Title: Evolutionary Enhancements to UO2

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Report on Evolutionary Enhancements to UO_2 Pellets

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SUMMARY

Sintered uranium oxide fuel pellets are the primary fuel used in civilian nuclear reactors. Due to extensive experience and established infrastructure, these ceramic fuels are likely to remain important for nuclear energy well into the future.

Fuel pellets are produced mainly through cold-pressing ceramic powder and high temperature sintering. The processing technique presented here is designed to fit into the current fuel pellet production infrastructure with minimal changes to fuel manufacturers and reactor operators. This study makes changes in the UO_2 powder before the pellets are pressed, possibly requiring only minor changes in the manufacturing process.

Oxide additives to UO_2 have been studied since the early days of nuclear energy. Additives can effect the performance of UO_2 in several ways, altering the grain size, sintering behavior, and mechanical behavior such as creep, toughness, and hardness. The first part of this study is to identify techniques to controllably alter pellet microstructure. The next step will be to test the mechanical properties of the doped UO_2. The ultimate goal in developing this processing technique is to produce well-defined microstructural features that can be tested in controlled studies to better understand their role in fuel pellet performance.

There are two unique aspects to this study. While the majority of research into additives has focused on producing large grain sizes, this study is also interested in restricting grain growth. In addition, most studies have introduced additives by the traditional method of blending oxide powders with UO_2. This study employs a metal precursor technique to introduce additives to the matrix. The additives being investigated thus far are aluminum oxide, titanium oxide, vanadium oxide, and yttrium oxide.

This report provides an update on progress thus far in enhancing the properties of UO_2 with oxide additives.

CONTENTS

ACRONYMS

ADS	Aluminum Di-Stearate
EBS	Ethylene Bis Stearamide
EBSD	Electron Back Scattered Diffraction
PCMI	Pellet Cladding Mechanical Interaction
SEM	Scanning Electron Microscopy
BEI	Backscattered Electron Image
SEI	Secondary Electron Image
SPEX	Manufacturer of SPEX brand high-energy mill

1. Introduction

Uranium oxide fuel pellets power most civilian nuclear reactors today. With over 400 civilian nuclear reactors worldwide, the combined operational experience and infrastructure of this user base implies that ceramic nuclear fuels will remain important well into the future. Despite the conservative approach taken by the nuclear industry, improvements in reactor operation are still being sought. The properties of the ceramic fuel itself have received substantial attention over the years. This report updates the progress of studies to enhance the behavior of UO_2 by altering its properties and microstructure with oxide additives.

This study envisions changes that can be applied with current equipment and processes. Fuel pellets are typically made by cold-pressing dry ceramic powder. Before being pressed into pellets, the powder may be blended with additives or binders. By introducing the additives at the mixing and blending step, this approach modifies the fuel with little change to the rest of the process.

Fuel rod performance is of great interest to operators of nuclear reactors. Fuel rod failures can lead to expensive maintenance and down time for the reactor. A common cause of these failures is pellet cladding mechanical interaction (PCMI), which can be caused by pellet fracture or swelling. Fuel pellets increase their dimensions under reactor conditions due to the formation of insoluble fission gasses that migrate to grain boundaries. Thermal expansion of the pellet can also cause contact between the pellet and the cladding. Additives have been studied to modify microstructure to improve fission gas retention as well as to alter the mechanical properties of the UO_2 to lessen PCMI. Therefore, techniques to tailor these characteristics for improving the performance of UO_2 fuel pellets could be highly valuable to the nuclear industry.

The standard average grain size in light water reactor fuel is around 10-12 µm. Grain size effects have been noted for both creep and release of fission gas, making control of grain size important to the properties and performance of fuel.[1,2,3,4,5] Solid solution chemistry and grain boundary phases can raise creep rates in ceramics through enhanced material transport or grain boundary sliding. Higher creep rates are desired for reducing PCMI. This study aims to use oxide additives to control grain size in UO_2 and to alter the mechanical properties of UO_2 towards the goal of reducing PCMI. For more even dispersion, a metal precursor technique is being used to distribute the additives within the UO_2 powder.

2. Grain Size Control – Additives to UO_2

2.1 Background

Over the past 60 years much effort has gone into using oxide additives to modify the properties and/or microstructure of UO_2. Despite this long history a few areas have not been well explored. Details are scarce in the open literature on creating fine-grained microstructures and on techniques to distribute the additives.

This work seeks to address the above areas by examining the use of additives to restrict grain size and by exploring an unconventional method of incorporating those additives into UO_2 powder. In this study metal precursors were used as additive sources as opposed to the more traditional route of oxide powder blends. Once the effects of the additives on microstructure have been characterized, tests are planned to determine the mechanical properties of the doped materials, such as hardness.

