ANL/CFCT-20/29

Preliminary results from Low Pressure Steam Oxidation Testing of ALD ZrN and ZrO2 Coating Deposited over UCN Fuel Kernels

Chemical and Fuel Cycle Technologies Division

About Argonne National Laboratory
Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago, at 9700 South Cass Avenue, Lemont, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see www.anl.gov.

DOCUMENT AVAILABILITY
Online Access: U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free at OSTI.GOV (http://www.osti.gov/), a service of the U.S. Dept. of Energy's Office of Scientific and Technical Information.

Reports not in digital format may be purchased by the public from the National Technical Information Service (NTIS):
U.S. Department of Commerce
National Technical Information Service
5301 Shawnee Rd
Alexandria, VA 22312
www.ntis.gov
Phone: (800) 553-NTIS (6847) or (703)
605-6000 Fax: (703) 605-6900
Email: **orders@ntis.gov**

Reports not in digital format are available to DOE and DOE contractors from the Office of Scientific and Technical Information (OSTI):
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
www.osti.gov
Phone: (865) 576-8401
Fax: (865) 576-5728
Email: **reports@osti.gov**

Disclaimer
This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor UChicago Argonne, LLC, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or UChicago Argonne, LLC.

ANL/CFCT-20/29

Preliminary results from Low Pressure Steam Oxidation Testing of ALD ZrN and ZrO2 Coating Deposited over UCN Fuel Kernels

---

prepared by

Sumit Bhattacharya[1], Rachel Seibert[2], Andrew Nelson[2],

Heather Connaway[1], Abdellatif Yacout[1]

1) Argonne National Laboratory

2) Oak Ridge National Laboratory

June 2021

(This page left intentionally blank)

Abstract

Steam oxidation testing was used to investigate as-developed 100 nm ALD ZrN and 1000 nm ZrO_2 coatings deposited over UC1-xNx fuel kernels. The results of these tests were compared against oxidation of uncoated kernels. This work was performed to support development of coatings which both provide high temperature Zr metal diffusion barrier and also provide resistance against oxidation, especially against high temperature steam and/or air. This work was performed in collaboration with Oak Ridge National Laboratory (ORNL), using ORNL-provided samples. The oxidation tests yielded valuable information, including relative differences in performance of different coating materials and coating thicknesses.

Table of Contents

1 Introduction

There is ongoing research at Argonne National Laboratory regarding high-temperature Zr metal diffusion barrier for $UC_{1-x}N_x$ fuel kernels received from Oak Ridge national laboratory (ORNL). One of the key technical requirements for this work is that the same coating needs to provide resistance against oxidation, especially against high temperature steam or air, or both in case of a loss of coolant accident (LOCA) scenario. To verify this requisite, a quick low-pressure (~ 100 Torr) steam oxidation test carried out for 30 minutes was devised.

This steam oxidation test was used to investigate as-developed 100 nm ALD ZrN and 1000 nm ZrO_2 coating deposited over the kernels, and results were compared against oxidation of uncoated kernels. The results accumulated from this test not only helped to understand the surface oxidation of $UC_{1-x}N_x$ fuel kernels under low pressure steam, but also helped to quantify that the deposited ALD coating is conformal, devoid of any defects or surface cracks over the rough textured exterior of the as received kernels.

In this report, the detailed discussion regarding the steam oxidation testing and the corresponding characterizations performed over both coated and uncoated $UC_{1-x}N_x$ fuel kernels are presented.

2 Experimental Procedure

2.1 $UC_{1-x}N_x$ fuel kernels and details of the deposited ALD ZrN and ZrO_2 coatings

Details regarding the microstructure, surface chemistry/condition of the as-received $UC_{1-x}N_x$ microspheres from ORNL, and complete details of the deposited ALD coatings can be found in a corresponding report titled "Selection and characterization of surrogate material for developing Zr barrier coatings for Uranium nitride particles", ANL/CFCT-20/30 [1]. This portion of the work is not repeated in the current report.

2.2 Low Pressure Steam Oxidation Testing Procedure and Sample Handling

The same commercial wafer coating ALD system used to develop the ALD ZrN and ZrO_2 was re-purposed to perform the quick steam oxidation test of coated and uncoated fuel kernels. Generally, under normal operational conditions in this ALD system the maximum pressure that can be achieved with a continuous water (supply bubbler maintained at room temperature) pulse is ~ 20-30 Torr, with the ALD reaction chamber maintained at ~ 280°C. This water pressure is more than enough for performing any ALD deposition, but to achieve observable changes from exposure to super-heated steam, the input pressure needs to be boosted to enhance the oxidation kinetics. To increase the net pulse pressure the bubbler is marginally heated from ambient conditions to 40°C, with external tape heaters. This temperature increase helps to propel the input pressure to ~ 100 Torr, achieved from a continuous water pulse inside the ALD reaction chamber maintained at ~ 280°C. The steam pressure is not increased beyond 100 Torr, because the fomblin oil-based vacuum roughing pump used for this ALD device, seemed to show signs of significant moisture accumulation in its coolant oil, when the steam pressure is taken to 120 Torr and continuously maintained for 30 minutes. Therefore, for safe operation a net steam pressure of 100 Torr is maintained for 30 minutes to accomplish the objectives. In addition, all the coated and uncoated fuel kernels were handled within an inert atmosphere glove box, such that there is not influence on the results due to external humidity, especially for the uncoated $UC_{1-x}N_x$ fuel kernels.

