

M. BRYKALA^{1*}, M. ROGOWSKI¹, D. WAWSZCZAK¹, T. OLCZAK¹, T. SMOLINSKI¹

MICROSPHERES AND PELLETS OF UO₂ PREPARED VIA ADU BY COMPLEX SOL-GEL PROCESS AND ICHTJ PROCESS

This study is devoted to synthesis and characterization of uranium dioxide microspheres ($\varnothing < 100 \mu\text{m}$) and pellets by application of powder-free process called the *Complex Sol-Gel Process*. The precursors of prepared sols were ascorbic acid solution with dissolved a freshly precipitated ammonium diuranate. The microspheres of uranyl-ascorbate gel were obtained using the *ICHTJ Process*. The pellets were formed by pressing and sintering of uranium dioxide powder. Studies allowed determining an optimal heat treatment of calcination, reduction and sintering processes at temperatures of 700°C, 900°C and 1300°C, respectively. The main parameters which play a key role in the process of synthesis method and features of the pellets and microspheres of uranium dioxide are described in this article.

Keywords: Uranium dioxide, microspheres, pellets, *Complex Sol-Gel Process*, *ICHTJ Process*

1. Introduction

The physico-chemical properties of the uranium fuel for nuclear reactors have a significant impact on the selection of the type and parameters of the reactor's operation, and also determine the economic results of its operation, due to the degree of fuel burn-out. Therefore, work on the selection of fuel material and improvement of fuel production technology remains one of the most important factors influencing the directions of development of nuclear energy. Currently, more than 85% of used nuclear fuel in the world is uranium dioxide (UO₂) pellets contained in cladding of fuel rods of a special alloy, mostly zirconium alloy. UO₂ has been used as the fuel material for the commercial thermal reactors all over the world, and powder metallurgical pellet fabrication process is also commercially well-established [1-8].

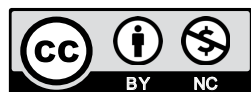
The second potential type of nuclear fuels is spherical one, which is proposed for High Temperature Gas Cooled Reactors, such as a generation IV reactor. A considerable progress in production of those nuclear fuels has been reported over the years [1,9-12]. One of the unique methods to produce them and the most perspective is a sol-gel process. It is the wet chemical method which mainly involves the gelation of a droplets of sol to gel microspheres. Afterwards, they are washed, dried, and heat treated to obtain high density microspheres [1,10].

In this paper, an alternative method of UO₂ pellets and microspheres with diameter below 100 μm synthesized directly from ammonium diuranate (ADU) was proposed. ADU, often named as "yellow cake", plays very important role in the fabrication of uranium oxide fuel. The name "ammonium diuranate" is controversial, but has widespread use. Reason of this is the composition and structure of ADU, which have often been investigated [13-15]. ADU is insoluble in water, therefore in order to obtain spherical grains it seems necessary to use the sol-gel method. One of them is a powder-free *Complex Sol-Gel Process* (CSGP), which combined with the *ICHTJ process* (name of the process from polish acronym of the Institute) of gelation, produce final ceramic material in spherical shape with desired size distribution. Moreover, the fabrication conditions with properties of microspheres and sintered pellets of UO₂ were investigated. The CSGP is an original variant of a sol-gel method, which has been elaborated in the Institute of Nuclear Chemistry and Technology. Utilization of ascorbic acid (ASC) is the main aim of this method where it plays a role as complexing agent to obtain a stable aqueous sols with a high degree of amorphization and a homogenous distribution of the components. The CSGP has been used to synthesize a variety of advanced ceramic materials e.g. Li₂TiO₃ [16], uranium carbide [17,18], and thorium dioxide [19].

The synthesis of different sized UO₂ microspheres by using internal-, external- and water extraction gelation techniques are

¹ INSTITUTE OF NUCLEAR CHEMISTRY AND TECHNOLOGY (INCT), CENTRE OF RADIOCHEMISTRY AND NUCLEAR CHEMISTRY, 16 DORODNA STR., 03-195 WARSZAWA, POLAND

* Corresponding author: m.brykala@ichtj.waw.pl



well known for more than a decade [10]. However, the explanation and characterization of parameters concerning fabrication of pellets and UO_2 microspheres directly from ADU with ASC, especially by extraction of water process, is rarely found. The conversion reactions into uranium oxides from different precursors are relevant for the fabrication of advanced nuclear fuels, particularly minor actinide-containing. The presented methods can be an attractive alternative to the conventional one used for the production of uranium fuel in the form of microspheres and pellets.

2. Experimental

2.1. Materials

The following reagents for preparation of sols were used: uranyl nitrate (Chemapol Praha, 99%) as a source of uranium; ascorbic acid (Takeda Europe GmbH, pharmaceutical grade) as a complexing agent. During the gelation step – 2-ethylhexanol-1 (2 EH, Acros Organics, 99%) was used as organic phase to extract water. The sorbitol monooleate – SPAN-80 (Fluka) served as surfactant. The purity of used nitrogen and nitrogen with 5% hydrogen mixture were 99.99%. All the other reagents were used as analytically pure compounds.

2.2. Preparation of uranyl-ascorbate sol solutions

The process flow sheet used for the preparation of uranium dioxide in the shape of microspheres and pellets is shown in Fig. 1.