Four additives were chosen based on their anticipated effect or utility, Al_2O_3, TiO_2, Y_2O_3, and V_2O_5. Al_2O_3 was chosen as a known grain growth inhibitor, TiO_2 was chosen because it is known to enhance grain growth in UO_2. Some evidence exists that Y_2O_3 may also inhibit grain growth [6], while the studies with V_2O_5 have shown varying results.[6,7,8,9]

The solid solubility of the additive in UO_2 is a key aspect to its effect upon grain growth.[9] All additives in solid solution are believed to increase material transport rates.[7] Insoluble second phases are expected to slow material transport and/or pin grain boundaries.[10] Therefore, the prediction is that additives at concentrations below their solid solution limit will result in larger grains than pure UO_2, whereas once the solution limit has been exceeded grain growth might be impeded by second phases.

Initial test samples provided encouraging results indicating that additives were indeed affecting the grain size in the UO_2 in expected ways. The remaining compositions proposed for this study have been prepared, and samples sintered and characterized. This update presents data from those results.

2.2 Experimental

As-received depleted UO_2 from Areva was milled for 15 minutes in a high energy SPEX mill and sieved through 60 and 200 mesh sieves. Powder retained on the 200 mesh sieve was recycled for use as part of additional batches of powder. This milled and sieved powder was collected and stored for mixing with metal precursors.

The precursors for the liquid mixing method were Ti-diisopropoxide (liquid), Y-nitrate (solid), and Vanadyl-acetyl acetonate (solid). The appropriate amounts of each precursor dissolved in ethanol to allow accurate measurements of the precursor solution. The solutions were assayed by pyrolyzing measured amounts of solution and determining the yield of oxide powder per gram of solution.

For the mixing step, eight grams of the conditioned UO_2 powder were measured into a weighing boat and spread out into a thin layer. Appropriate amounts of solution were poured onto the powder. Some dry ethanol was then used to rinse remaining solution from the transfer bottle into the powder in the weighing boat. Using a metal spatula, the powder and solution were mixed by hand.

Aluminum dis-stearate (ADS) was chosen to determine whether a solid precursor technique might also be effective at distributing a precursor. For the Al_2O_3 doped samples eight gram batches of UO_2 were placed in a plastic mixing jar. The appropriate amount of assayed ADS was measured into the mixing jar. For comparison with the ADS containing samples, ethylene bis stearamide (EBS) binder was added to powders containing no inorganic components to reach consistent total amounts of solid additive. The amounts were 0.25, 0.5 and 1.0 wt% total solid additive. These batches of powder were then mixed for 5 minutes in the mill with a plastic ball. The jar and ball were cleaned in between batches.

Pellets were pressed at 100 MPa with a 5.7 mm pellet punch and die set using a uniaxial hydraulic hand press. A thin layer of oil was added to lubricate the die. All samples were heated to 450°C at 2°C/min and held for 1 hour to burnout organic matter under an environment of ultra high purity Ar containing ~100 ppm O_2. Specimens were then heated to 1600°C for 4 hours at 8°C/min. The furnace environment at 1600°C was ultra high purity Ar with ~10 ppm O_2.

Table I lists the composition matrix for this study. The compositions have been chosen in accordance with the solubility limit in order to sample materials at, below, and above the solid solubility limits of the addtive in UO_2, with the exception of Y_2O_3, which is expected to be in solid solution at all of these concentrations.[11] All other solubility limits are from Peres et. al.[12] which publishes the Ph.D. thesis work of Bourgeois.[9]

Table I. Composition matrix for additive experiments.

Composition (ppm)	Al_2O_3	TiO_2	V_2O_5	Y_2O_3
50	🟩 X	🟩	🟩	🟩
100	🟩 X	🟩 X	🟩 X	🟩 X
500	X	🟩 X	🟩 X	🟩 X
700		🟩	X	🟩
1000	X*	🟩 X	X	🟩 X
2000		X	X	🟩 X

*1100 ppm for Al_2O_3. Green shading indicates at or below the solid solution limit in UO_2 for each additive.

2.3 Results & Discussion

A complete set of samples from the composition matrix has been sintered, and characterized for grain size data. Evidence of precipitates was found by scanning electron microscopy (SEM) in the 1000 ppm compositions of Al_2O_3 and TiO_2 doped UO_2.[13] SEM images have thus far not shown similar precipitates in the Y_2O_3 or V_2O_5 doped materials. Figure 1 shows SEM backscattered electron images (BEI) from the 2000 ppm TiO_2 and the 1000 ppm Y_2O_3 samples, and a secondary electron image (SEI) of the 1000 ppm V_2O_5 samples. Precipitates are highlighted with arrows in the TiO_2 sample (fig. 1a). As expected, no precipitates are observed in the Y_2O_3 doped samples, which are well within their solubility limits (fig. 1b). The image of the V_2O_5 sample also shows no signs of precipitates or second phases (fig. 1c). Given the large mass difference between vanadium and uranium, any vanadium rich phase could reasonably be expected to show up via z-number contrast, despite this being a secondary electron image.