Twenty as-received $UC_{1-x}N_x$ fuel kernels were loaded on an aluminum tray and placed inside of the ALD reaction chamber. The ALD chamber temperature was brought down to room temperature before any powder loading to prevent any unwanted reactions of the uncoated fuel kernels in particular. Once the Al tray was placed, the chamber was closed, and brought under vacuum. The pressure is brought to ~ 1.2 to 1.5 Torr with a 40 sccm of N_2 flow. At this pressure, the temperature is slowly ramped up in steps of 20 degree Celsius /ten minutes to finally reach the target of 280°C. The temperature is maintained overnight, and then the following day the steam oxidation test is performed.

Before the initiation of the testing, the water bubbler temperature is slowly raised to 40°C, and once the temperature is stabilized the water vapor is pulsed continuously for 30 minutes (2 total pulses, each pulse is for 15 minutes, 30 second purge and followed by another water pulse) inside the reaction chamber. After completion of the net 30 minute of exposure from 100 Torr steam, the ALD chamber is again cooled down slowly to room temperature before taking out any samples for post oxidation characterization studies.

2.3 Characterization Techniques

Microstructure of the steam oxidized coated and uncoated $UC_{1-x}N_x$ fuel kernels were characterized by scanning electron microscope (SEM), model JSM-IT100 In Touch Scope and detailed cross sections of the coated spheres were characterized with focused ion beam (FIB), model FEI HELIOS Nano Lab 600 Dual Beam FIB/SEM.

3 Results

3.1 Microstructural and sub-surface chemical pre-analysis of the as received UC1-xNx

The as-received uncoated $UC_{1-x}N_x$ fuel kernels were pre-characterized to document the surface and the sub-surface conditions before performing the low-pressure steam oxidation studies. With help of the FIB, individual areas of dimensions 40-micron x 40 micron were dug over multiple as-received fuel kernels. Over each dug zone, 5 EDS line scans were performed. The observed result can be explained through the BSE image of a typical dug zone, shown in Figure 1 (a). From the corresponding two-line scans performed (Figure 1 (b, c)) over the cross section unambiguously detects even though there is some amount of surface oxidation present, but the sub surface area is free of any such unwanted interactions. In figure 1 (b), the grey line signifies the O intensity plot measured over the cross section, and from the result it can be concluded that not much oxygen is present below the subsurface, and only the intensity rises as it goes to the exposed external surface of the kernel. Similar conclusions can be drawn from Fig 1 (c). Based on the results following the O line mapping across the cross section, there is no concern for finding pre-oxidized kernels which may have interfered with the steam oxidation results.

