducted without stage heating on Si substrate. The condensation of precursor molecules on the substrate was observed – the temperature difference was too significant. The initial beam current was 20 keV.

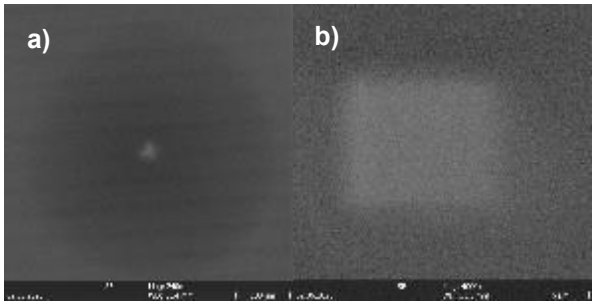

Figure 1. a) Spot deposit and b) square-shaped deposit; T_{GIS} = 80°C, no stage heating, deposition time: 1–2 h.

[1] This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

Applying a GIS temperature of 80°C and stage temperature of 80°C (2–4 h process) results in a lack of precursor condensation process on the Si substrate.

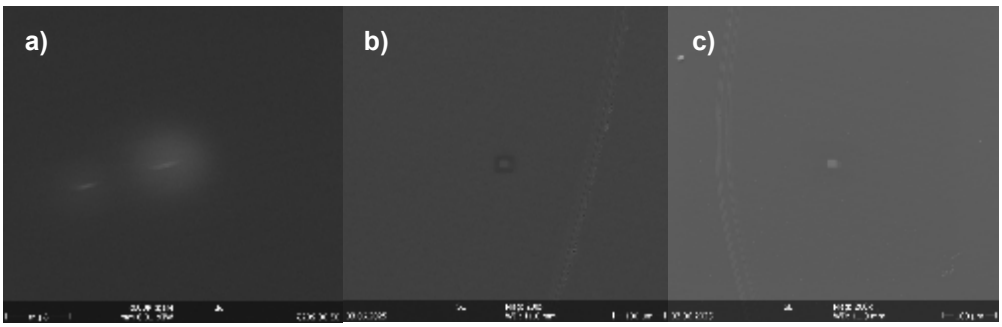

Figure 2. a) Spot deposit, b) and c) square deposits; T_{GIS} = 80°C, T_{stage} = 80°C, deposition time: 2–4 h.

The composition of deposits was determined with X-ray spectroscopy (15 kV). The strong Si signal is typical for the substrate; its presence indicates that the fabricated deposit is thin.

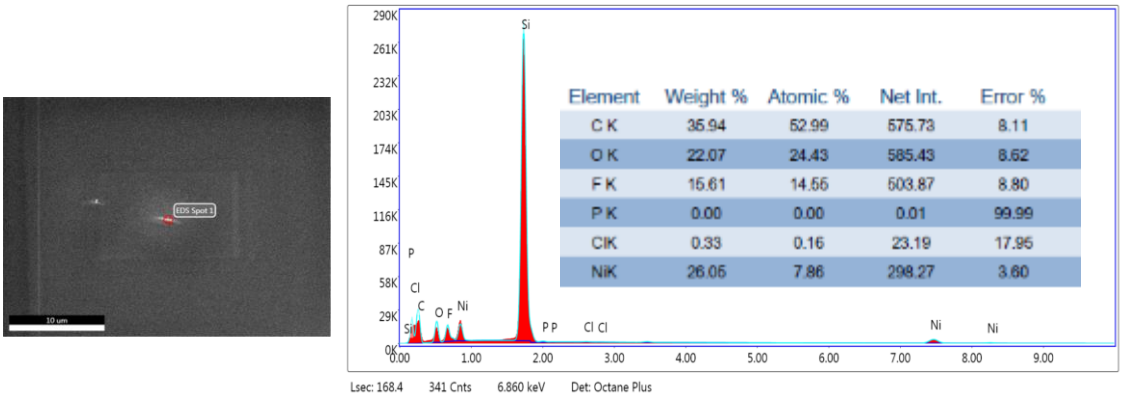

Figure 3. SEM image, EDX spectrum, and the composition of the spot deposit (T_{GIS} = 80°C, T_{stage} = 80°C).

Ni:C:F at.% ratio is approximately 1:7:2.