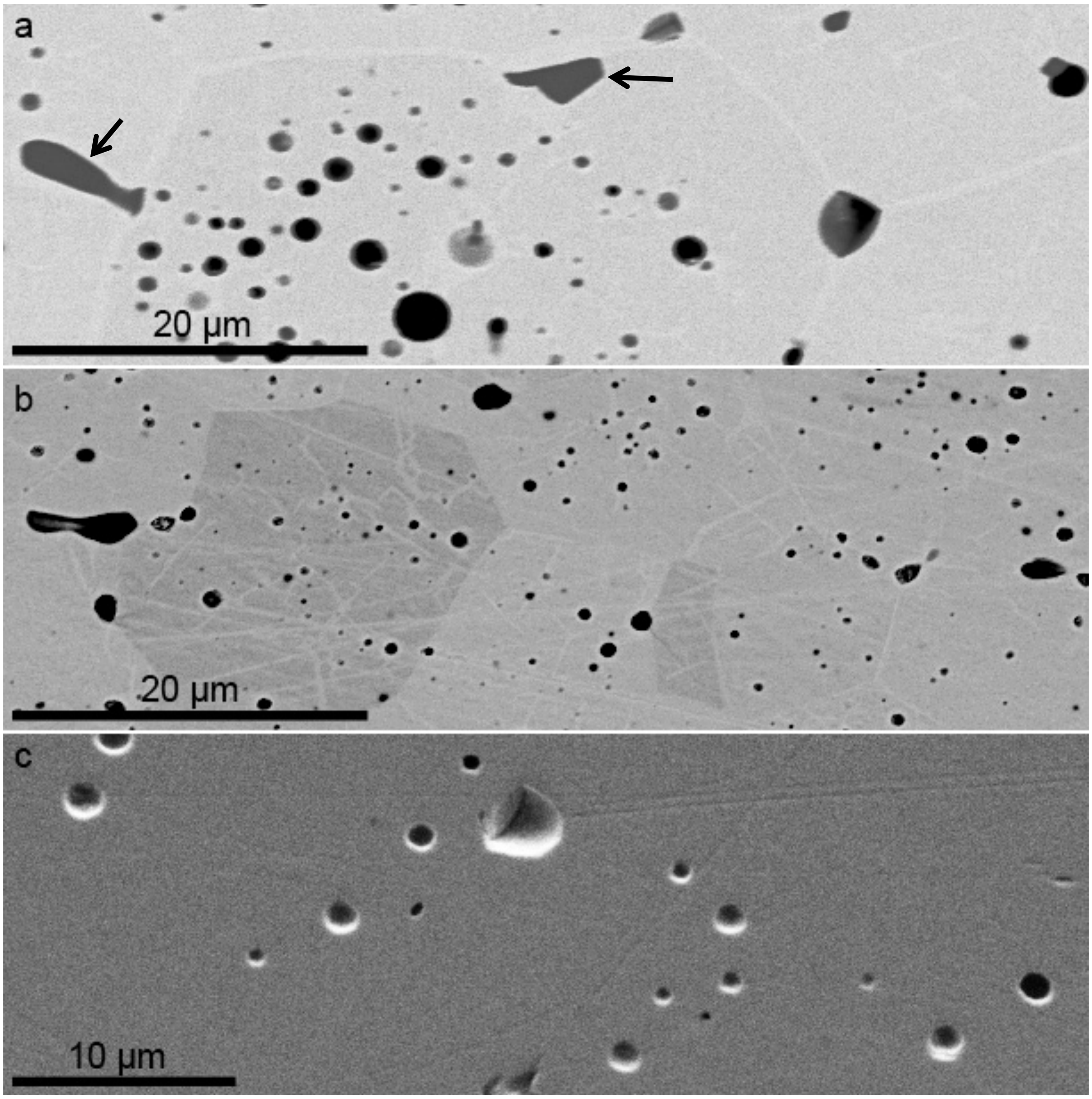

Figure 1. SEM images of sintered doped pellets a) 2000 ppm TiO_2, BEI image. b) 1000 ppm Y_2O_3, BEI image. c) 1000 ppm V_2O_5, SEI image.