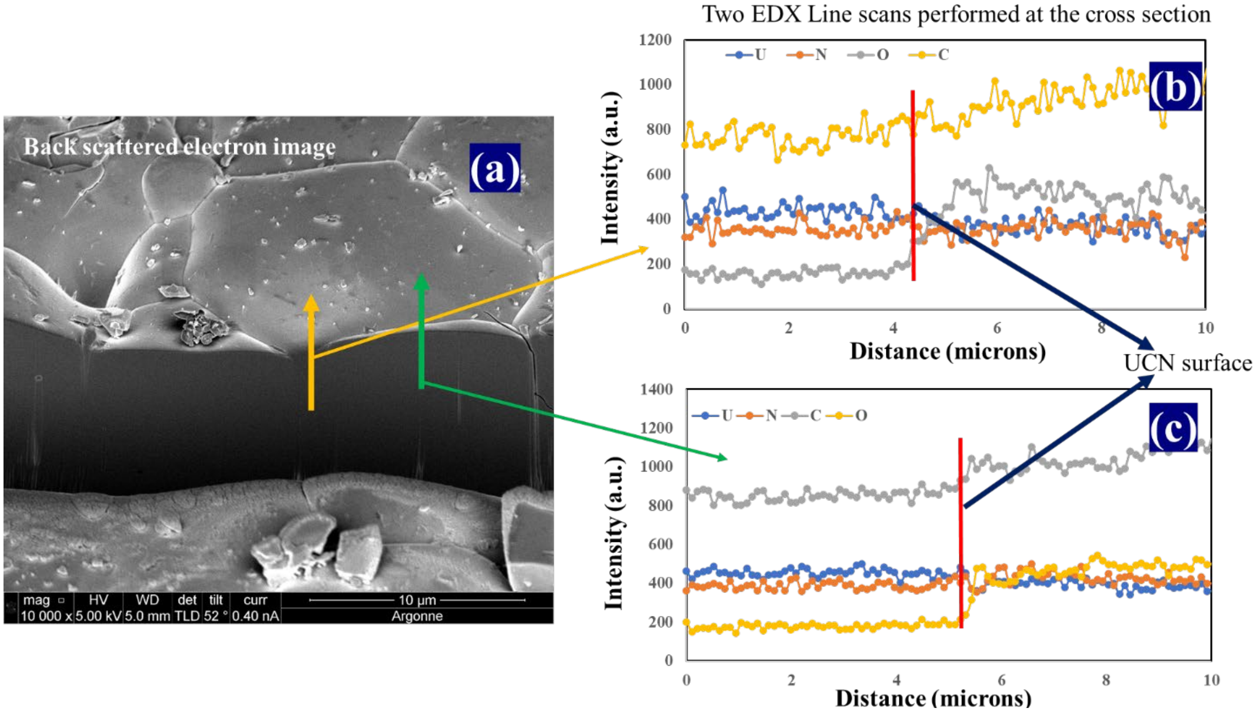


Figure 1: (a) FIB cross section of the uncoated UC$_{1-x}$N$_x$ fuel kernels, (b) Two EDS Line scans performed at the dug cross section of the particle, the red line over the line scan plot indicates interface between top exposed surface and the sub-surface region.

3.2 Microstructural and sub-surface chemical post analysis after steam oxidized UC1-xNx

After the steam oxidization test was completed over the uncoated twenty fuel kernels, 5 particles were recovered from the tray, for determining the net effect over the fuel kernels due to exposure to super-heated steam. The immediate variation observed is the change in net amount of surface oxygen when compared to the as-received kernels, presented in Figure 2 (a, b). This is evident from comparing to the information in the corresponding report, “Selection and characterization of surrogate material for developing Zr barrier coatings for Uranium Nitride particles”, ANL/CFCT-20/30 [1]. The net amount of at. % of Oxygen jumps from 10% (as-received) to 28% (post steam oxidation), whereas the net surface N contribution decreases from ~ 16 at. % to 7.45 at. % (results shown in Table 1).

The oxidized samples were then further characterized for determining any changes that may have occurred in the sub-surface region. Before the oxidation test, the sub-surface region was almost pristine; thus any observed changes will be a direct result from the exposure to the super-heated steam for 30 minutes. This characterization is accomplished with help of the FIB. Individual area of dimensions ~40-micron x 40 micron were dug over 5 collected steam oxidized fuel kernels. Over each dug zone, 5 EDS line scans were performed. Overall, with consistent increase in oxygen amount in the sub-surface region, there are two distinct regions which are forming. These features can be seen directly over the kernel surface and also when cross sections are examined. The observed result can be explained through the BSE image of a typical dug zone, shown in Figure 3 (a, b). Figure 3 (a) demonstrates the pre-oxidation surface and the corresponding sub surface region. In Fig. 3 (b) significant surface cracks, consistently distributed over the whole kernel surface area are detected, which were not seen in the pre-oxidation surface (Fig 3 (a)). In general nitrogen rich UN when exposed to high temperature steam, will initially form UO2 or a mixture of UO_2 and U_2N_3. More details regarding the reaction mechanism can be found in reference [2].

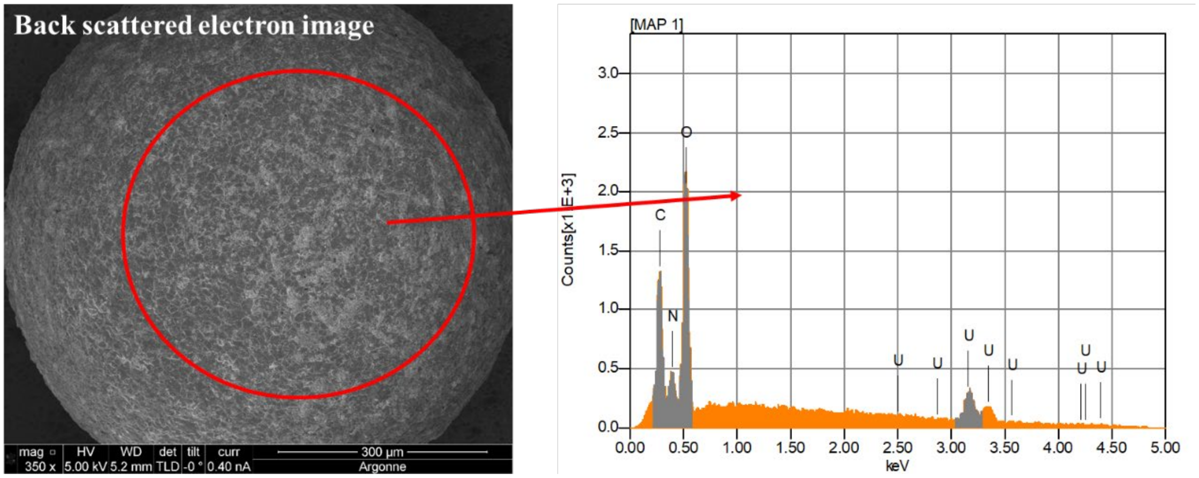


Figure 2: (a) UC$_{1-x}$N$_x$ fuel kernels as received from ORNL after 30 minutes of low-pressure steam oxidation at 100 Torr; (b) EDS spectrum (5 KeV) performed over the kernel surface (marked by red circle) showing significant oxidation.