The first step of UO_2 synthesis by the CSGP was preparation of a homogeneous uranyl-ascorbate sol with various concentration and molar ratio of uranyl ions to ASC. The initial form of uranium substrate was ADU, which was obtained by precipitation from $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution with $\text{NH}_3(\text{aq})$. The addition of $\text{NH}_3(\text{aq})$ to $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to MR $\text{NH}_3(\text{aq})/\text{UO}_2^{2+} = 2$ corresponds to the polymerization of uranyl ions according to the possible mechanism (equation (1)). An increase of ratio $\text{NH}_3(\text{aq})/\text{UO}_2^{2+}$ causes precipitation of ADU (with a simplified formula $(\text{NH}_4)_2\text{U}_2\text{O}_7$) according to the equation (2) [15]. The precipitation conditions affecting its physical form, which determines the sinterability of UO_2 were investigated. Literature survey has shown that fine powders obtained from ADU with high density and specific surface are better sintered [20]. The precipitation of ADU was carried out at equilibrium, which was achieved by addition of ammonia solution in portions and allowing the solution to adjust pH after each portion added. The precipitate was washed twice with water and then air dried.

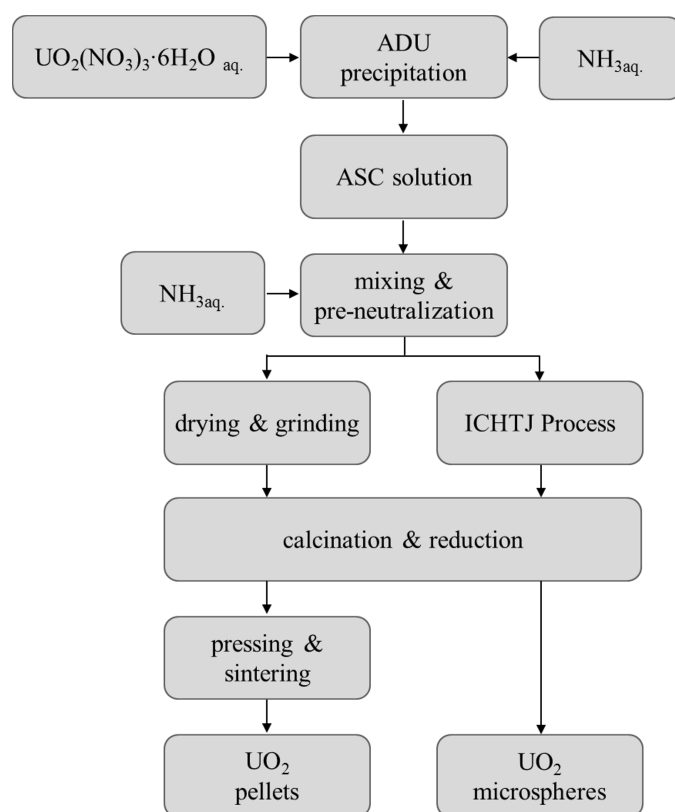
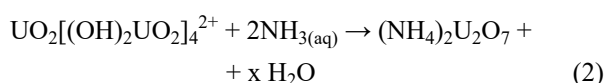
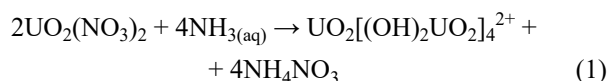
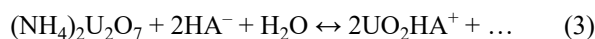


Fig. 1. Flow sheet for the preparation of UO_2 pellets and microspheres ($\text{Ø} < 100 \mu\text{m}$) by the Complex Sol-Gel Process

Subsequently, a ADU powder was added during intensive mixing of 1M ASC water solution according to the equation (3). The molar ratio of ASC to ADU equalled 2, which corresponds to MR ASC/U equal 1.



A – ascorbate anion.

Afterwards, partial hydrolysis by addition of $\text{NH}_3(\text{aq})$ to a certain pH value was carried out. To ensure slow and homogeneous pre-neutralization, $\text{NH}_3(\text{aq})$ was added to sol solution dropwise before precipitation at pH = 4.0 ~ 5.0.

2.3. Formation of microspheres of uranyl-ascorbate gel

In this work, the small sized spherical particles of uranyl-ascorbate gel were obtained by applying the *ICHTJ Process* in a 1000 mL glass-enclosed reactor with rapid stirring agitator. There are many factors influencing optimal conditions of gelation by the *ICHTJ Process*, such as concentration of aqueous phase, sol to organic phase volume ratio, type and concentration of surfactant, flow rate of sol, mixing intensity, and time of gelation. The effect of each factors were earlier investigated and reported [21]. At the beginning of gelation process a formation of sol emulsion in long-chained aliphatic alcohol 2-ethylhexanol-1 containing 1 vol.% of surfactant SPAN-80 takes place. The surfactant has a low-HLB (hydrophilic-lipophilic balance) to prevent coalescence and sticking of sol droplets. During contact of droplets

of sol with organic emulsion the extraction of water with 2EH is carried out. Removing of water from sols droplets concentrates the colloid until it becomes unstable and coagulates to solid microspheres of gel. After switching off a stirrer the microspheres fall to the bottom of reactor and neither have tendency to stick together no form some larger aggregates. The last stage is separation of spherical powders and washing them with acetone to remove the residual organic compounds, which can cause agglomeration of microspheres in the further thermal treatment steps.

The chosen optimal parameters for gelation to microspheres by the *ICHTJ Process* are presented in Table 1.