Grain size measurements were made using Electron Back Scatter Diffraction (EBSD) providing quantitative measurements. Figure 2 charts the grain size data for the Al_2O_3, TiO_2, and Y_2O_3 doped pellets versus additive concentration. The importance of the solid solubility of the additive is clearly demonstrated. For both Al_2O_3 and TiO_2 doped UO_2 the grain size increases up to the solid solubility limit and declines when the additive concentration exceeds the limit. For Al_2O_3, the 50 ppm sample's average grain size is similar to the control's, showing little effect at this concentration of Al_2O_3. However, near the solubility limit of 100 ppm, there is a clear increase in grain size. As the amount of Al_2O_3 is increased above 100 ppm, the grains decrease in size, which is pronounced for the 1100 ppm Al_2O_3 sample. The TiO_2 doped pellets show the same trend. Up to the solid solubility limit of 1000 ppm TiO_2 the average grain size increases, falling at 2000 ppm. The Y_2O_3 doped materials show a small increase in grain size independent of concentration. This may be related to the high solubility limit of Y_2O_3 in UO_2 (~48 mole % [11]). Within this concentration range the Y_2O_3 may not alter the UO_2 matrix enough to cause greater material transport rates. It also does not precipitate out of solution and therefore would not be expected to restrict grain growth.

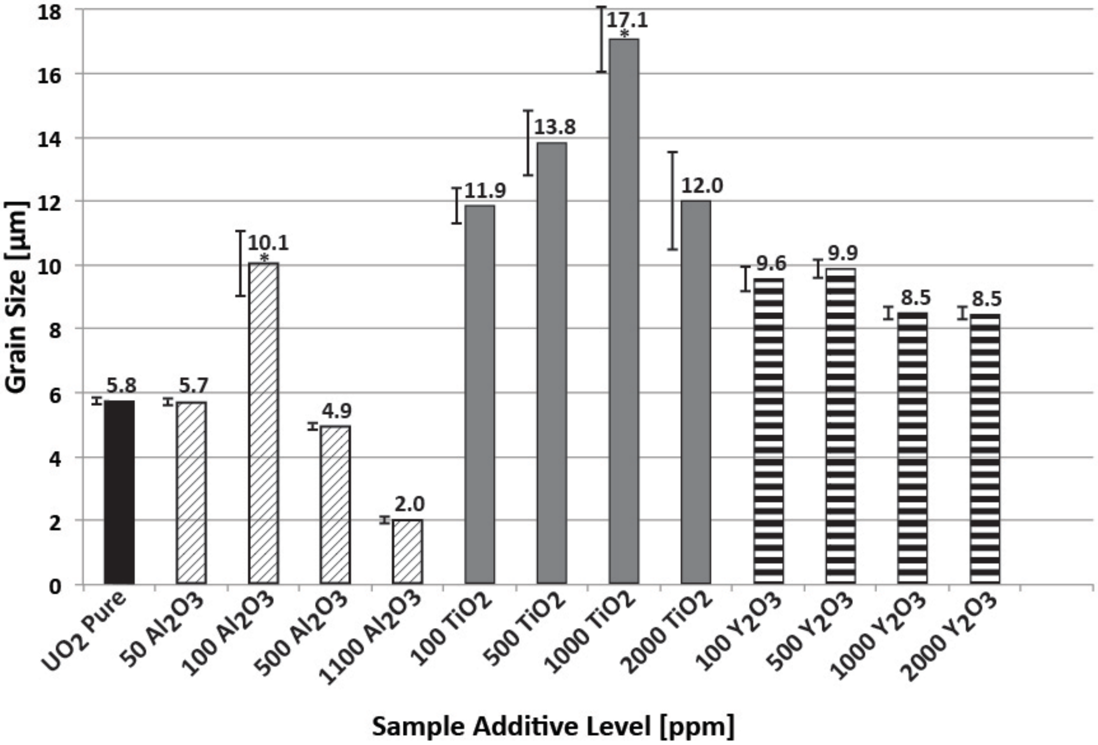

Figure 2. Chart of average grain size vs. additive level for Al_2O_3, TiO_2 and Y_2O_3 doped samples. Average grain size value is given at the top of each column for that sample. Reported values for solid solubility limits of the additive in UO_2 at 1700°C are noted with an asterisk at the top of relevant column.[9]

Figure 3 charts average grain size versus additive concentration for the V_2O_5 doped UO_2 samples. This data follows the same trend as the Al_2O_3 and TiO_2 materials, with increasing grain size until the solubility limit has been exceeded. While this data indicates that the solubility limit at 1600°C is higher than the reported limit at 1700°C (1000 ppm vs. ~500 ppm [9]), the error in the data for the 2000 ppm V_2O_5 sample is too high for certainty. The samples doped with V_2O_5 will be recharacterized to verify the statistics. One anomaly was found in the V_2O_5 sample data, the pure UO_2 control run with these pellets shows a much higher average grain size that the other controls (11.6 µm vs. 5.8 µm). Because the control sample was in the same crucible as V_2O_5 containing pellets, it is speculated that V_2O_5 vapor from the doped samples may have affected the control sample. To test this hypothesis, another set of pellets has been made with control samples sintered either in a separate crucible or a crucible along side a V_2O_5 containing sample. These samples will be characterized for grain size in the near future.