Table 1: $UC_{1-x}N_x$ fuel kernels surface composition after steam oxidized at 100 Torr for 30 min.

Elements	Mass%	Atom%
C	1.54	15.79
N	0.84	7.45
O	3.62	27.96
U	94.00	48.80

To determine and confirm that regions affected by fine cracks and breaking is a direct result of UN oxidizing against steam to form UO_2 more EDS line scans were performed to quantify the oxidation chemistry. The corresponding line scans performed (Figure 4 (a, c)) over the shown cross section clearly detects increase in the oxygen intensity. In Figure 4 (b), the orange line signifies the O intensity plot measured over the cross section, and from the result it can be concluded O has diffused in to the sub-surface region, but when compared to Figure 4 (d) the oxygen seems to have traveled/diffused a long way inside the sub-surface region. This may be a result of the surface cracks that are contiguous to the line scan measurement region. From the BSE surface images Fig 3 (b), significant swelling of individual grain surface along with few propagating cracks can also be observed, when compared with Fig 3 (a) where the grain profiles are flatter.

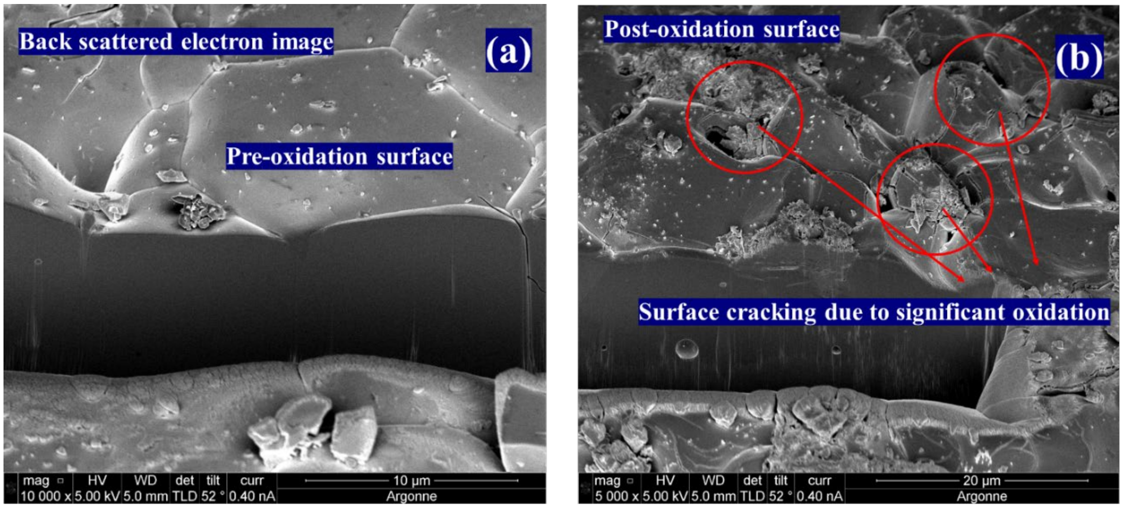
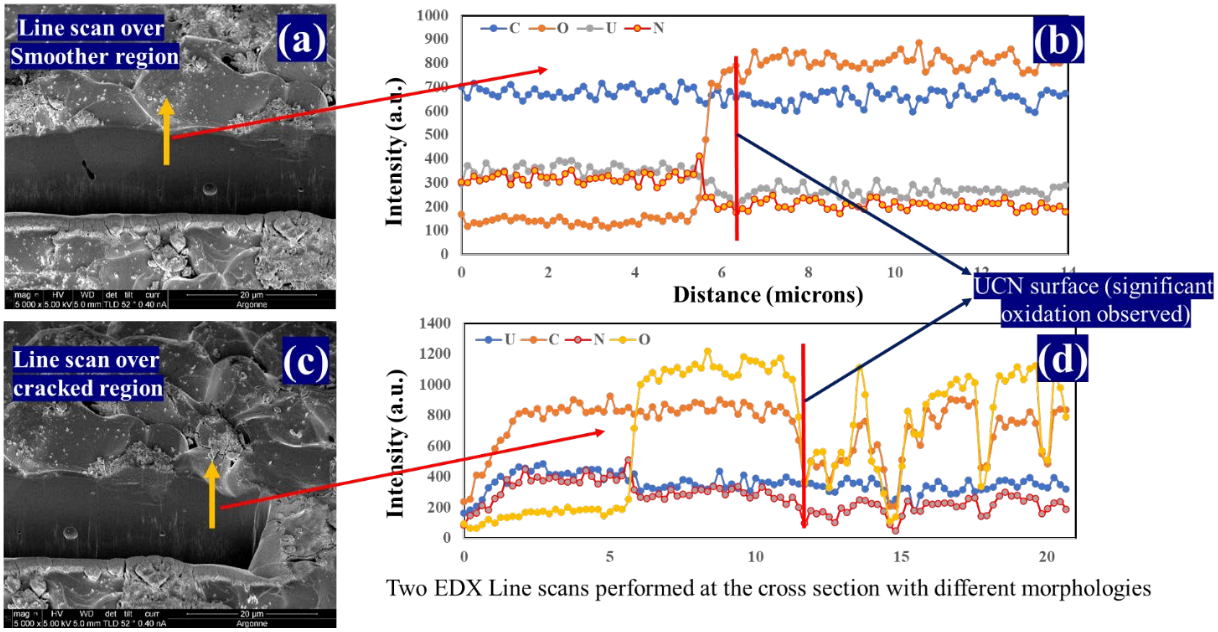


