



**Fuel Recycle and Experimentally Demonstrated
Manufacturing of Advanced Nuclear Solutions for Safety
Project Number: 101060800**

DELIVERABLE D1.2

Report on mechanical conditioning of the educts

Lead Beneficiary: CHALMERS

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EXECUTIVE SUMMARY

This report summarizes the work performed aiming at determining conditioning and production processes of UO₂ materials for obtaining powders suitable for additive manufacturing. The work has focused on preparatory techniques for fabrication of both pure and doped UO₂ powders by classical precipitation techniques and techniques for direct precipitation of nanometric UO₂. The work has focused on preparation of powders that are converted to UN powders by subsequent carbothermic reduction. Due to the complexity of these powders and processes work was done on UO₂ materials and suitability of powders for additive manufacturing was estimated through the powders sintering properties. The main result obtained indicates that the application of nanometric powders strongly promotes sintering and constitutes a promising candidate for fuel powder suitable for performing additive manufacturing.

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1 INTRODUCTION

The FREDMANS' Working package 1 is the evaluation of novel fuel production methods, which are optimized for the refabrication of highly active fuels with improved properties and potentially added functionality. The work package mainly focuses on the methods and their applicability to this special purpose from the chemical and mechanical conditioning, the shaping methods, up to the solidification of the material, also including the safety aspects of all process steps.

At the end the methods shall qualify to provide nitride fuel, which is the most sophisticated fuel form, as it implies advanced chemical processing steps with for example a carbothermal reduction and an exposure to nitrogen gas. However, oxide fuel is targeted in a first step, as a basis for the further development of the processing steps.

2 DELIVERABLE D1.2

Chemical and mechanical conditioning of the educts (CHALMERS, PSI, JRC)

Timing of the task: M1 - M36

The conditioning of the educts is a critical aspect and an important part of the advanced manufacturing methods, as they often require very high quality of chemical solutions, powders or suspension to properly work (e.g., power for additive manufacturing, chemical solutions for gelation processes, etc.).

In nuclear field, and especially when working with highly active starting materials, there is the additional aspect, that these processes should be compatible with remote operations and emitting as few as possible contamination into the production environment. Additionally, the ability for remote maintenance must be considered

2.1 Particle/powder production

2.1.1 Task description

Production of high-quality powder with well-defined particle size and shape, and therefore the flowability, from solutions or solid scrap to be expected from waste recycling and/or reprocessing. Depending on the educt form, different precipitation approaches can be addressed and tested if coming from a liquid phase, and milling procedures, additionally for the final conditioning, and especially if coming from a solid phase.

Depending on the targeted process, and if the oxidation of transformation of into nitride is part of it or not, both, the production of metallic and ceramic particles must be envisaged. Especially when talking about non-oxide particles, there is a direct crosslink to the Safety of the processes task, where the safety aspects are to be considered. In all cases, the contamination of the environment is a major issue to be addressed here.

2.1.2 Task progress

A series of different powder types has been produced using the co-precipitation of uranyl nitrate. The main powder type is UO_2 with lanthanum additives, in order to investigate the solubility of the additives in the starting solution and to produce a series of simulated burn-up fuel. Smaller quantities of UN, UC and UCN were also produced with the co-precipitation technique.

The powders were examined with SEM and ICP-MS in order to evaluate the particle size and the composition of the final product, especially for the simulated fuel powder which contained the additives. The results proved that the production of the powders with this method was successful and fulfilled the requirements.

Additionally, a research work was conducted on the electrochemical precipitation route for synthesis of pure and doped nanocrystalline UO_2 . This method was also successful to produce simulated fuel pellets with homogeneous distribution of dopants. The scientific literature describes the technique used during this work as a method of preparing “nanometric UO_2 ”. The powders produced and presented here are thus referred to as “nanometric” though no TEM work has been performed in the work to confirm precise particle or crystallite sizes. The powders prepared were studied with respect to their sintering behavior, though the name “nanometric UO_2 ” is still used here for the powders to differentiate them from UO_2 powders prepared by conventional precipitation techniques from U(VI).

As additive manufacturing requires consolidating powders into cohesive macroscopical objects it was considered of interest preparing nanocrystalline UO_2 and Ce-doped UO_2 in order to study the increased sinterability of such powders. UO_2 powders of significantly increased sinterability is considered to potentially be of great use and importance for additive manufacturing techniques.

