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UO_2 fuel pellets fabrication via Spark Plasma Sintering using non-standard molybdenum die

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Abstract. The article investigates spark plasma sintering (SPS) of commercial uranium dioxide (UO_2) powder of ceramic origin into highly dense fuel pellets using non-standard die instead of usual graphite die. An alternative and formerly unknown method has been suggested to fabricate UO_2 fuel pellets by SPS for excluding of typical problems related to undesirable carbon diffusion. Influence of SPS parameters on chemical composition and quality of UO_2 pellets has been studied. Also main advantages and drawbacks have been revealed for SPS consolidation of UO_2 in non-standard molybdenum die. The method is very promising due to high quality of the final product (density 97.5-98.4% from theoretical, absence of carbon traces, mean grain size below 3 μm) and mild sintering conditions (temperature 1100 ºC, pressure 141.5 MPa, sintering time 25 min). The results are interesting for development and probable application of SPS in large-scale production of nuclear ceramic fuel.

1. Introduction

Fabrication of high mechanically stable compounds based on uranium dioxide (UO_2), which is a high melting oxide with melting temperature 2800 ºC, is a tough technological challenge. World's practice widely uses sintering technologies with and without external load (pressurizing) at high temperatures ranging in 1700-1800 ºC and are carried out in reductive medium with hours-long holding [1]. In this case conventional sintering conditions provide mechanically stable ceramic compounds in the form of UO_2 pellets with density ranging from 10.40 to 10.70 g/cm^3 (95-97.5 % from theoretical) and with various porosity and microstructure peculiarities. However, experts indicate significant drawbacks of the mentioned methods related to properties of the final product, e.g., non-uniform contraction and density of the material along the height dimension as well as distortion of geometrical shape. These increase the number of defected products, which don't meet the quality requirements.

To date as a high-tech approach to efficient synthesis of ceramic nuclear fuel electrophysical method of sintering are pointed out, in particular, the technology of spark plasma sintering (SPS). The technology is a brand new one in powder metallurgy and is actively applied for production of various ceramics [2,3]. The process is based on powder consolidation in constant electric field under the impact of high energy pulse of low voltage under constant pressure [4,5]. Obvious advantages of SPS are lower sintering temperatures due to high speed heating of consolidated powder by electric pulse current and also short process time. In this case grain growth is limited, microstructure is preserved and mechanical strength increases greatly without using any linking (reinforcing) agents that contaminate final product. Successful application of SPS to synthesis of ceramic fuel based on UO_2 is

presented in [6,7], where authors showed that the method allowed producing compounds with density of 96 % from theoretical at 1050 °C, holding time from 30 s and pressure of 40 MPa.
Despite the obvious advantages SPS technology has significant drawbacks that limit its development for synthesis of fuel products for industry. The main reason is the type of dies used that are usually such conducting materials as graphite and its composites. In this case, negative factors are active carbon diffusion from the surface of the dies and graphite surroundings into the bulk of sintered material, where it agglomerates as described in [8,9]. While known and described methods of carbon elimination by aluminum, molybdenum and tungsten foils as well as absorbing layers that interact with carbon and isolate it from the sintered material are not appropriate for fuel production because radioactive byproducts are formed after the contact of isolating materials with fuel composition and additional contamination of the material can occur. Besides that, graphite has a rather limited compression limit that does not allow higher pressures applied onto sintered powder that provide maximal stability of grain growth. Carbon diffusion into the sintered compound can reduce the degree of uranium oxidation due to its partial carbothermic reduction. The presence of carbon impurities in the fuel tablet product can be cause uncontrolled deceleration of neutrons during irradiated in the reactor. Mentioned factors impact such quality parameters as density, stability, thermal conductivity, resistance to bulk gas formation under radiation, full combustion. It is obvious that indicated drawbacks can be avoided using carbon-free dies. However, there is nothing to prove this fact because such research is absent in the literature.
Taking this into account, this work is aimed on investigating peculiarities of SPS consolidation of commercial UO_2 ceramic powder using different die instead standard graphite die. In particular, we tested molybdenum die for production of highly dense UO_2 pellets of required quality.