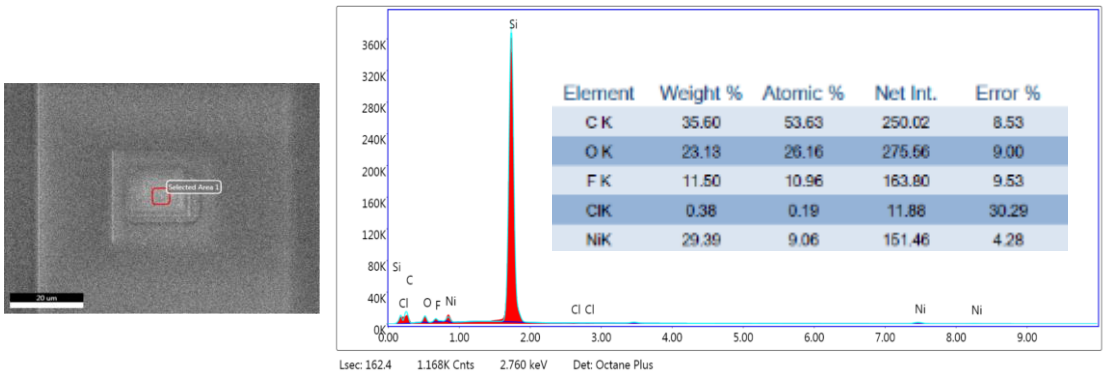

Figure 4. SEM image, EDX spectrum, and the composition of the square deposit (T_{GIS} = 80°C, T_{stage} = 80°C).

Ni:C:F at.% ratio is approximately 1:6:1.

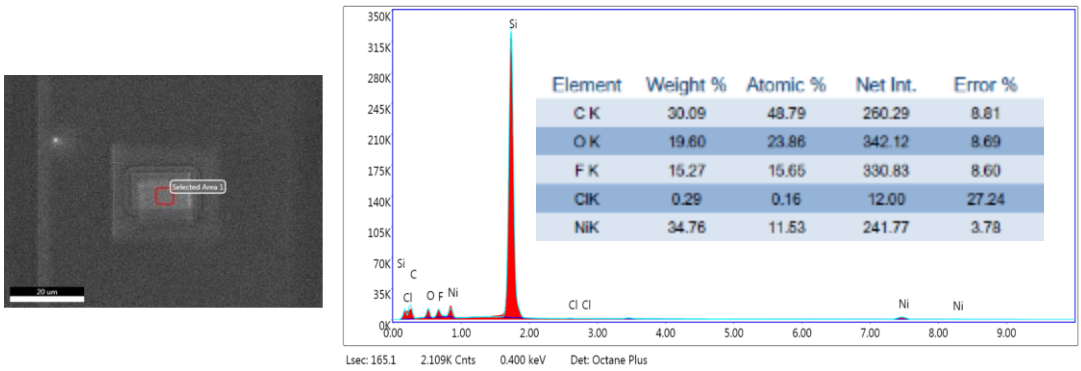

Figure 5. SEM image, EDX spectrum, and the composition of the square-shaped deposit (T_{GIS} = 80°C, T_{stage} = 80°C).

Ni:C:F at.% ratio is approximately 1:4:1.

SEM EDX analysis confirms the fabrication of nickel-containing deposits. Nickel content is significantly higher, and the carbon and fluorine content are lower in the obtained deposits compared to the complex. The atomic element composition in the pure compound is Ni:C:F =1:10:10, and changed in the fabricated deposits from 1:7:2 (Figure 3), by 1:6:1 (Figure 4) to 1:4:1 (Figure 5). The signal from nitrogen is not observed.

Next experiments were conducted with GIS temperature of 70°C and the stage temperature of 55°C; deposition times: 4 h (Figure 6a) and 12 h (Figure 6b), respectively. The next day, an experiment on the same substrate was conducted. The GIS temperature was increased to 75°C, and the stage temperature to 60°C for more effective evaporation and adsorption (Figure 6c), but the microscope stopped working in the middle of the process, and the remaining precursor condensed on the substrate surface.