The preparation of directly precipitated UO_2 from U(IV) solution was started by preparation of suitable aqueous media. Uranyl nitrate hexahydrate was dissolved in water and the nitrate was separated from the uranium by precipitation of uranium using aqueous ammonia. The precipitated $\text{UO}_3 \cdot \text{H}_2\text{O}$ was redissolved in 1M perchloric acid to a concentration of 0.1M U. This stock solution served as the start point for all work done on U(IV) precipitation.

Cyclic voltammetry was performed on the stock solution to determine the potential required versus a reference electrode. The electrochemical reduction of the uranium from U(VI) to U(IV) progresses according to the half-cell reactions:



Combining the two half-cell reactions form the full summary reaction:



By this method uranium stock solution was reduced to tetravalent uranium and confirmation of complete reduction of uranium to U(IV) was performed using UV-Vis spectrometry. In case of Ce-doping of powders, trivalent cerium was added to the reduced U(IV) solution.

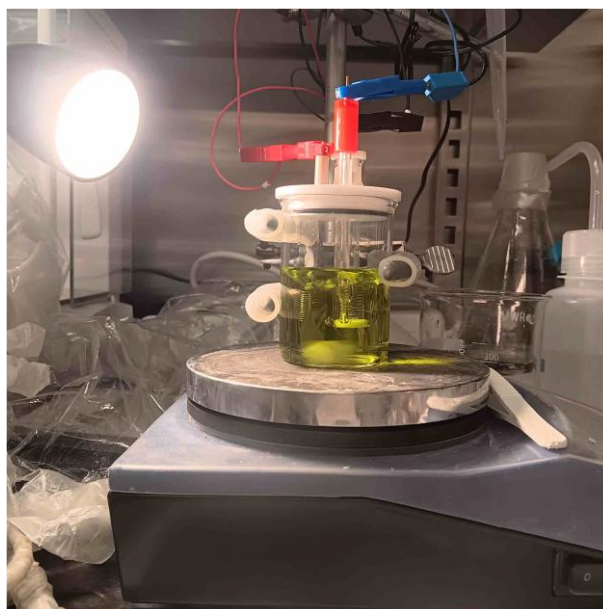


Figure 1. Electrochemical reduction setup during reduction of U(VI) to U(IV). Image from Julia Bergströms Master thesis “Synthesis and characterization of nano-metric simulated nuclear fuel (SIMfuel)” carried out at Nuclear chemistry’s laboratories 2024.

Precipitation of nanometric UO_2 was performed by increasing the pH of the reduced stock solution using 0.5-1M Aqueous ammonia. pH was slowly increased to between 1-2 in a duration between 1-2 hours and was kept stirring at roughly constant pH for time periods ranging between some hours to a few days to allow the nanometric UO_2 particles to form. The formation of the nanometric particles turned the stock solution from transparent green into homogeneously black. When the formation of

the black UO_2 particles were completed pH was increased to about 8.5 causing the individual particles to coalesce into small granules that were collected as final product.

Due to the inability to perform additive manufacturing on UO_2 at Chalmers, the suitability of powders for additive manufacturing was evaluated by investigating the produced powders sinterability in both conventional sintering and by spark plasma sintering (SPS).

Two sets of pellets were pressed by conventional cold pressing techniques at about 250 MPa. The first set of pellets were pressed from material prepared from the batches of nanometric UO_2 produced and the second set of pellets were pressed from UO_2 powder prepared by precipitation of $\text{UO}_3 \cdot \text{H}_2\text{O}$ from uranyl nitrate solution, followed by thermal reduction of the $\text{UO}_3 \cdot \text{H}_2\text{O}$ into UO_2 in hydrogen atmosphere.

The pellet samples were sintered together at three different temperatures, 1200, 1650 and 1750 °C. In between each sintering experiment the pellets were examined for densification before being resintered at the next temperature in the series.

Sintering of conventional UO_2 powders generally require significant temperatures and sintering encountered in literature frequently sinters in the range of 1600-1800 °C. The pellets pressed from conventional powder preparation did not sinter at all at the sintering experiment at 1200 °C. The pellets pressed from nanometric powders did however display significant size reduction and were from an average of three pellets, estimated to have sintered to about 68% of the theoretical density.