2. Experimental

2.1. Materials and methods

We used uranium dioxide powder with lean isotope U-235 of ceramic type produced by “PJSC MSZ” (Russia). Powders have bulk density ranging in 1.0-2.0 g/cm^3, specific surface area 3.0-5.0 m^2/g and particle size from 20 to 1000 μm.
We conducted sintering on a device SPS-515S produced by “Dr. Sinter*LAB^{TM}” (Japan) using molybdenum die (type of molybdenum is TC 48-19-203-85) 6.5 mm in diameter and 30 mm in height.

2.2. Synthesis technique

Sample of initial uranium dioxide powders was place into the die, moved into the vacuum chamber with residual pressure 6 Pa, after that sintering was conducted at optimal temperature and pressure followed by cooling and removing sample from the chamber.
Due to uranium dioxide easily undergoes oxidation in air into U_3O_8 we conducted sintering in vacuum to preserve the initial O/U ratio in the range 2.06-2.16. Sintering conditions: SPS temperature 1100 °C, applied pressure 141.54 MPa, heating rate 58 °C/min, holding time at maximal temperature 5 min and cooling time 30 min. The impulse ON/OFF regime was 12/2 frequency and duration 3.3 to 329 ms.

2.3. Characterization methods

Crystal phases of initial powders and sintered pellets based on uranium dioxide were identified by XRD on a multipurpose X-ray diffractometer D8 Advance “Bruker AXS” (Germany). Microstructure of the samples was carried out using scanning electron microscopy (SEM) on TM 3000 and S 5500 “Hitachi” (Japan) devices. Samples’ elemental composition based on quantitative and qualitative determination of the elements in the investigated materials was carried out using energy dispersive microanalysis (EDX) on Bruker station within TM 3000 microscope “Hitachi” (Japan). Specific density of the samples was determined using hydrostatic weighting in various liquids on a balance AdventurerTM “OHAUS Corporation” (USA).

3. Results and discussions

The main idea of implementing molybdenum die is to fully eliminate carbon diffusion from working die surfaces into the bulk of the compound. Additional advantage is the increased upper limit of applied pressure due to higher mechanical stability of molybdenum as compared to graphite. Such approach enables one to decrease considerably process' temperature and to obtain samples of desired geometrical shape close to the practical products without loss of quality.

In this experiment we used powder of ceramic type, which microstructure is defined by small crystallites not bigger than 500 nm (Fig. 1).

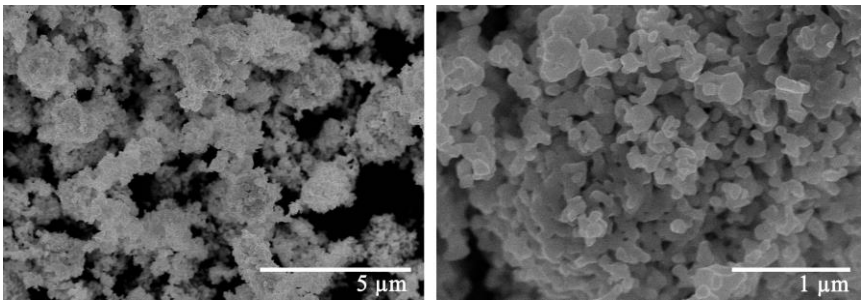

Figure 1. SEM images of UO_2 powder of ceramic type.

SPS consolidation of powder was conducted stepwise with periodical holding at certain temperature and at constant pressure as shown on Fig. 2.