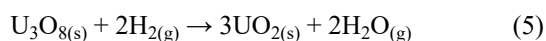
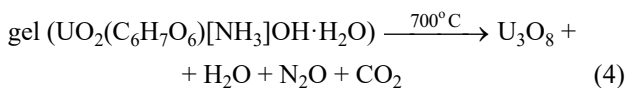
TABLE 1

Summary of optimal gelation process parameters to microspheres of uranyl-ascorbate gel by the *ICHTJ Process*

Parameter	Value / Quantity
Concentration of metal	1 M
Amount of ASC	MR ASC/ $\text{UO}_2^{2+} = 1$
pH	~4.5
Composition of gelling organic phase	Volumetric proportion 2EH:SPAN-80 = 100:1
Volume of organic phase	1000 mL
Volume ratio (sol/organic)	1 mL/100 mL
Temperature of gelation	Approx. 25.0°C
Diameter of needle	0.5 mm
Flow rate	0.5 mL/min
Stirring rate	800 rpm
Gelation time	45 min

2.4. Thermal treatment to uranium dioxide

The wet microspheres of gel were dried in an air oven at 100°C for 12 h. Then, dry powders were thermally treated - calcined to triuranium octoxide (U_3O_8) and reduced to UO_2 , according to the proposed equations (4) and (5). A suitable conditions have to be selected to achieve the desired properties – spherical shape and non-cracked surface of the product. The flow chart of thermal treatment of gel to UO_2 is presented in Figure 2.



The selected thermal treatment program was used to ensure calcination at 700°C in air atmosphere of the gels and full reduction at 900°C in N_2/H_2 mixture of obtained U_3O_8 to UO_2 . The heating rate of calcination was slow (2°C/min) to avoid stress cracking of particles while decomposition of organic compounds. The heating rate of reduction was faster (5°C/min) but with preservation of features in final product both sphericity, undamaged surface of grains, and their flowability.

2.5. Production and sintering of uranium dioxide pellets

The next subject of research was pressing of UO_2 as irregular grains into pellets, and sintering under inert atmosphere. The uranyl-ascorbate sol, prepared from ADU and ASC, was gelled by evaporation of water in an oven at 70°C. The resulting gel was grounded and then calcined and reduced (according to the aforementioned conditions) to UO_2 . Afterwards, powders were pressed on a hand press in double-sided dies for compacts with a diameter of 20 mm under a pressure of 10 MPa. To increase the strength of the compacts and reduce friction during pressing, 3% glycerol in alcohol, 3% polyethylene glycol in alcohol, distilled water or 2% aqueous polyvinyl alcohol solution were added to the powders.

The sintering was carried out in a high-temperature chamber furnace at 1300°C for 5 hours under vacuum ($p \leq 10^{-3}$ mbar). The heating and cooling rates were not higher than 180°C/h.

2.6. Characterization

The sedimentation times of formed ADU powders after complete precipitation from $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and uranyl-ascorbic acid complex solutions were investigated. A sol pH measurements were performed using pH-meter HANNA Instruments HI 2223. Spherical particles of gels and oxides were characterized by Scanning Electron Microscopy (SEM) with a Zeiss DSM 942, and optical microscope Motic BA300. The powders of gels and oxides were mechanically screened with an AS200 Digit (Retsch) apparatus through Multiserw-Morek sieves (20 μm , 50 μm , 100 μm , and 125 μm) for 4-6 h.

The thermogravimetric analysis using Derivatograph OD-102 (MOM, Hungary) was employed to analyse mass changes

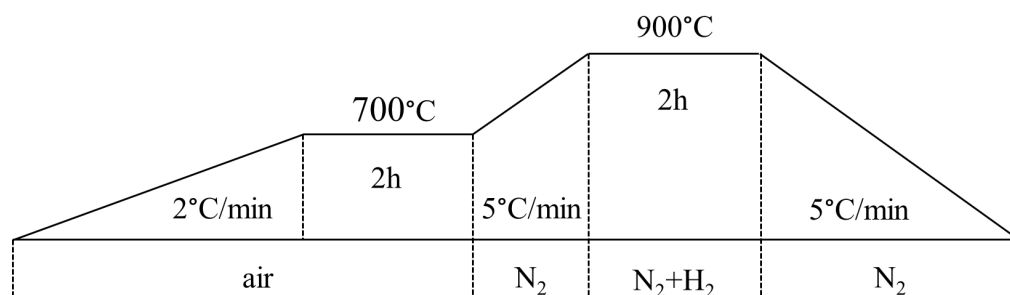


Fig. 2. Flow chart of calcination of uranyl-ascorbate gels and reduction of U_3O_8 to UO_2

of uranyl-ascorbate gels heated at 10°C/min in air atmosphere. Drying and calcination of uranyl-ascorbate gels were performed in a muffle furnace (Nabertherm L15/13/P330). The crystal-line structure of uranium oxides were characterized by the powder X-ray diffraction (XRD) on the Bruker D8 Advance unit. The reducing to UO_2 and sintering process were carried out in a chamber furnace (Nabertherm VHT 08/18 GR, 8 dm³ volume).

3. Results and discussion

3.1. UO_2 microspheres

The preparation of stable and homogenous uranyl-ascorbate sol solutions from ADU were studied at first. ADU was produced by reaction of 0.8M $\text{NH}_3(\text{aq})$ with 0.4M $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The precipitation reactions between $\text{NH}_3(\text{aq})$ and uranyl-ascorbic acid complex with different MR ($\text{ASC}/\text{U} = 0.5\text{--}2.0$) were also investigated (Table 2).