The second sintering cycle at 1650 °C resulted in an average density of about 90% of the theoretical density and that density was retained during the third sintering experiment under the sintering conditions used. The pellets made from conventional UO_2 powder reached a density of about 87% of theoretical density after the third sintering experiment. Considering the small number of pellets sintered in the experiment, one should not overinterpret the results and the final densities of 90% and 87% between the two sets of pellets are practically considered to be more or less equal values. It did however appear apparent that the sintering properties of the nano-powder UO_2 was significantly improved compared to conventional powder.

Microstructural characterization using SEM was performed on the pellets sintered from nanometric UO_2 powder to determine the grain structure developed during sintering.

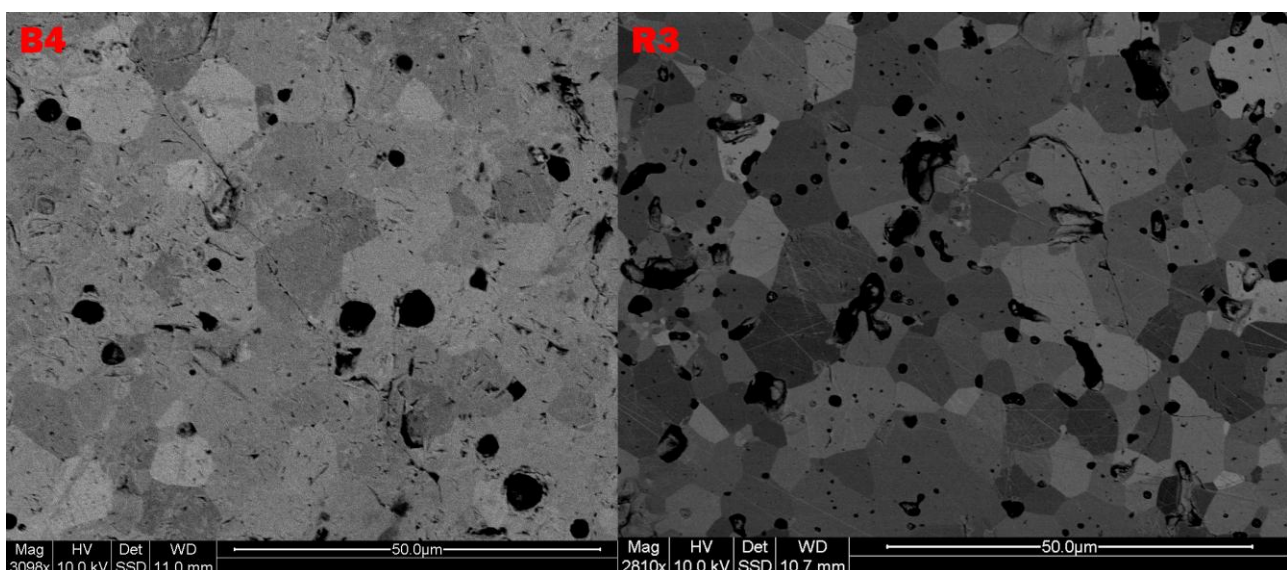


Figure 2. Comparison between grain structures developed when sintering nanometric (B4) and conventional (R3) UO_2 powders. Domains of grains reaching characteristic lengths of about $10\mu\text{m}$ could be observed in both samples, indicating that similar grain structures could be obtained during sintering. Image from Julia Bergströms Master thesis “Synthesis and characterization of nano-metric simulated nuclear fuel (SIMfuel)” carried out at Nuclear chemistry’s laboratories 2024.

As figure 2 indicates there were areas observable in pellets from both types of powders that displayed similar microstructural features. The sequence of sintering parameters applied in the experiments resulted in pellets with grains on the size order of about $10\mu\text{m}$. When studying the pellets made from nanometric UO_2 it was however also possible to locate pellet domains where clusters of smaller grains persisted in the pellet as illustrated in figure 3.