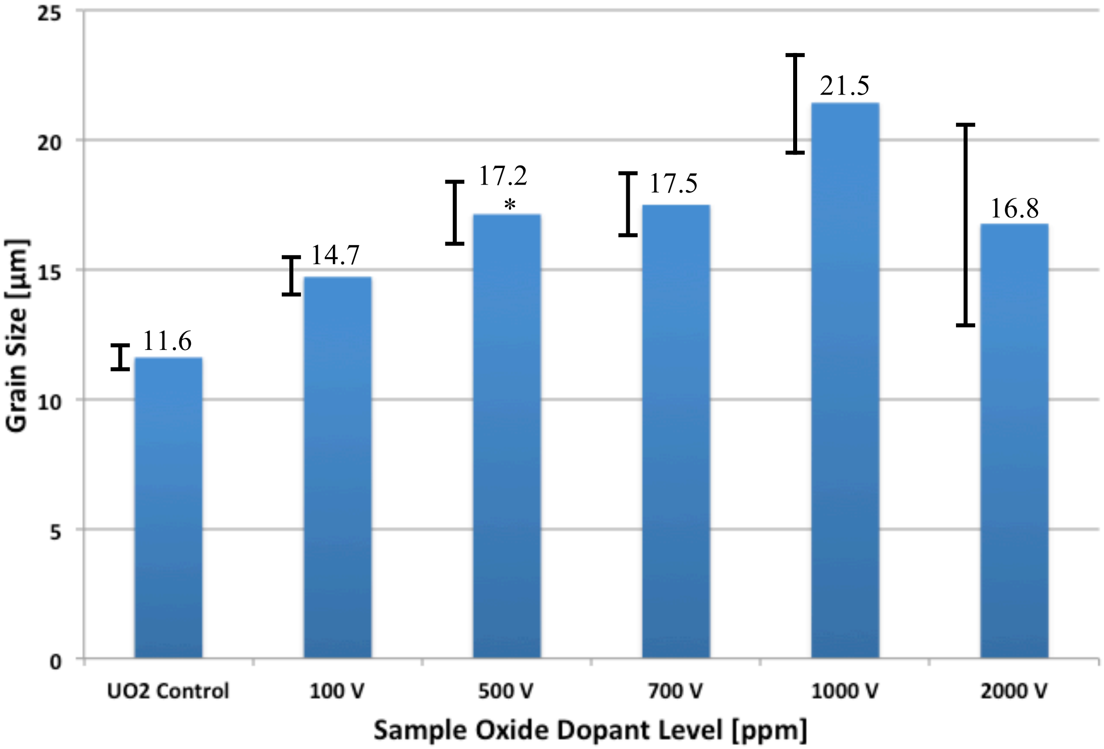

Figure 3. Chart of average grain size vs. additive level for V_2O_5 doped samples. Average grain size value is given at the top of each column for that sample. Approximately 500 ppm V_2O_5 is the reported solid solubility limit at 1700°C, indicated with asterisk.[9]

Images from the EBSD scans are shown in figures 4, 5, 6 and 7. Figure 4 shows the grain size images of the control sample and the Al_2O_3 doped materials. The Al_2O_3 images most clearly show the effect of solid solubility on grain growth or restriction. The 50 ppm image is similar to the control, showing little effect at this concentration of Al_2O_3. Near the solubility limit of 100 ppm, grain size is increased. The grain size decreases with increasing additive concentration until at 1100 ppm of Al_2O_3 it is much smaller than in the control.