TABLE 2

Studies on the amount of precipitate and sedimentation time of powders after reaction of $\text{NH}_3(\text{aq})$ with $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and uranyl-ascorbic complex solutions

MR ASC/U	Volume of precipitate [ml]	Time of sedimentation [min]
—	12.5	35
0.5	28.0	150
1.0	36.0	210
1.5	34.5	1200
2.0	58.5	1140

The results presented in Table 2 show increasing of the necessary amount of $\text{NH}_3(\text{aq})$ needed to full precipitation as molar ratio ASC/U increases. The smallest volume to complete precipitation was observed for pure $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. A higher ASC concentration in solution causes volume increase of resulting sediment and a longer sedimentation times were observed. In addition, the shortest drying time was obtained for pure ADU. Remaining samples with ASC , proportionally with increasing ASC/U , showed longer drying times. Therefore, there was decided that the precipitated pure ADU would be used as the uranium substrate for preparation of uranyl-ascorbate sols.

The sedimentation time of formed ADU powders was investigated. ADU was precipitated from a 1 mol/dm³ $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ by ammonia added “quickly” (continuously dosing) and “slowly” (in portions until the precipitate dissolved). The resulting precipitate was then washed three times with water. Sedimentation tests of ADU suspensions in distilled water under static conditions were carried out. Analyses were conducted in graduated cylinders placed vertically. The ADU powders precipitated in the abovementioned manner, unwashed and washed with water, were examined. The sedimentation curve was determined

by reading a level of interface between clarified liquid and the suspension. Sedimentation curves obtained on the basis of these measurements are shown in Figure 3.

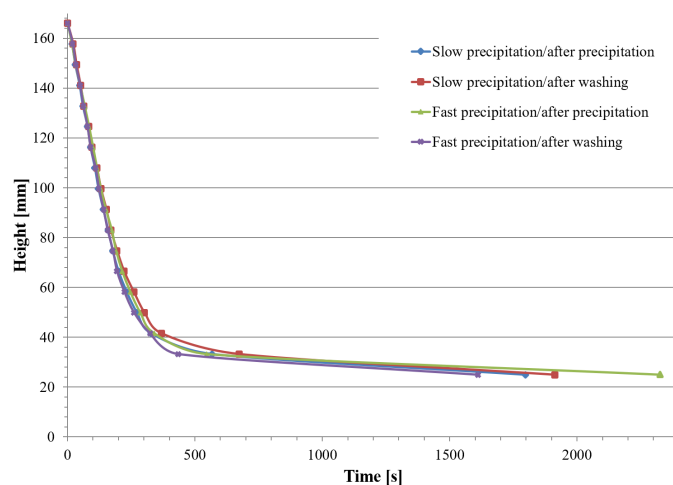


Fig. 3. Sedimentation curves for the ADU suspension obtained in various ways

The shape of the curves varies slightly depending on the ADU precipitation conditions. For 4 types of suspensions, the sedimentation rates were similar, which indicates the presence of particles with similar sizes.

ADU is insoluble in water, which makes it impossible to obtain uranium microspheres using the *ICHTJ Process*. Therefore, it is necessary to combine it with the *CSGP*. The preparation of uranyl-ascorbate sol were carried out by the addition of ADU to ASC solution in a 2:1 molar ratio, what it results in the brown complex $[\text{UO}_2\text{A}]^+$ (equation 3). Two hydroxyl groups of ASC are readily available for metal cations, including UO_2^{2+} , which allows complex formation. The dissociation constants for ASC are respectively for C (3) $\text{p}K_1 = 4.04$ (25°C) and C (2) $\text{p}K_2 = 11.34$ (25°C) [22].

A partial pre-neutralization step of uranyl-ascorbate sol were important in order to proper gelation into microspheres. Raising sol's pH increases its viscosity. The value of pH ~4.5 seems to be optimal, after which a beginning of gelation was observed. Too high viscosity of sol decreased the possibility to generate droplets of sol by a needle to an organic solvent. However, too low viscosity also decreased the possibility to obtain stable emulsion droplets and obtaining of the desired size and sphericity of spheres were not possible.

The gelation by *ICHTJ Process* to spherical particles of uranyl-ascorbate gel was conducted by water extraction from the sols drops by 2EH. There were many parameters, which had a influence on the shape and size of the final products [21]. Basing on this an optimal parameters were selected, and presented in Table 1. The sol flow rate and stirring rate of mixture have a predominant influence on size of microspheres and is shown in Fig. 4.

The particle size distributions of dried gel microspheres were characterized based on image (Fig. 5) and sieve analysis.

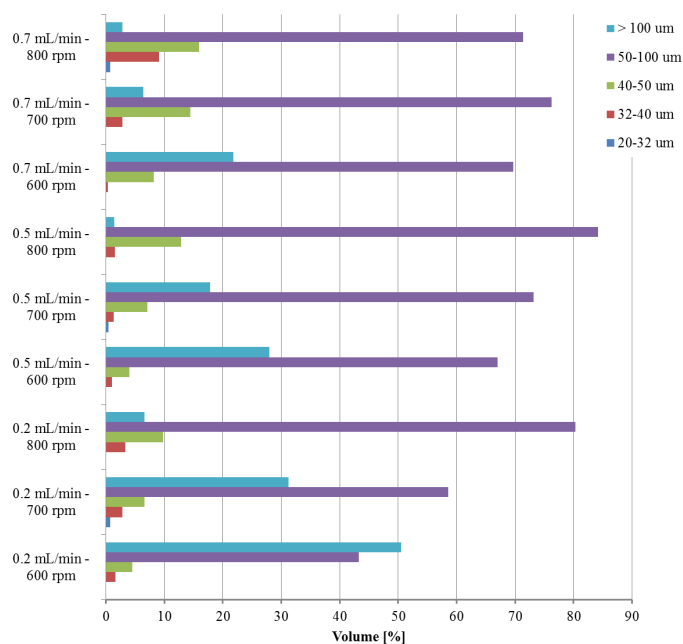


Fig. 4. Diagram of the distribution of gel microspheres diameters obtained by ICHTJ Process for the different value of flow rate and stirrer rotation rate (other parameters are present in Table 1)