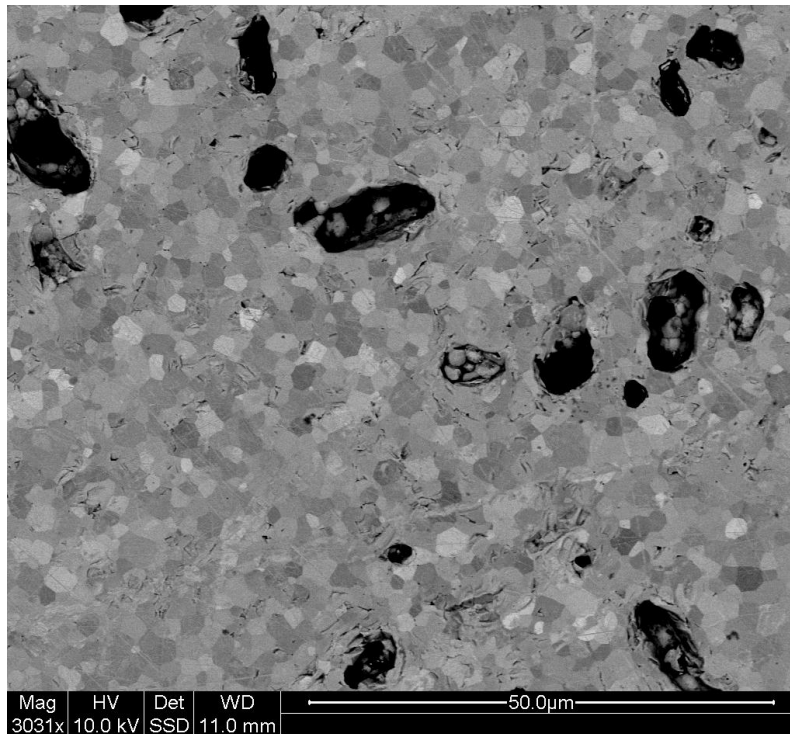


Figure 3. Microstructural domain of pellet B4 (from nanometric UO_2) exhibiting residual reduced grain sizes. A significant fraction of the grains observed in such domains were estimated to be in the range of about $1\text{-}3\mu\text{m}$ in size which is significantly smaller than the more predominant domains of pellets observed as illustrated by figure 2. Image from Julia Bergströms Master thesis “Synthesis and characterization of nano-metric simulated nuclear fuel (SIMfuel)” carried out at Nuclear chemistry’s laboratories 2024.

The data obtained from the sintering studies implied that the powders produced by direct precipitation from U(IV) solution displayed a significant improvement in sinterability, indicating a good potential for being a suitable candidate powder in additive manufacturing techniques.

The improved sintering qualities in the prepared powders could only be inferred by the decreased sintering onset temperature observed during the $1200\text{ }^\circ\text{C}$ sintering experiment. As a compliment, spark plasma sintering (SPS) was performed to get an online monitored comparison between the densification behavior of the nanometric UO_2 powder and the conventionally produced powder. SPS of both powders was performed by heating to $400\text{ }^\circ\text{C}$ in two minutes and from that point by $100\text{ }^\circ\text{C}$ per minute to $1300\text{ }^\circ\text{C}$ where a 5 minute isothermal sintering time was maintained before cooling the samples to room temperature. The compaction pressure used during the experiments was 100 MPa and sintering was performed in vacuum.

The logged compaction behavior of the SPS experiments for nanometric and conventional UO_2 powders are presented in figures 4 and 5.