Figure 3: (a) FIB cross section of the uncoated $UC_{1-x}N_x$ fuel kernels, (b) FIB cross section of the uncoated $UC_{1-x}N_x$ fuel kernel after 30 minutes of steam exposure at 100 Torr for 30 minutes. Substantial surface cracks, some amount of swelling can be observed from the cross-sectional image.



Two EDX Line scans performed at the cross section with different morphologies

Figure 4: (a) FIB cross section of the uncoated $UC_{1-x}N_x$ fuel kernel after 30 minutes of steam exposure at 100 Torr for 30 minutes, the yellow arrow marks the region where O_2 has diffused into the sub surface but without significant effect (c) FIB cross section of the uncoated $UC_{1-x}N_x$ fuel kernel after 30 minutes of steam exposure at 100 Torr for 30 minutes, the yellow arrow marks the region where O_2 has diffused in deep inside of the sub surface. (b and d) Corresponding EDS line scans displaying the net O_2 intensity across the cross-sectional region in (a, b)

3.3 Microstructural and sub-surface chemical post-analysis, after steam-oxidized $UC_{1-x}N_x$ coated with 100 nm ALD ZrN.

After the steam oxidization test was completed over the 100 nm ALD ZrN coated twenty fuel kernels, similar to the uncoated characterization process, 5 particles were recovered from the tray for use in determining the net effect over the fuel kernels due to exposure to super-heated steam.

The direct variation observed is the change in net amount of surface oxygen and nitrogen, when compared to the as coated kernels, presented in Figure 5 (a, b). This is evident from comparing to data in the corresponding report “Selection and characterization of surrogate material for developing Zr barrier coatings for Uranium Nitride particles”, ANL/CFCT-20/30, where the net amount of at. % of Oxygen jumps from 5% (as-received) to 25% (post steam oxidation), whereas the net surface N contribution decreases from ~ 43 at. % to 27 at. % (as shown in Table 2). This is evidence that the ALD ZrN coating has been oxidized as a result of exposure to steam.

The oxidized coating samples were then further characterized for determining any changes that may have occurred in the coating interface region. Before the oxidation test the sub-surface, and the interface region was almost pristine; thus any observed changes will be a direct result from the exposure to the super-heated steam for 30 minutes, diffusing through the ZrN barrier coating. This examination was accomplished by using the FIB. Individual area of dimensions ~40-micron x 40 micron were dug over 5 collected steam oxidized ALD ZrN coated fuel kernels. Over each dug zone, 5 EDS line scans were performed to document any changes.

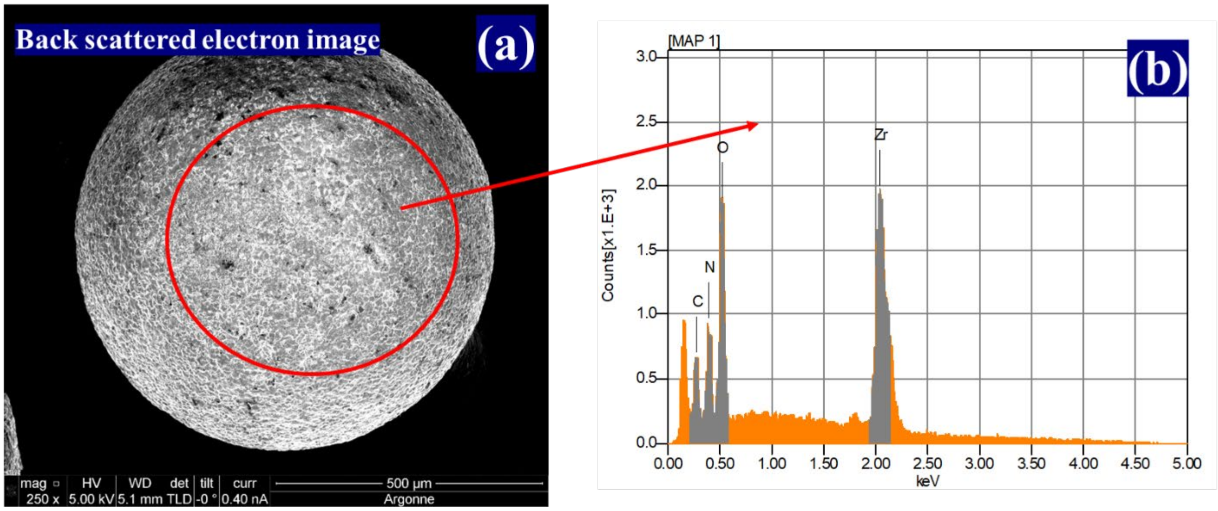


Figure 5: (a) $UC_{1-x}N_x$ fuel kernels coated with 100 nm ALD ZrN after 30 minutes of low-pressure steam oxidation at 100 Torr; (b) EDS spectrum performed over the kernel surface (marked by red circle) showing significant oxidation.