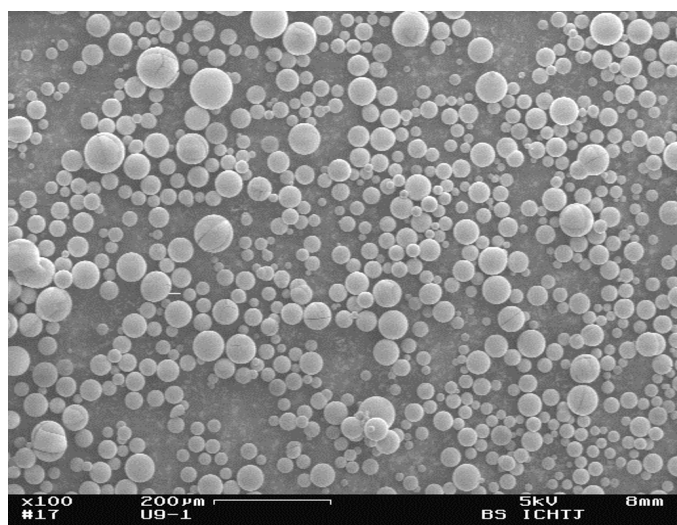


Fig. 5. SEM micrographs of microspheres morphology of uranyl-ascorbate gel

Results of size analysis shown that the size of microspheres was inversely proportional to the flow rate of sol dispensing and stirrer rotation rate in organic solvent. The content of spherical particles with larger diameters was smaller if mixing speed and dosing rate were higher. This is related to size of drops sol formed in the organic solvent. The increasing of external forces acted on the droplets caused the formation of smaller microspheres. The main population of spherical particles of gels were mainly 50-100 μm in the range mainly 70-80% regardless of the mentioned parameters. Moreover, considering Figure 5 the efficiency of fabrication of the small microspheres was practically 100%.

The conditions of thermal treatment (Fig. 2) were determined on the basis of differential thermal analysis and thermo-

gravimetric analysis (DTA-TG) in air atmosphere and the results are shown in Fig. 6.

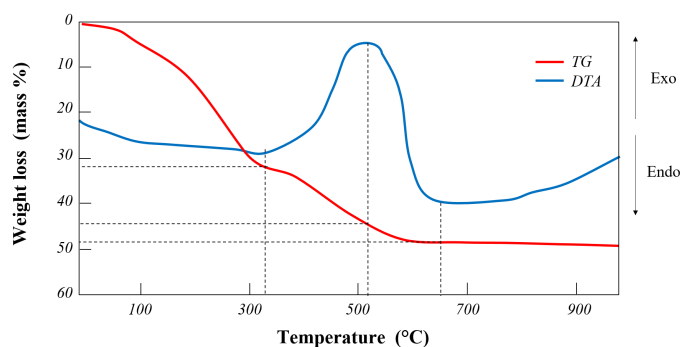


Fig. 6. Thermal analysis (TG, DTA) of uranyl-ascorbate gel obtained from ADU (heating rate 10°C/min)

The first mass loss at temperatures of 100-200°C was connected to evaporation of molecular water and hydroxide groups. The small exothermic effect at 220-320°C was connected with decomposition of the amorphous gel with CO_2 and CO release. The next mass change connected with a broad exothermic effect between 400-700°C was caused by combustion of ASC and products of its decomposition. After that, the mass started to stabilize what presents the formation of U_3O_8 . The total mass loss of gel to oxide equalled about 47%.

The obtained microspheres after calcination stage was the $\alpha\text{-U}_3\text{O}_8$ (Fig. 7), characterized by a orthorhombic structure in which all U-atoms have a coordination number equal 7 and it is a double pentagonal pyramid. The second form is the $\beta\text{-U}_3\text{O}_8$, which does not occur in this case, because arises when the $\alpha\text{-U}_3\text{O}_8$ is heated to 1350°C in air and slowly cooled to room temperature. The octagonal coordination (distorted octahedron) and coordination number equal 7 (double tetragonal pyramid) is observed for the $\beta\text{-U}_3\text{O}_8$.

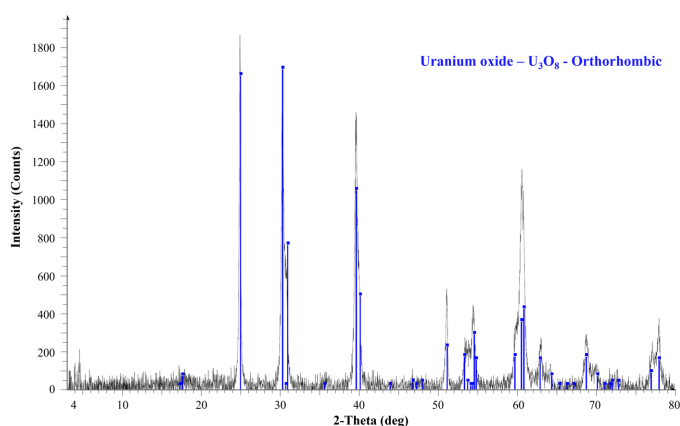


Fig. 7. XRD pattern of U_3O_8 formed after calcination under air of uranyl-ascorbate gel

The U_3O_8 was then reduced to final UO_2 in 5% H_2 . The heating rate and cooling rate were also very important in this process. Too high speeds (above 5°C/min) caused significant

cracking of the grains, which in turn leads to a loss of their sphericity (Fig. 8).