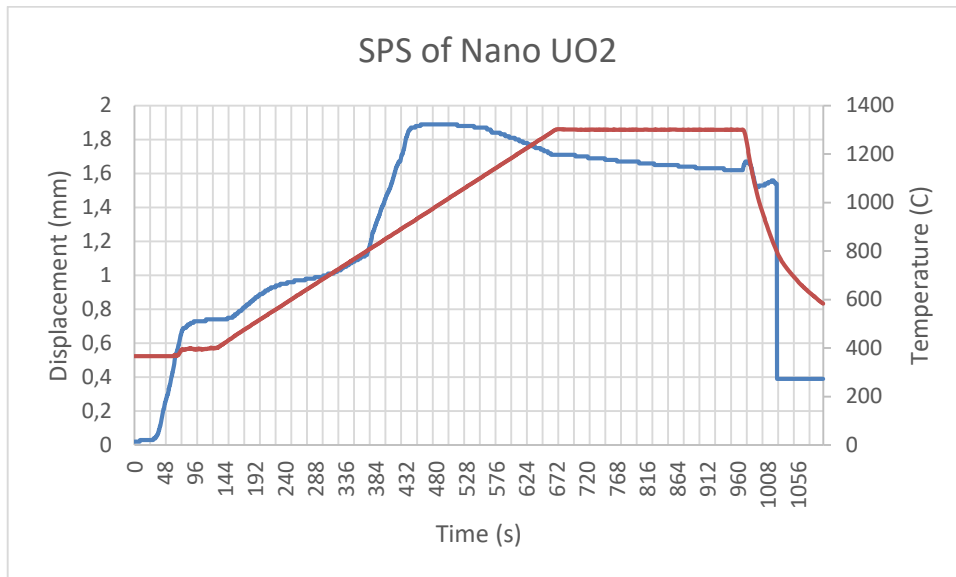


Figure 4. Compaction behavior and temperature profile during SPS of nanometric UO_2 . The blue line refers to the material compaction and the orange to temperature during the experiment.

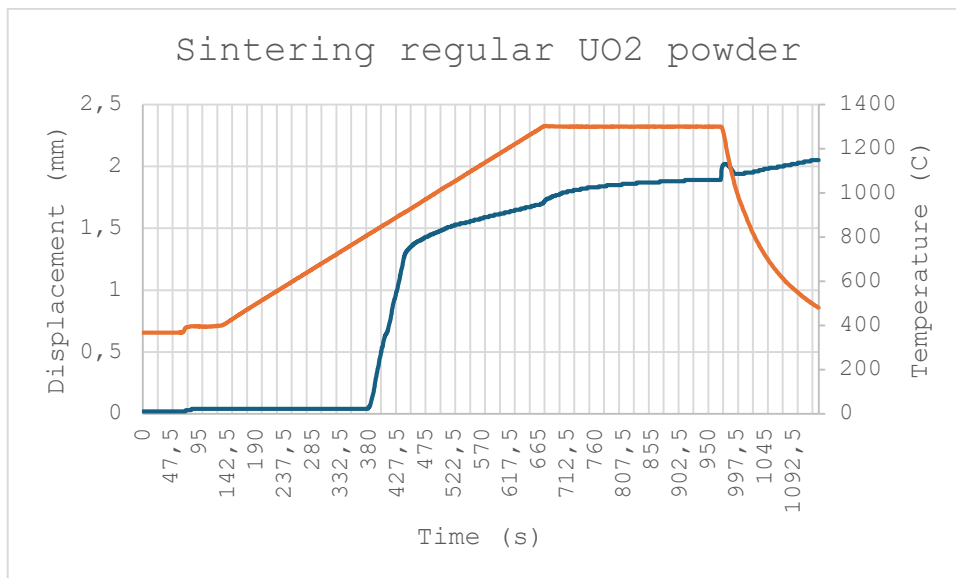


Figure 5. Compaction behavior and temperature profile during SPS of conventional UO_2 powder. The blue line refers to the material compaction and the orange to temperature during the experiment.

The system pyrometer operated during experiments did not measure below 367 °C, causing the initial heating ramp to not appear linear in the logged data. From figures 4 and 5 it becomes clear that the nanometric UO_2 powder sinter faster and maximum densification was obtained at about 920 °C compared to the conventional powder sintering which reached its final compaction almost 4 minutes into the isothermal stage at 1300 °C. The initial compaction of the nanometric powder, occurring before the reliable temperature measurement range of the pyrometer, clearly show that something happens in the material below the measurement threshold of 367 °C. By looking at the system pressure during sintering it is believed that this compaction was caused by evaporation of volatile compounds.