Table 2: $UC_{1-x}N_x$ fuel kernels coated with 100 nm ALD ZrN surface composition after steam oxidized at 100 Torr for 30 min.

Elements	**Mass%**	**Atom%**
C	2.84	10.30
N	8.61	26.73
O	9.26	25.16
Zr	79.29	37.81

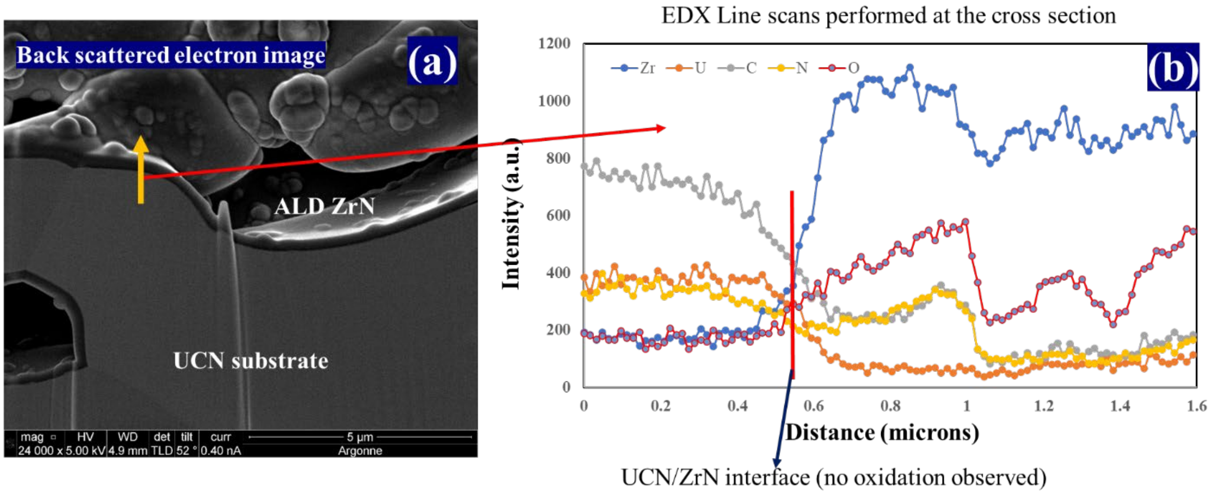


Figure 6: (a) FIB cross section of the 100 nm ALD ZrN coated $UC_{1-x}N_x$ fuel kernel after 30 minutes of steam exposure at 100 Torr for 30 minutes, the yellow arrow marks the region where EDS line scan will be performed. (b) Corresponding EDS line scans displaying the net O_2 intensity across the cross-sectional region.

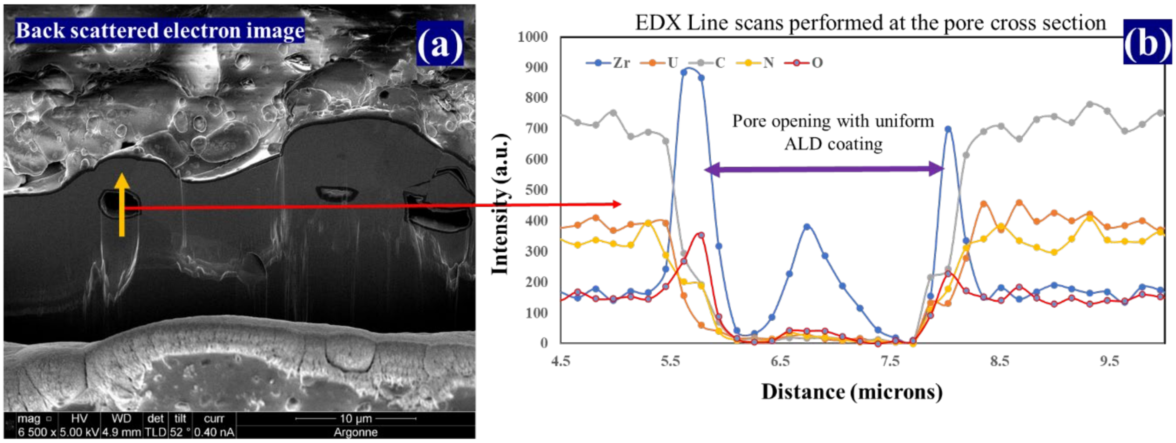


Figure 7: (a) FIB cross section of the 100 nm ALD ZrN coated $UC_{1-x}N_x$ fuel kernel after 30 minutes of steam exposure at 100 Torr for 30 minutes, the yellow arrow marks the region where EDS line scan will be performed which is a ALD coated open channel cross section. (b) Corresponding EDS line scans displaying the net O_2 intensity across the cross-sectional region.