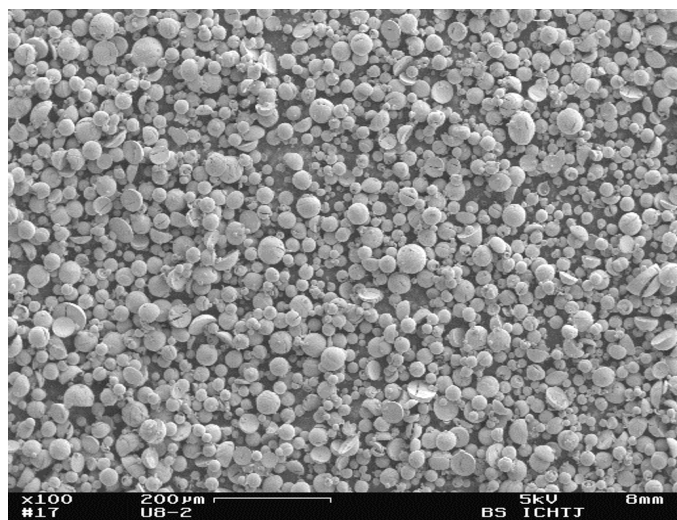


Fig. 8. SEM micrographs of cracked microspheres of UO_2 with to high heating rate ($10^\circ\text{C}/\text{min}$)

The correctness of selected parameters of the reduction process was confirmed by the results of the XRD analysis. The analyzed product was cubic UO_2 (Fig. 9).

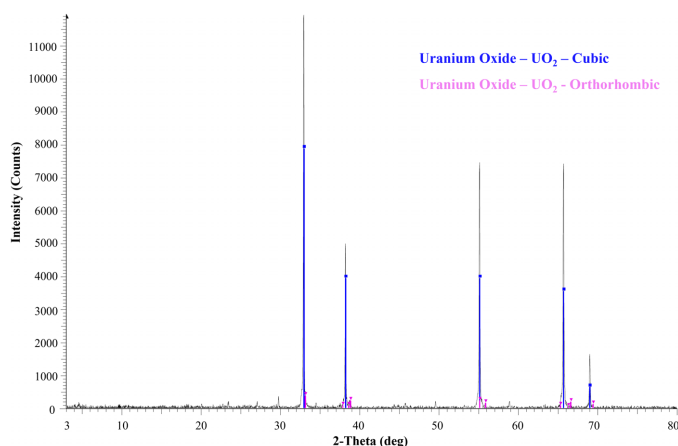


Fig. 9. XRD pattern of UO_2 formed after reduction under oxygen-free atmosphere of U_3O_8

The particle size distributions of U_3O_8 and UO_2 were characterized based on sieve analysis (Fig. 10). The results of size analysis showed that the main population of spherical particles of uranium oxides were predominant in number in range $50\text{-}100\ \mu\text{m}$ (60%) and 20% with diameter $40\text{-}50\ \mu\text{m}$. There were not too big differences in diameters between microspheres after calcination and reduction, but between uranyl-ascorbate gel and U_3O_8 were significant. It seems that during calcination the shrinkage by almost a half of diameter of gels was observed. The mass changes analysis (Table 3) of calcined uranyl-ascorbate gel microspheres showed a mass loss of 41.7%. The difference in mass loss between the calcination and reduction stages was not so significant – 4.7%. Moreover, from 1 gram of ADU taken

for synthesis by the CSGP method the 0.815 gram of UO_2 microspheres were obtained. It should be noted that the selected parameters of the CSGP & ICHTJ methods were appropriate and the obtained dioxide microspheres characterized by good size distribution.

TABLE 3

Mass balance of the synthesis spherical particles of UO_2 from ADU by the Complex Sol-Gel Process

ADU [g]	ASC/U gel [g]	U_3O_8		UO_2	
		mass [g]	mass loss [%]	mass [g]	mass loss [%]
1.000	1.467	0.855	41.7	0.815	4.7

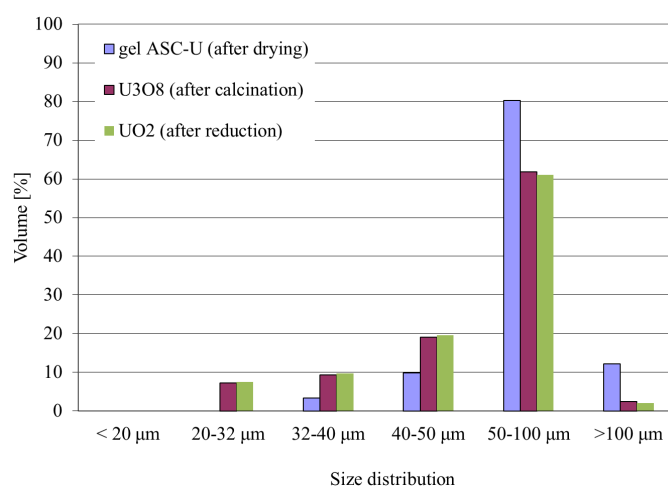


Fig. 10. Diagram of the ASC-U gel, U_3O_8 and UO_2 size distributions microspheres obtained by ICHTJ Process (parameters are present in Table 1)

3.2. UO_2 pellets

The irregular particles of uranyl-ascorbate gel were used to obtain of UO_2 pellets. The preliminary studies on cold pressing to pellets were carried out on UO_2 powder without any addition of binder. To increase the strength of the compacts and to reduce friction during pressing, plasticizers and a lubricant were added to the powders. Their lack caused a heterogeneity of pellets which after removed from the press just crumbled. Therefore, the influence of the various binders on the properties of the obtained pellets was investigated.

