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Documentation Package Supporting Fabrication of Doped UO_2 Samples for MiniFuel Irradiation and Fission Gas Release Benchmarking

Nuclear Technology Research and Development

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S. C. Finkeldei,
R. D. Hunt, J. O. Kiggans
C. A. Hobbs, and B. D. Eckhart
Oak Ridge National Laboratory
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SUMMARY

The Oak Ridge National Laboratory (ORNL) is looking into the fabrication of high performance UO_2 fuel candidates via the addition of dopants to the UO_2. The addition of dopants is proposed to cause enlarged grains that will slow down fission gas release from the irradiated fuel pellet candidates. The Cr-doped UO_2 pellets were fabricated from a microspherical feedstock, and enlarged grains were observed during the microstructural characterization. Irradiation under the Miniature Fuel program in the High Flux Isotope Reactor at ORNL will enable the study of irradiation response of such potential fuel candidates and will allow fission gas release benchmarking for these fuel candidates.

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ACRONYMS

AFC	Advanced Fuels Campaign
HFIR	High Flux Isotope Reactor
ICP-MS	inductively coupled plasma mass spectrometry
ORNL	Oak Ridge National Laboratory
ppm	parts per million
RMS	root mean square
SEM	scanning electron microscopy
SGMP	sol-gel microsphere pelletization
TD	theoretical density

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DOCUMENTATION PACKAGE SUPPORTING FABRICATION OF DOPED UO_2 SAMPLES FOR MINIFUEL IRRADIATION AND FISSION GAS RELEASE BENCHMARKING

1. INTRODUCTION

The Oak Ridge National Laboratory (ORNL) is looking into the fabrication of high performance UO_2 fuel candidates. The addition of dopants such as Cr, Ti, and Mn is proposed to enhance UO_2 grain growth [1]. Due to the enlarged grains, the diffusion pathway of the fission gases to the grain boundaries is elongated and is therefore proposed to slow down the fission gas release from the irradiated fuel. In relation to UO_2 with dopants prepared via the conventional solid-state route, ORNL has a long history of UO_3 microsphere feedstock fabrication. The UO_3 microspheres can be fabricated in a variety of sizes and are highly porous, enabling the infiltration of dopants. Moreover, the high porosity of the feedstock is favorable for a direct pelletization of the spherical feedstock, a procedure known as the *sol-gel microsphere pelletization process* (SGMP) [2][3][4]. The fabrication of fuel pellets via SGMP omits any grinding step and is thereby a completely dust-free fabrication avenue. In this effort, the UO_3 microspherical feedstock was infiltered with different Cr concentrations to obtain enlarged grains. Pellets fabricated from a powder feedstock obtained from Areva are used as reference pellets with common UO_2 grain sizes of about 10–12 µm in fuel pellets.

2. FEEDSTOCK FABRICATION

The UO_3 microspheres were fabricated via an established internal gelation process at ORNL [5]. UO_3 spheres between 300–850 µm were dried at 200°C. The desired amount of Cr was infiltered into the dried UO_3 spheres by adding $Cr(NO_3)_3{\times}9H_2O$ (Sigma Aldrich) to aim for 1,000 ppm and 2,000 ppm Cr initial concentration. Just enough deionized water was added to cover the UO_3 spheres and to dissolve the $Cr(NO_3)_3{\times}9H_2O$. The spheres were allowed to take up the dopant solution for about 30 min. Afterwards, the spheres were dried at 200°C on a hot plate, and after cooling to room temperature, water was added to enable the dopant uptake to proceed. This step was repeated about 4 times. The doped spheres were thermally denitrated for 10 h at 500°C in air.

In this report, the dopant concentration is reported as dopant/uranium weight concentration in ppm rather than referring to the oxides.

UO_2 powder that was received from Areva was used as feedstock to prepare undoped UO_2 reference pellets. This feedstock has seen extensive use within AFC over the past decade at both ORNL and Los Alamos National Laboratory and is considered the ‘reference’ feedstock for UO_2 pellet production.