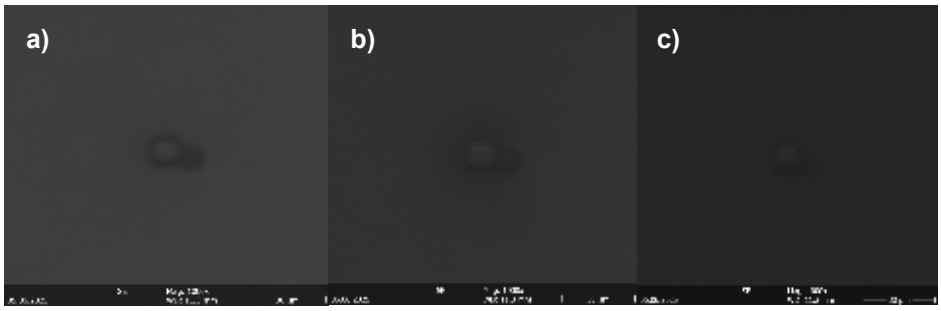

Figure 6. Square deposits; T_{GIS} = 70/75°C, T_{stage} = 55/60°C, deposition time: 4–12 h.

For the last experiments, the evaporation temperature was 75°C, the stage temperature was 70°C, the beam current was 20 kV, the acceleration voltage 1,3 nA, deposition time was 17 h and 18 h, respectively.

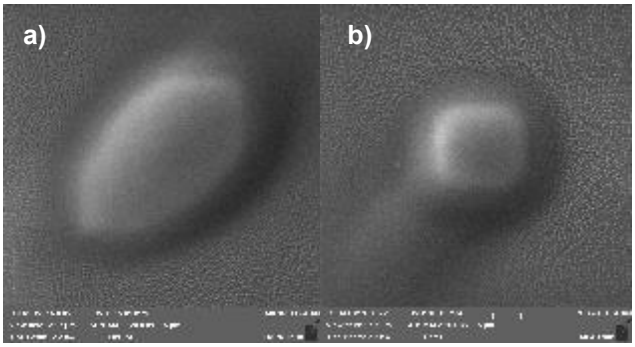

Figure 7. a) deformed square deposit; T_{GIS} = 75°C, T_{stage} =70°C, deposition time: 17 h, b) square deposit; T_{GIS} = 75°C, T_{stage} = 70°C, deposition time: 18 h.

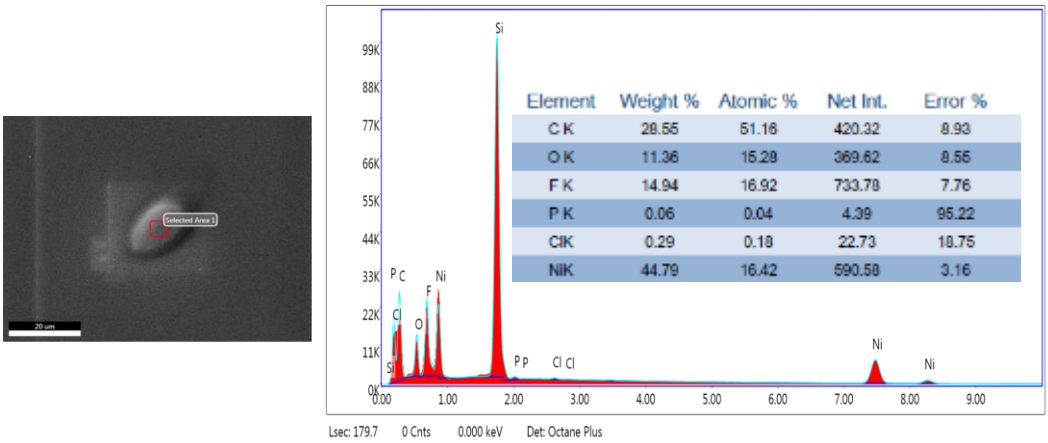

Figure 8. SEM image, EDX spectrum, and the composition of the deposit (T_{GIS} = 75°C, T_{stage} = 70°C, deposition time: 17 h).

Ni:C:F ratio is approximately 1:3:1.