The results can be explained with a BSE image of a typical dug zone, shown in Figure 6 (a). From the corresponding line scan performed (Figure 6 (b)) over the cross section, it is clearly detectable that even though there is significant oxidation of the ALD ZrN coating, the sub surface and the interface area is free of any such unwanted oxygen interactions. In Figure 6 (b) the red line signifies the O intensity plot measured over the cross section, from this result it can be concluded that not much O has managed to diffuse through the coating and reach the interface or the sub-surface area. The O intensity rises as it goes to the coating zone and the subsequent exposed/external surface of the coated kernel.

In case of Figure 7 (a), (where the focus of the study has been to validate the ALD's ability to infiltrate through open porous channels and also provide protection against diffusion and oxidation) the BSE image shows the ALD coating is still present in those sub-surface channels even after getting exposed to super-heated steam. As a result, a line scan has been performed right over the ALD coated channel cross section to determine whether similar diffusion barrier against oxidation has been achieved. Figure 7 (b) unmistakably presents that the ALD ZrN coating deposited in the channels has been oxidized, similar to the external coating,. It also shows that even though the coating has turned to oxide, the fuel kernel area around the channel cross section is still pristine and no oxidation is observed.

3.3.1 Microstructural and sub-surface chemical post analysis after steam oxidized $UC_{1-x}N_x$ coated with 1000 nm ALD ZrO_2.

After the steam oxidization test was completed over the 1000 nm ALD ZrO2 coated twenty fuel kernels, 5 particles again were recovered from the tray for determining the net effect over the fuel kernels due to exposure to super-heated steam. For this test case, there is not direct evidence of any change in the net amount of surface oxygen and nitrogen when compared to the as-coated kernels, as presented in Figure 8 (a, b). Both coatings shows the exact same final coating surface composition before and after steam oxidation.

The ALD ZrO2 samples were then further characterized for determining any changes that may have occurred in the sub surface/interface region. Using the FIB, individual area of dimensions

~40-micron x 40 micron were dug over 5 collected steam oxidized fuel kernels. Instead of line scans, EDS mapping was performed over the dug cross sections as shown in Figure 9 (a, b, c, d). From the elemental distribution results, no changes have occurred due to steam oxidation. Therefore, ALD ZrO_2 is the most effective coating in terms of providing oxidation barrier properties.

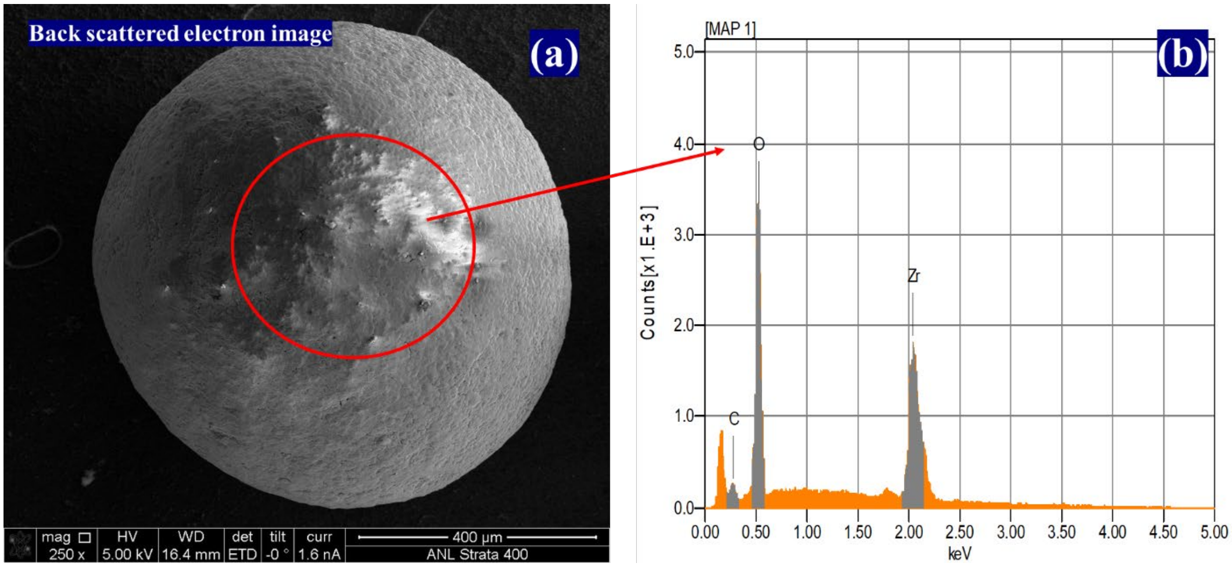


Figure 8: (a) $UC_{1-x}N_x$ fuel kernels coated with 1000 nm ALD ZrO_2 after 30 minutes of low-pressure steam oxidation at 100 Torr; (b) EDS spectrum performed over the kernel surface (marked by red circle) showing no changes in surface composition.