The applying only additives such as 3% glycerol in alcohol, 3% polyethylene glycol in alcohol, distilled water or 2% aqueous polyvinyl alcohol solution did not guaranteed production of compacts. After the first pressing, the compacts were again crushed and grounded. After second pressing a durable and dense compacts were obtained. Their strength has not been tested.

The sintering process was carried out in a high-temperature chamber furnace in a vacuum ($p \leq 10^{-3}$ mbar). The maximum sintering temperature was 1300°C (5 h), heating and cooling rate $180^\circ\text{C}/\text{h}$. The results of experiments describing features of the compacts and sinters are summarized in Table 4.

Geometric density analysis of sintered UO₂ pellets with various additives

No	Binder	UO ₂ mass [g]	volume of binder [μl]	pellet before sintering		pellet after sintering			
				height [mm]	radius [mm]	height [mm]	radius [mm]	mass [g]	density d_{geom} [g/cm ³]
1	3% glycerol in alcohol	23.91	150	11.0	10.0	10.1	9.4	23.32	8.53
2	3% glycerol in alcohol	21.00	125	9.4	10.0	8.4	9.7	20.30	8.46
3	3% polyethylene glycol in alcohol	26.46	175	12.5	10.0	11.2	9.6	26.13	8.24
4	3% polyethylene glycol in alcohol	21.01	225	9.5	10.0	8.6	9.5	20.60	8.62
5	H ₂ O	21.03	125	9.8	10.0	8.8	9.6	20.60	8.26
6	2% aqueous polyvinyl alcohol	21.03	125	9.9	10.0	8.8	9.6	20.30	8.16
7	2% aqueous polyvinyl alcohol	21.01	150	9.6	10.0	8.5	9.4	20.89	8.91

The sinterability of the powder would be better characterized by measuring the density in gas or liquid. This density is slightly higher than the geometric density measured with a micrometer screw gauge. The difference is due to the fact that the sintered pellets do not have the shape of a cylinder, and their diameter at half height is smaller than the diameter at the ends. The geometric density of sintered pellets was assessment and treated as a preliminary value to answer the question whether a given the works with those type of powder and sintering conditions should be continued. As shown in Table 4, the highest geometrical density (8.91 g/cm³) was obtained for UO₂ with 150 μl of 2% polyvinyl alcohol and cold-pressed at 10 MPa. It was found that the amount of additives effects on obtaining the sintering density, which was confirmed by the results obtained for 2% polyvinyl alcohol and 3% polyethylene glycol in alcohol. However, the pellets used as fuel element require the highest possible density. In the production on technical scale, a density approx. 10 g/cm³ are required. For a better understanding of the method UO₂ pressing and sintering the parameters such as grain refinement, quantity and type of additives, pressing pressure, pressing frequency, sintering atmosphere, and sintering time and temperature should be investigated. This paper present only preliminary studies on the preparation of sintered UO₂ pellets obtained by the CSGP.

4. Conclusions

This paper presents the results of a series of multi-stage works, which were completed with obtaining of the uranium dioxide in the forms of pellets and microspheres with diameters less than 100 μm by applying the *Complex Sol-Gel Process* with sintering under oxygen-free atmosphere.

- ADU, as substrate of uranium, is insoluble in water, so it was necessary to use of combination the *CSGP* and *ICHTJ* methods for obtaining uranium microspheres directly from ADU. The main population of spherical particles of gels were mainly 50-100 μm in the range mainly 70-80% regardless of the analyzed parameters.
- An optimal calcination temperature of 700°C with low heating rate 2°C/min and maximum 900°C in oxygen-free atmosphere for reduction process enabled receiving

a crack-free surface of small microspheres of monophasic UO₂ in cubic type crystal structure. The size distribution of obtained microspheres of U₃O₈ and UO₂ were in range of 50-100 μm (approx. 60% from all obtained).

- Using 1 gram of ADU taken for synthesis by the CSGP method gives 0.815 gram of UO₂ microspheres.
- In the research on pressing and sintering under inert condition to UO₂ pellets, the influence of the addition of various binders, on the properties of the resulted pellets was investigated. The pellets with a density above 8 g/cm³ (with the highest geometrical density 8.91 g/cm³ for of 2% polyvinyl alcohol and cold-pressed at 10 MPa) were obtained, whereas in industrial production the density of about 10 g/cm³ is obtained.
- Powder and sintered microstructure, mechanical and thermal strength, and behavior in the reactor should also be tested. This type of data is missing, but it was beyond the scope of research in the project. The obtained microspheres of U₃O₈ and UO₂, as well as its compacts and pellets were characterized with available possibilities.