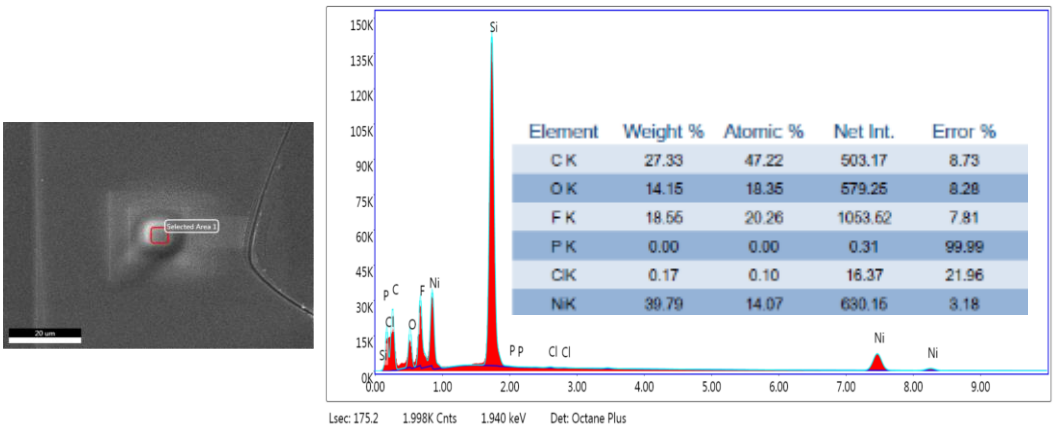

Figure 9. SEM image, EDX spectrum, and the composition of the deposit (T_{GIS} = 75°C, T_{stage} = 70°C, deposition time: 18 h).

Ni:C:F ratio is approximately 1:3:1.

The fabricated materials were significantly thicker based on SEM images and EDX spectra. The atomic element composition significantly changed in the fabricated deposits from 1:3:1 (Figure 8 and Figure 9) compared to the pure compound (Ni:C:F =1:10:10). There were also spherical structures around both deposits that might be worth analysing.

The selected compound $[Ni_2(^sBuNH_2)_2(\mu\text{-}O_2CC_2F_5)_4]$ is promising as an FEBID precursor; however, further tests should be performed. The experiments confirmed that longer deposition time results in forming thicker deposits with higher nickel content in the obtained materials.

The second complex $[Ni_2(^iPrNH_2)_2(\mu\text{-}O_2CC_2F_5)_4]$ could not be tested yet, because of time limits and an apparatus problem, but the samples have been delivered to the EMPA Institute, and the experiments can be continued.

Description of the STSM main achievements and planned follow-up activities

Description and assessment of whether the STSM achieved its planned goals and expected outcomes, including specific contribution to Action objective and deliverables, or publications resulting from the STSM. Agreed plans for future follow-up collaborations shall also be described in this section.

(max. 500 words)

The planned goals of the STSM have mostly been achieved – preliminary parameters (GIS and substrate temperatures, electron beam voltage and current, interaction time) for FEBID experiments were determined, and then modified to perform deposits with better quality. The 3D deposit wasn't obtained, but an attempt was taken to fabricate a thick square-shaped material (17/18 hour experiment). The morphology and composition of deposits were characterised.

The research results are the basis for scientific paper preparation, which will consist of complexes synthesis, composition, volatility, and thermal studies data obtained already in our research group in Toruń. The paper will also include new data that have been obtained as a result of the FEBID experiments conducted at EMPA, about the compounds molecules interaction with electrons, adjusted FEBID process parameters such as temperatures of effective evaporation for precursors, focused electron beam acceleration voltage and current, and morphologies and compositions of performed materials, including validation of the extent of metal content and defining the atomic ratio in obtained deposits. The mentioned experiments allowed a better understanding of the electron irradiation impact and electron-induced formation and growth of nickel-containing nanostructures from the carboxylate-amine complex precursor. The data will also be presented as results during the poster session (poster title „New nickel(II) complexes as promising precursors in FEBID method") on MultIChem-ISACC 2025 Conference: The Final Conference of the COST Action "Multiscale Irradiation and Chemistry Driven Processes and Related Technologies" and the 12th International Symposium "Atomic Cluster Collisions".

Moreover, the STSM was a great opportunity to gain experience in working with electron microscopes and FEBID equipment, and also to work with a big international group for the first time.

The collaboration between Ivo Utke's research group and our group will be further developed, to continue current work and to possibly take new 10 and 11 group compounds into account as new promising precursors dedicated to FEBID experiments.