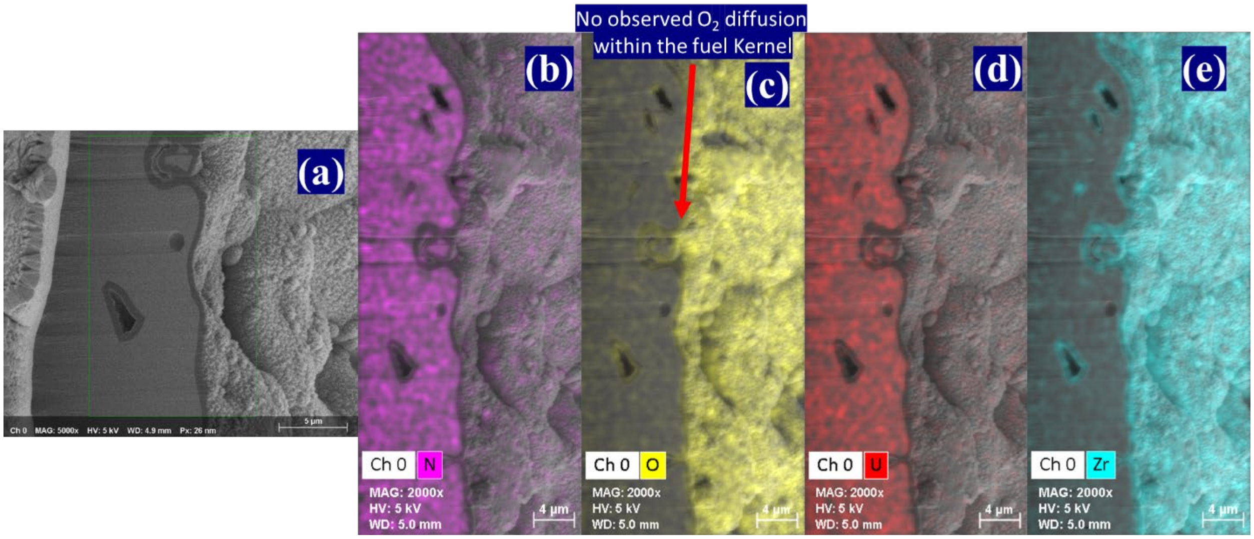


Figure 9: (a) FIB cross section of the 1000 nm ALD ZrO_2 coated $UC_{1-x}N_x$ fuel kernel after 30 minutes of steam exposure at 100 Torr for 30 minutes (b) Corresponding EDS mapping displaying Nitrogen distribution, (c) Oxygen distribution, (d) Uranium distribution, (e) Zirconium distribution.

4 Future Work

To accurately test the oxidation resistance against high pressure steam at temperatures greater than 600 ºC, a dedicated thermogravimetric analyzer (TGA) device is more appropriate, Therefore high pressure steam oxidation should be performed within the TGA setup, as it will alert any miniscule changes that may happen with the coating as it measures any slight changes in the net weight of the studied material during steam oxidation testing.

Additional applications of coatings will also be performed at Argonne in future activities, using new sample fuel kernels provided by ORNL.

5 Conclusions

A number of important conclusions can be drawn from the preliminary low pressure steam oxidation testing of ZrN and UO_2 ALD coatings deposited over UCN fuel kernels. Key observations from this work are as follows:

(1) Low pressure steam oxidation testing seems to be an effective way to determine if the developed ALD coatings can provide surface oxidation resistance to $UC_{1-x}N_x$ fuel kernels. This is due to the fact that the 100 Torr steam pressure combined with the testing temperature of 280ºC provides enough oxidation kinetics to generate observable changes over the uncoated fuel kernel, while also ensuring a sufficient supply of O ions which can amplify any coating defect issues that may have been generated during deposition process.

(2) 100 nm ALD ZrN provided good oxidation barrier protection, even though it turned into zirconium oxide during steam oxidation testing. This shows the ALD ZrN coating has significantly large defect concentration, which allowed the oxygen ions to diffuse through the coating and completely oxidize the coating.

(3) 1000 nm ALD ZrO_2 provides the best oxidation protection against 280ºC steam and shows no observable or chemical changes in the coating stoichiometry.

(4) Both coatings remains mechanically stable and well adhered during steam oxidation testing, and no cracking, spalling is observed.

(5) Both coatings can infiltrate through surface open porosities and have the ability to deposit an ultra-conformal coating layer which is equally effective as possible diffusion barrier against steam.

Acknowledgement

This work was sponsored by the U.S. Department of Energy, Office of Nonproliferation Research and Development in the U.S. National Nuclear Security Administration Office of Defense Nuclear Nonproliferation under Contract DE-AC02-06CH11357.

References

[1] Sumit Bhattacharya, Andrew Nelson, Heather Connaway, and Abdellatif Yacout, “Selection and Characterization of Surrogate Material for Developing Zr Barrier Coatings for Uranium Nitride Particles”, ANL/CFCT-20/30, Argonne National Laboratory, 2020.

[2] Mikael Jolkkonen, Pertti Malkki, Kyle Johnsonand Janne Wallenius, “Uranium nitride fuels in superheated steam”, Journal of Nuclear Science and technology, 2017.

Nuclear Science & Engineering Division
Argonne National Laboratory
9700 South Cass Avenue, Bldg. 208
Argonne, IL 60439

www.anl.gov

Argonne National Laboratory is a U.S. Department of Energy
laboratory managed by UChicago Argonne, LLC