3. PELLET FABRICATION

The Cr-doped spheres and the Areva powder were calcined for 5 h at 600°C in Ar-4% H_2 in a metal tube furnace to obtain UO_2. The 1,000 ppm and 2,000 ppm Cr-doped spheres were biaxially pressed into a pellet with a 4 mm die at 480 lb for 2 min. The Areva powder was biaxially compressed into a pellet in the 4 mm die with 710 lb for 2 minutes. For the Areva pellets, a higher pressing force was needed due to the different nature of the feedstock being a fine powder rather than coarse grains. Sintering for the Cr-doped UO_2 took place for 6 h at 1500°C in Ar-4% H_2 in a metal furnace to limit the dopant sublimation. It is known from the literature that about 50% of the Cr volatizes during thermal treatments [6]. The same was observed for the microspherical feedstock, and details about the Cr concentration within the spheres are reported elsewhere [7]. The Areva UO_2 pellets were sintered under the same atmosphere for 6 h at 1700°C. The higher sintering temperature was used for pure UO_2 since dopant volatility is not a concern, and excessive grain growth does not occur in the reducing environment. All fabricated pellets were polished on both sides to meet the required thickness criteria of < 0.4 mm.

4. PRE-IRRADIATION CHARACTERIZATION

To ensure the pellets meet the criteria for irradiation in HFIR, they were characterized as described below. The Cr- doped UO_2 pellets were fabricated from the item 165–756 (0.23 % ^{235}U). The Areva UO_2 pellets also comprise depleted uranium and were fabricated from the item Areva NTP (0.26 % ^{235}U).

4.1 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) of Sintered Spheres

The dopant concentration was determined via ICP-MS of the sintered spheres and is reported elsewhere [7].

4.2 Density and Dimensional Inspections

The density of the polished pellets was geometrically determined and is reported in Table 1. All pellets have a density above 90% theoretical density (TD).

4.3 Roughness Determination

The fabricated pellets need to have a roughness less than 1.6 μm root mean square (RMS). The surface roughness was characterized by means of using a non-contact measurement system, the Keyence VR-5200. The pellet is first cast in a silicon rubber compound using Struers RepliSet-GF1. This casting provides an exact 3D copy of the surface and sides of the pellet down to 0.1 μm. This compound is an accepted replicating system for ASTM standard E 1351 "Standard Practice of Field Metallographic Replicas." Next, the cast is scanned using the Keyence VR-5200 line roughness measurement. The roughness measurement results conform to the ISO 4287 requirements. An area from edge to edge is selected, and multiple parallel line scans are used to validate that the RMS surface roughness is less than 1.6 μm. The same software will be used in the future to create a 3D model of the pellet. This will be accomplished by scanning both sides and stitching the images together and will be used later when comparing the as-fabricated pre-irradiated pellet to the post-irradiated pellet. The roughness of both sides of the pellets is presented in Table 1.

4.4 Microstructural Characterization

Due to charging effects on the pellets' surfaces, a detailed microstructural characterization of every individual pellet was not feasible. Additional pellets that were prepared in the same batch will be characterized by scanning electron microscopy (SEM) after carbon coating to characterize the microstructure of representative pellets that will be irradiated within the MiniFuel experiment at HFIR. Figure 1 shows a representative area of the 2,000 ppm Cr doped UO_2 pellet with enlarged grains.

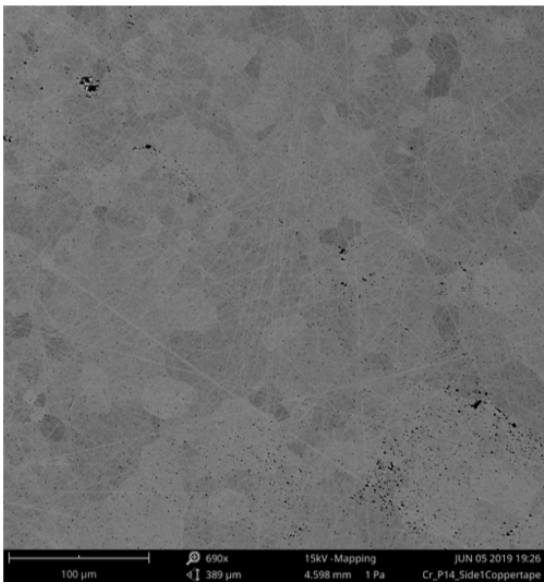

Figure 1. SEM image of a representative area of a 2,000 Cr-doped UO_2 pellet (pellet 14) fabricated from the microspherical feedstock showing large UO_2 grains

Table 1. Dimensions of Cr-doped UO_2 pellets and reference UO_2 pellets with the corresponding pellet ID, arithmetic mean roughness, mass, average diameter, height, and geometrically determined TD.