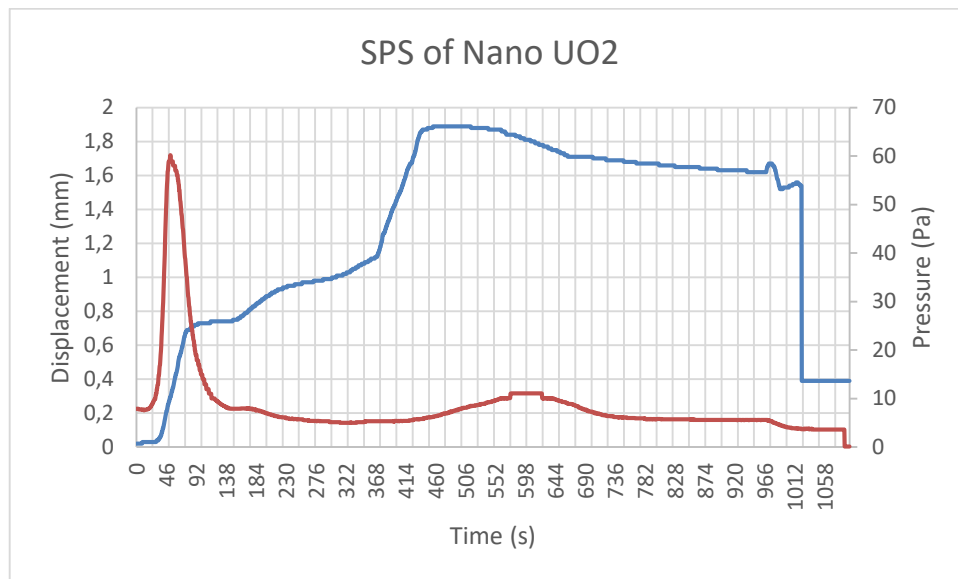


Figure 6. Pressure evolution in the SPS system during sintering of nanometric UO₂.

No analysis is installed on the SPS equipment to perform analysis on the off gases during sintering but given the conditions under which the powders were precipitated the likely compounds to degas would be H₂O and possibly some NH₃. All prepared powders were dried in glovebox to apparent dryness before any experiments were conducted. Therefore, it stands to reason that the gas coming from the sample most likely is H₂O crystal bonded to the UO₂ or strongly enough chemisorbed on the particle surfaces to not be removed by simple drying.

Powder X-ray diffraction was performed on the pellets sintered by conventional sintering from the nanometric UO₂ powders to confirm the formation of pure UO₂ in the fabricated pellets.

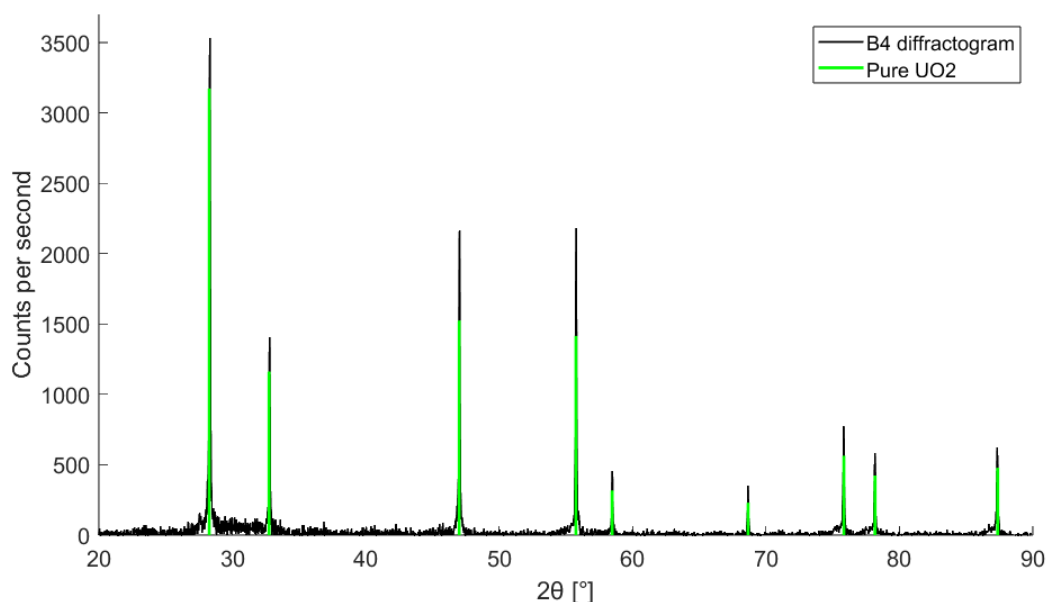


Figure 7. PXRD pattern measured on pellet produced by conventional sintering of nanometric UO₂ powder. Image from Julia Bergströms Master thesis “Synthesis and characterization of nano-metric simulated nuclear fuel (SIMfuel)” carried out at Nuclear chemistry’s laboratories 2024.