It should be emphasized, however, that the obtained results showed that the production of UO₂ pellets and microspheres using the modified CSGP method was possible, and it seems beneficial to develop further research on UO₂ in the various forms.

Acknowledgments

This work is one part of the studies in the Polish Governmental Project "Technology Supporting the Development of Safe Nuclear Power," (SP/J/3/143 045/11), from The National Centre for Research and Development (NCBiR), Poland over the period 2011-2014.

The authors give special thanks to R. Laskowska and K. Godlewska for works on preparation of sol solutions and gelation to gels microspheres, Dr A. Deptula and MSc W. Lada for their support and friendly help, Dr. B. Sartowska for SEM analysis.

REFERENCES

- [1] V.N. Vaidya, J. Sol-Gel Sci. Technol. **46**, 369-381 (2008), <https://doi.org/10.1007/s10971-008-1725-0>

- [2] M. Cologna, V. Tyrpekl, M. Ernstberger, S. Stohr, J. Somers, *Ceram. Int.* **42**, 6619-6623 (2016), <https://doi.org/10.1016/j.ceramint.2015.12.172>
- [3] H. Wang, H. Huang, J. Liu, *Ceram. Int.* **40**, 5671-5674 (2014), <https://doi.org/10.1016/j.ceramint.2013.11.004>
- [4] T. Fujino, T. Shiratori, N. Sato, K. Fukuda, K. Yamada, H. Serizawa, *J. Nucl. Mat.* **297**, 176-205 (2001), [https://doi.org/10.1016/S0022-3115\(01\)00609-2](https://doi.org/10.1016/S0022-3115(01)00609-2)
- [5] J. Arborelius, K. Backman, L. Hallstadius, M. Limback, J. Nilsson, B. Rebensdorff, G. Zhou, K. Kitano, R. Lofstrom, G. Ronnberg, *J. Nucl. Sci. Technol.* **43** (9) 967-976 (2006), <https://doi.org/10.1080/18811248.2006.9711184>
- [6] J.K. Fink, *J. Nucl. Mat.* **279**, 1-18 (2000), [https://doi.org/10.1016/S0022-3115\(99\)00273-1](https://doi.org/10.1016/S0022-3115(99)00273-1)
- [7] D. Olander, *J. Nucl. Mat.* **389**, 1-22 (2009), <https://doi.org/10.1016/j.jnucmat.2009.01.297>
- [8] S.C. Finkeldei, J.O. Kiggans, R.D. Hunt, A.T. Nelson, K.A. Ter-rani, *J. Nucl. Mat.* **520**, 56-64 (2019), <https://doi.org/10.1016/j.jnucmat.2019.04.011>
- [9] International Atomic Energy Agency, High Temperature Gas Cooled Reactor Fuels and Materials, IAEA-TECDOC-CD-1645, IAEA, Vienna (2010).
- [10] D.D. Sood, *J. Sol-Gel Sci. Technol.* **59**, 404-416 (2011), <https://doi.org/10.1007/s10971-010-2273-y>.
- [11] K.C. Jeong, M.S. Cho, *Nucl. Eng. Technol.* **48**, 175-181 (2016), <https://doi.org/10.1016/j.net.2015.10.003>
- [12] International Atomic Energy Agency, Sol-gel Processes for Fuel Fabrication, IAEA-TECDOC-161, IAEA, Vienna (1974).
- [13] S. Manna, R. Kumar, S.K. Satpati, S.B. Roy, J.B. Joshi, *Nucl. Eng. Technol.* **49**, 541-548 (2017), <https://doi.org/10.1016/j.net.2016.09.005>
- [14] R. Eloirdi, D. Ho Mer Lin, K. Mayer, R. Caciuffo, T. Fanghänel, *J. Mater. Sci.* **49**, 8436-8443 (2014), <https://doi.org/10.1007/s10853-014-8553-0>
- [15] A. Deptula, *Nukleonika* **7**, 265-275 (1962).
- [16] A. Deptula, M. Brykala, W. Lada, T. Olczak, B. Sartowska, A.G. Chmielewski, *Fusion Eng. Des.* **84**, 681-684 (2009), <https://doi.org/10.1016/j.fusengdes.2008.12.077>
- [17] M. Brykala, M. Rogowski, *Prog. Nucl. Energy* **89**, 132-139 (2016), <https://doi.org/10.1016/j.pnucene.2016.02.015>
- [18] M. Brykala, M. Rogowski, T. Olczak, *Nukleonika* **60** (4), 921-925 (2015), <https://doi.org/10.1515/nuka-2015-0122>
- [19] M. Brykała, M. Rogowski, *J. Nucl. Mat.* **473**, 249-255 (2016), <https://doi.org/10.1016/j.jnucmat.2016.03.004>
- [20] S. Paik, S. Biswas, S. Bhattacharya, S.B. Roy, *J. Nucl. Mat.* **440**, 34-38 (2013), <https://doi.org/10.1016/j.jnucmat.2013.04.011>
- [21] M. Brykala, A. Deptula, M. Rogowski, W. Lada, *Ceram. Int.* **41**, 13025-13033 (2015), <https://doi.org/10.1016/j.ceramint.2015.07.002>
- [22] J.S. Casas, M.V. Castano, M.S. Garcia-Tasende, T. Perez Alvarez, A. Sanchez, J. Sordo, *J. Inorg. Biochem.* **61**, 97-108 (1996), [https://doi.org/10.1016/0162-0134\(95\)00034-8](https://doi.org/10.1016/0162-0134(95)00034-8)