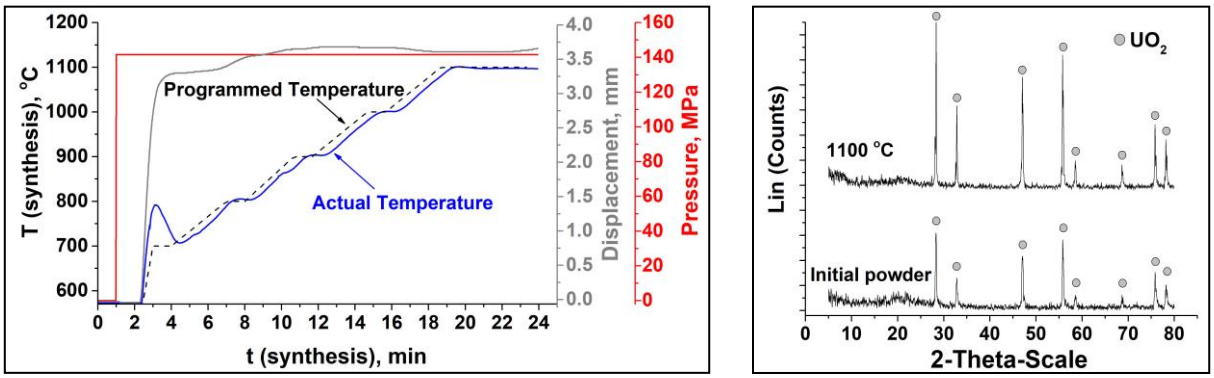

Figure 2. SPS parameters of UO_2 powder consolidation in molybdenum die and XRD patterns of initial powder and UO_2 pellets obtained via SPS.

According to presented trends the main compaction of sintered powder occurs during the first 5 min in 600-800 °C temperature range under the conditions of stepwise heating and high pressure (141.5 MPa) that is several times higher than in earlier experiments. Full densification is reached within 10 min of sintering and doesn't change significantly further. The peculiarity is proved by microstructural investigation discussed below (Fig. 3).

Initial powder according to XRD is a crystal uranium dioxide UO_2 (Fig. 2). In the course of SPS sintering at 1100 °C in molybdenum die its composition doesn't change. However, diffraction peak intensities increase indicating the improvement of crystallinity (transformation of amorphous phase into crystal one) and also possible oxide's crystallite growth.

While investigating microstructure of the sample obtained via SPS in molybdenum die (Fig. 3) we revealed that particles of the initial powder are actively sintered forming crystallites with well-defined planes and open porosity along intergranular contacts and in the bulk. The main factor deserving attention is the crystallite size below 3 µm in average.

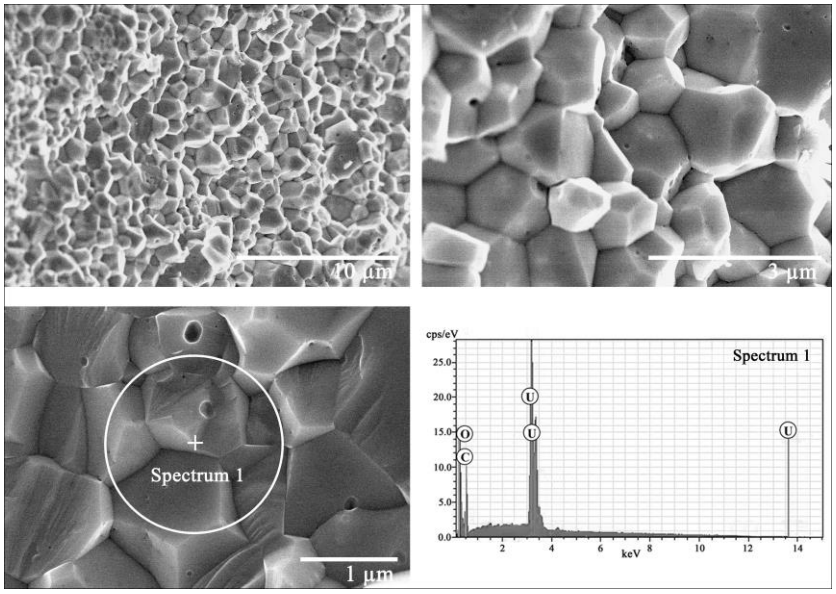

Figure 3. SEM images and EDX analysis (spectrum 1) of UO_2 pellet obtained via SPS of powder in molybdenum die at 1100 °C and under 141.5 MPa.

In addition, SEM images clearly evidence the absence of agglomerated carbon in the bulk of consolidated pellet (Fig. 3). Carbon traces are observed only in small amount on the sample's surface (Table 1) and can be explained by the EDX error introduced due to using carbon adhesive to fix the sample to the support. Carbon can also come into the sample during the treatment (polishing and smoothing) by abrasive. Despite this, it is obvious that bulk diffusion into the sample during SPS as described for previous experiments does not occur in this case.