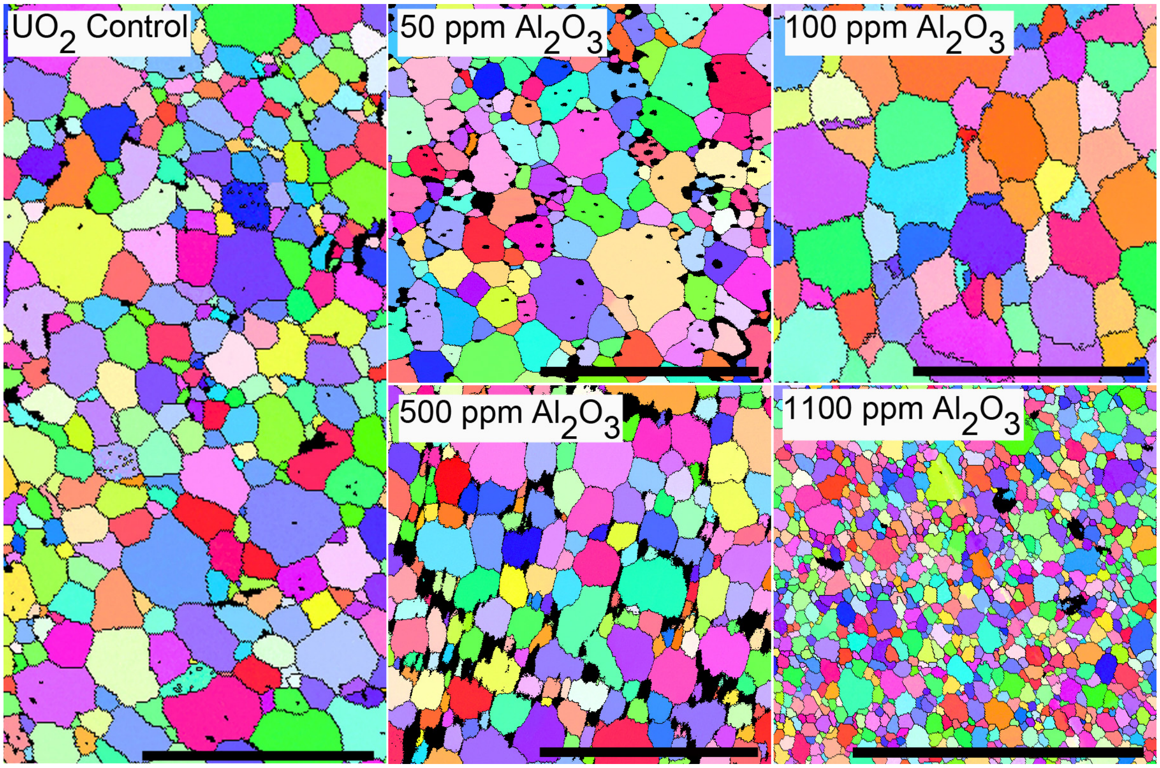

Figure 4. EBSD images for the Al_2O_3 doped UO_2 pellets. Solid solubility is exceeded after 100 ppm Al_2O_3.[9] Scale bars represent 50 µm.

Figure 5 shows the EBSD images from the TiO_2 doped UO_2 pellets. For the TiO_2 doped materials, the grain size increased until the solid solution limit was reached at 1000 ppm TiO_2. The decrease in average grain size is not visibly obvious in the EBSD image shown, but is clearly seen in the statistical data presented in figure 3. Figure 6 shows the EBSD images from the series of samples doped with Y_2O_3. Although average grain size increases with Y_2O_3 additions, there is no clear trend because these additive levels are well below the solid solution limit and therefore there is no grain boundary pinning effect from precipitates.