Figure 7 compares the recorded diffractogram to the reference peak positions of UO₂ recorded in the Joint powder diffraction file (PDF) database. It was confirmed that the pellet indeed consisted of UO₂,

indicating that the substances degassing from the material during sintering do not affect the final composition of the material when sintered in reducing conditions.

The sintering behavior of the powders prepared by precipitation from U(IV) stock solution thus displays promising sintering properties that might make the technique suitable for preparing powders for additive manufacturing techniques with regards to powder sintering properties.

2.2 Suspensions

2.2.1 Task description

As an extension of the previous task the best powder conditioning for the establishing of ideal suspensions is to be considered. These suspensions will be used as printing inks in some of the additive manufacturing approaches.

2.2.2 Task progress

The progress of this task was limited to evaluating the methodology of producing a suspension of uranyl nitrate using the sol-gel technique. Further research should be conducting in the improvement of the gel solution in order to meet the requirements of the fuel 3D-printing techniques.

2.3 Chemical solutions

2.3.1 Task description

The production of chemical solutions (e.g., metal nitrate solutions) is essential for production methods, which remain in the pure aqueous regime, and are therefore beneficial when it comes to non-contamination issues and continuous production processes. These can be gelation-based techniques, including additive manufacturing with gels. The exact pre-conditioning of such solutions must be defined and tested. Again, different potential source forms must be considered, which might even imply a dissolution step.

2.3.2 Task progress

2.4 Microspheres

2.4.1 Task description

A novel electrospray-driven atomization process will be developed to create composite UO_2 microspheres with optimized carbon content. Key advantages of this technique are a simple setup and great process flexibility in terms of composition of the feeding solution, gelation conditions and productivity. The composite spherical aggregates will serve as precursors for the carbothermal conversion from oxide to nitride fuel. A homogeneous distribution of organic/inorganic carbon donors throughout the microsphere and balanced overall carbon content are expected to improve the yield of carbothermal conversion and reduce C and O impurities, thanks to the intimal contact between the reactants. The impact of size and morphology of oxide/nitride microsphere on the sintering behavior by SPS or other processes will be addressed in the project. In particular, a strict control over microsphere size and dispersity is expected to generate aggregates with better flowability, die filling and packing density, potentially resulting in better sinterability with reduction of processing temperature and time. Size and morphology of the microspheres produced by electrospray-driven atomization can be controlled acting on the atomization parameters and composition and physical properties of the feeding metal solution.

2.4.2 Task progress

A series of preliminary tests on microspheres production was conducted in this period. The microspheres could be produced using a vibrating nozzle. The produced kernels had a wide size and shape distribution, so another technique started to be investigated. The technique is based on a Electrohydrodynamic printing nozzle that it's capable of producing microspheres of controlled size and production rate. The components of this setup have been bought and the first tests are expected to start in the following months.

The solidification of the microspheres is currently made with the use of a warm silicon oil bath. This method enables a quick solidification but requires an additional washing of kernels step. An additional solidification technique using microwaves is going to be tested on a further time during this project.

3 SUMMARY

Methods for doping of uranium based materials through co-precipitation have been developed through direct precipitation of mixed nitrate solutions based on uranyl nitrate and precipitation by pH increase using aqueous ammonia. Additionally, a methodology for direct precipitation both of pure nanometric UO_2 particles and Ce doped particles from oxidation state controlled U(IV) solutions have been investigated. The pellets produced from nanometric UO_2 powders proved to sinter more readily and at lower temperature than corresponding powders prepared by traditional precipitation techniques. The nanometric powders do however contain relatively large quantities of sorbed water, which does not inhibit sintering using SPS but could in conventional sintering techniques result in slightly cracked pellets. This does however not seem to be a limiting property with respect to additive manufacturing since all moisture is gassed off during low temperature heating and should not inhibit additive printing which will occur at much higher temperatures than what the moisture gasses off at. Starting from nanometric UO_2 does seem like a promising route for efficient additive fuel manufacturing, though conversion from nanometric UO_2 to UN will reduce the specific surface area of the powders. It is still believed that UN produced from nanometric UO_2 will be a promising material for additive manufacturing of UN fuel pellets compared to UN produced from “regular” UO_2 powders.