Table 1. EDX analysis of UO_2 pellet obtained via SPS that presented at Fig.3.

Element	**Spectrum 1**		
	U	**O**	**C**
Content, wt. %	85.57	11.33	3.10
Content, at. %	27.12	53.42	19.45

Density measurements of obtained UO_2 pellet as one of the main quality criterion clearly indicate the efficiency of SPS process applied to sintering of UO_2 powders. According to them (Table 2) apparent density of the sample consolidated in molybdenum die varies in the range 97.5-98.4% from theoretical value depending the liquid type.

Given the data above it is obvious using molybdenum die for SPS consolidation allows consolidating uranium dioxide powder at lower temperature with high compaction due to considerable increase of pressure as compared to less mechanically stable graphite. In addition, carbon contamination is avoided. All these are crucial, when assessing the quality of produced fuel pellets based on UO_2.

Table 2. Apparent density of UO_2 pellet measured in various liquids, g/cm^3.

Water	**Alcohol**	**Toluene**	**Benzene**	**Chloroform**
0.991	0.803	0.860	0.870	1.470
10.7238	10.6947	10.7890	10.7729	10.7795

4. Conclusions

The work has investigated peculiarities of SPS consolidation of commercial uranium dioxide ceramic powder using no-standard die, in particular, the applicability of molybdenum die vs. graphite one was studied with respect to fabrication of highly dense fuel products (pellets) of required quality. Investigations have shown the SPS technology provides high-rate synthesis of UO_2 compounds with required physico-chemical characteristics. SPS consolidation of UO_2 powders in molybdenum die as alternative approach has proved to have a number of advantages. SPS consolidation of ceramic UO_2 powder is conducted at 1100 °C and 141.5 MPa during 25 min resulting in high quality product (density 97.5-98.4% from theoretical, grain size below 3 μm and carbon-free). In addition, molybdenum die prevents carbon diffusion during SPS and, therefore avoids sample's contamination.
According to obtained data it is obvious that SPS technology is promising for fabrication of UO_2 pellets with various ceramic properties. Suggested alternative approach using carbon-free equipment is rational for improving the product's quality. These results can be recommended for development and possible implementation of SPS technology in the industry.

References

[1] Carrea A J 1963 Sintering of uranium dioxide in an atmosphere of controlled hydrogen content *J. Nucl. Mater.* **8** 275–7
[2] Orru` R, Licheri R, Locci A M, Cincotti A and Cao G 2009 Consolidation/synthesis of materials by electric current activated/assisted sintering *Mater. Sci. Eng. R Reports* **63** 127–287
[3] Munir Z A, Quach D V. and Ohyanagi M 2011 Electric current activation of sintering: A review of the pulsed electric current sintering process *J. Am. Ceram. Soc.* **94** 1–19
[4] Tokita M 1993 Trends in Advanced SPS Spark Plasma Sintering Systems and Technology *J. Soc. Powder Technol. Japan* **30** 790–804
[5] Mamedov V 2002 Spark plasma sintering as advanced PM sintering method *Powder Metall.* **45** 322–8
[6] Ge L, Subhash G, Baney R H, Tulenko J S and McKenna E 2013 Densification of uranium dioxide fuel pellets prepared by spark plasma sintering (SPS) *J. Nucl. Mater.* **435** 1–9
[7] Cologna M, Tyrpekl V, Ernstberger M, Stohr S and Somers J 2016 Sub-micrometre grained UO2 pellets consolidated from sol gel beads using spark plasma sintering (SPS) *Ceram. Int.* **42** 6619–23
[8] Bertrand A, Carreaud J, Delaizir G, Duclère J R, Colas M, Cornette J, Vandenhende M, Couderc V and Thomas P 2014 A comprehensive study of the carbon contamination in tellurite glasses and glass-ceramics sintered by spark plasma sintering (SPS) *J. Am. Ceram. Soc.* **97** 163–72
[9] Bokhonov B B, Ukhina A V., Dudina D V., Anisimov A G, Mali V I and Batraev I S 2015 Carbon uptake during Spark Plasma Sintering: investigation through the analysis of the carbide "footprint" in a Ni–W alloy *RSC Adv.* **5** 80228–37

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