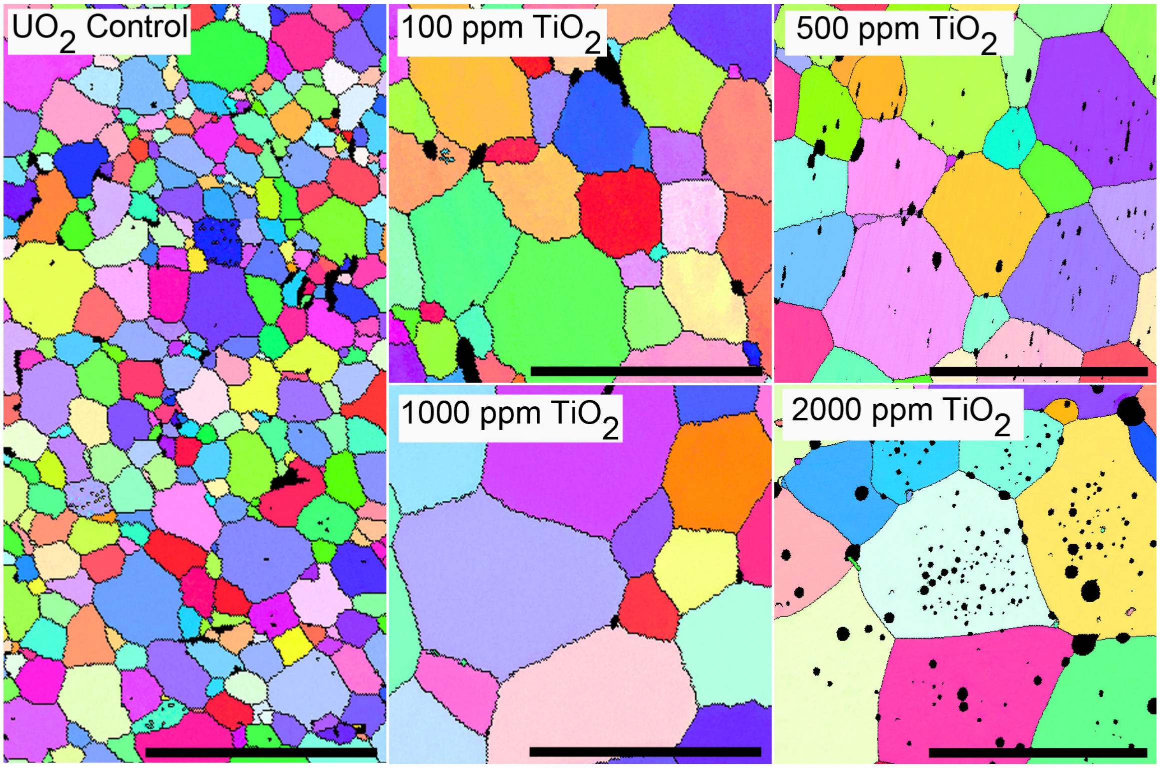

Figure 5. EBSD images for the TiO_2 doped UO_2 pellets. Solid solubility limit is 1000 ppm.[9] Scale bars represent 50 µm.

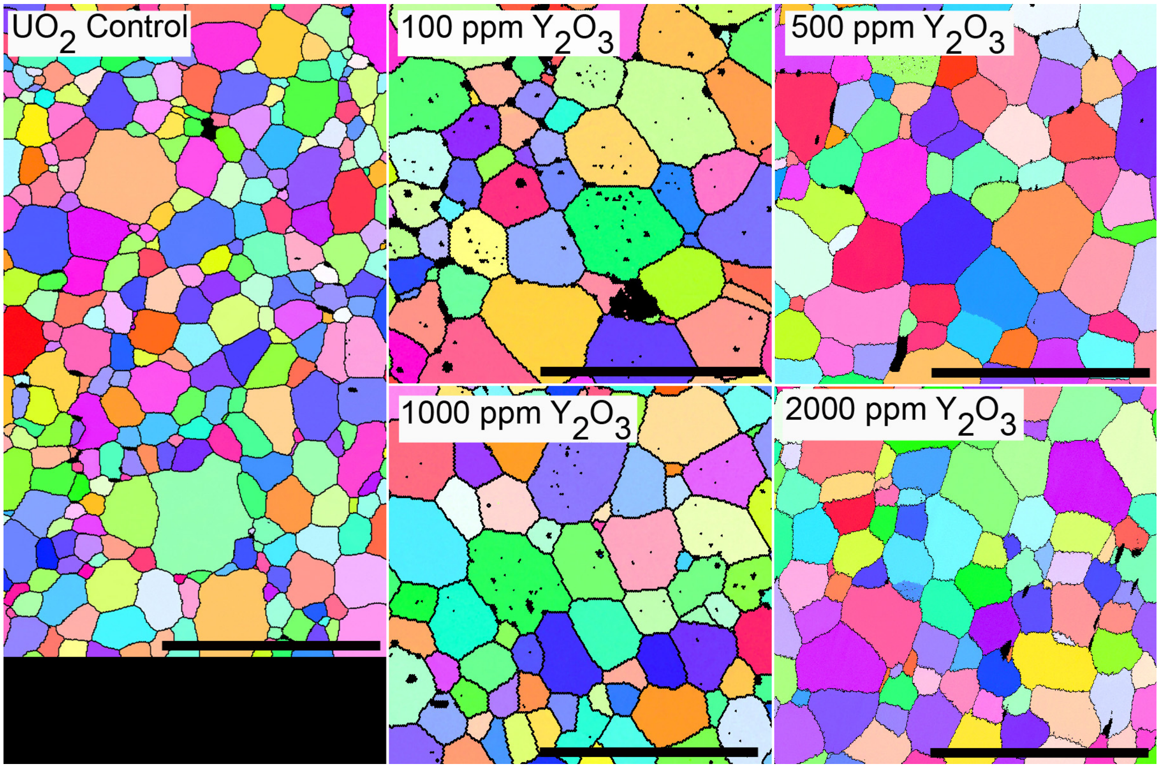

Figure 6. EBSD images for the Y_2O_3 doped UO_2 pellets. Scale bars represent 50 µm.

Figure 7 reveals the large amount of grain growth displayed by V_2O_5 additions. The 1000 ppm V_2O_5 doped sample has the largest average grain size of this study. The reduction in average grain size from 1000 ppm to 2000 ppm V_2O_5 is not clear in this image due to the small number of grains being shown, however this is highlighted in the chart of the grain size statistics shown in Figure 3. This data will be verified with furhter characterization of the V_2O_5 doped samples. Nevertheless, the trend is the same for Al_2O_3, TiO_2, and V_2O_5 doped materials, grain growth up to the point of solid solution, with grain size decreasing with additions above the solid solution limit.