Fabrication feedstock	***Pellet ID***	***Roughness (µm)***		***m***	$\bar{d}$	h_{final}	h_{final}	$\%TD_{final}$
		Ra, Side A	***Ra, Side B***	**(mg)**	**(mm)**	**on mount**	**Dig. Ind.**	
Cr 1000 ppm	1000-21	0.279	0.387	23.7	3.070	0.336	0.308	94.8
Cr 1000 ppm	1000-22	0.464	0.552	26.7	3.070	0.383	0.349	94.2
Cr 1000 ppm	1000-26	0.203	0.301	22.4	3.090	0.345	0.283	96.2
Cr 1000 ppm	1000-28	0.231	0.390	20.6	3.087	0.299	0.268	93.6
Cr 2000 ppm	2000-12	0.165	0.167	24.0	3.077	0.354	0.309	95.2
Cr 2000 ppm	2000-13	0.160	0.194	21.5	3.077	0.332	0.279	94.4
Cr 2000 ppm	2000-14	0.168	0.179	17.5	3.063	0.277	0.219	98.8
Cr 2000 ppm	2000-15	0.181	0.135	18.7	3.087	0.313	0.250	91.1
AREVA	A-04	0.130	0.135	26.3	3.270	0.324	0.295	96.8
AREVA	A-06	0.118	0.122	30.7	3.283	0.369	0.337	98.1
AREVA	A-07	0.124	0.121	32.3	3.283	0.377	0.358	97.1
AREVA	A-10	0.107	0.129	30.4	3.290	0.360	0.327	99.7

5. CONCLUSIONS AND OUTLOOK

The addition of Cr as dopants to UO_2 is expected to promote grain growth within the UO_2 pellets [1]. Cr-doped UO_2 pellets synthesized via an internal gelation route and subsequent infiltration were fabricated to investigate the irradiation response of such potential fuel candidates. UO_2 pellets without dopants were fabricated as reference pellets from a powder feedstock. The 12 pellets will be loaded within the MiniFuel capsules for two different irradiation durations. Two pellets of each composition will be loaded in mirrored axial positions to ensure they are exposed to the same flux. The second subset of pellets (2× 2,000 ppm Cr-doped UO_2, 2× 1,000 ppm Cr doped UO_2, 2 × UO_2) will be located in the same axial positions at similar radial positions to allow for a direct comparison of the same fuel candidates with different burn-ups. The irradiation will enable study of the irradiation response of such potential new fuel candidates and will allow fission gas release benchmarking for these fuel candidates.

6. REFERENCES

[1] M. W. D. Cooper, C. R. Stanek, and D. A. Andersson, The role of dopant charge state on defect chemistry and grain growth of doped UO_2, *Acta Mater.* **150** (2018) 403–413. doi:https://doi.org/10.1016/j.actamat.2018.02.020.

[2] E. Zimmer, C. Ganguly, J. Borchardt, and H. Langen, SGMP — an advanced method for fabrication of UO_2 and MOX fuel pellets, *J. Nucl. Mater.* **152** (1988) 169–177. doi:https://doi.org/10.1016/0022-3115(88)90323-6.

[3] S. C. Finkeldei, J. O. Kiggans, R. D. Hunt, A. T. Nelson, and K. A. Terrani, Fabrication of UO_2-Mo composite fuel with enhanced thermal conductivity from sol-gel feedstock, *J. Nucl. Mater.* **520** (2019) 56–64. doi:https://doi.org/10.1016/j.jnucmat.2019.04.011.

[4] N. Kumar, R. V. Pai, J. K. Joshi, S. K. Mukerjee, V. N. Vaidya, and V. Venugopal, Preparation of $(U,Pu)O_2$ pellets through sol–gel microsphere pelletization technique, *J. Nucl. Mater.* **359** (2006) 69–79. doi:https://doi.org/10.1016/j.jnucmat.2006.07.018.

[5] R. D. Hunt and J. L. Collins, Uranium kernel formation via internal gelation, *Radiochim. Acta.* **92** (2004) 909. doi:10.1524/ract.92.12.909.55110.

[6] S. Kashibe and K. Une, Effect of additives (Cr_2O_3, Al_2O_3, SiO_2, MgO) on diffusional release of ^{133}Xe from UO_2 fuels, *J. Nucl. Mater.* 254 (1998) 234–242. doi:https://doi.org/10.1016/S0022-3115(97)00356-5.

[7] S. C. Finkeldei, R. D. Hunt, J. O. Kiggans, C. A. Hobbs, B. D. Eckhart, J. W. McMurray, D. R. Brown, G. Helmreich, K. A. Terrani, and A. T. Nelson, Synthesis and Characterization of UO_2 Feedstocks Containing Controlled Dopants, Oak Ridge, forthcoming, 2019.