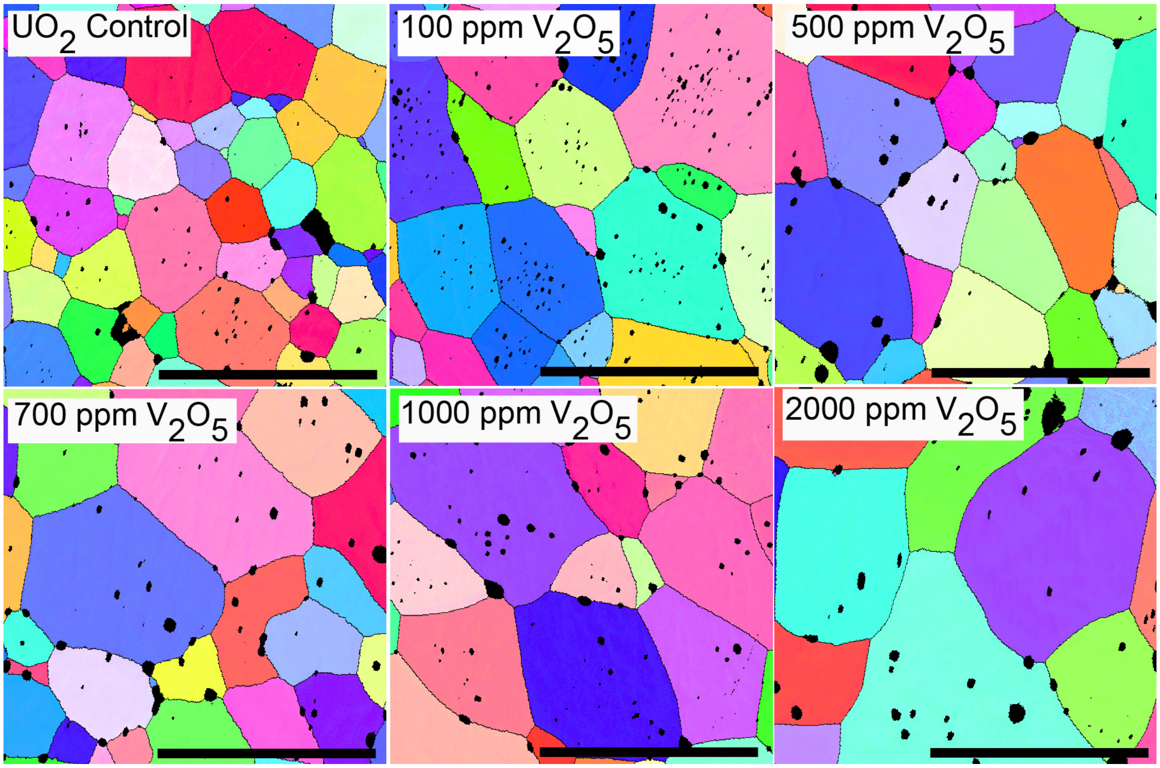

Figure 7. EBSD images for the V_2O_5 doped UO_2 pellets. Control sample is from the same sintering run as the V_2O_5 doped pellets. The literature reports the solid solubility limit for V_2O_5 in UO_2 at 1700°C as ~500 ppm.[9] Scale bars represent 50 μm.

3. Future Work

With this success in manipulating grain size and distributing additives into UO_2, future work will expand the study to explore the mechanical properties of the modified UO_2. Further, additional precursor materials are being prepared to introduce the oxides Cr_2O_3 and SiO_2. These may be added individually, or in concert with the current oxides. Mechanical testing of the current materials is in the early stages. Preliminary hardness testing shows some softening effect in the doped Al_2O_3 samples, but the tests will be redone to improve the quality of the data. Hot hardness testing is also being pursued, with samples already sintered and prepared from the existing doped UO_2 powders. By the end of the fiscal year, data will be collected and analyzed to downselect which additives show promise in modifying the mechanical properties of UO_2 in order to minimize the PCMI effects.

4. Conclusions

Al_2O_3, TiO_2, Y_2O_3, and V_2O_5 oxides have been added to UO_2 and sintered successfully using new liquid and solid mixing techniques. Grain size analysis revealed that the additives influenced grain growth in a manner consistent with reported solubility limits for the additives. In the case of Y_2O_3 the solubility limit is not reached; therefore grain growth is modestly enhanced regardless of concentration. This technique demonstrates the ability to both increase and restrict the grain growth of UO_2 through the use of oxide additives.

5. References

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