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Data Summary for Nominal 500 μm DUO_2 Kernels

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Data Summary for Nominal 500 μm DUO_2 Kernels

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1. Scope of report:

This document is a compilation of characterization data obtained on the nominal 500 μm DUO_2 kernels produced by ORNL for the Advanced Gas Reactor Fuel Development and Qualification Program to satisfy the FY03 WBS 3.1.2 task milestone #2. 2 kg of kernels were produced and combined in two composite lots. DUN-500 was a 1630 g composite sieved between 500±2 μm and 534±2 μm ASTM E161 electroformed sieves. DUN-482 was a 385.6 g composite sieved between 482±2 μm and 518±2 μm ASTM E161 electroformed sieves. Size, shape, density, and microstructural analysis were performed on a 100 g sublot (DUN-500-S-1) riffled from the DUN-500 composite. Size and shape were also measured on a 100 g sublot (DUN-482-S-1) riffled from the DUN-482 composite. For comparison, analysis was also performed on kernels extracted from the German reference fuel EUO 2358-2365 (AGR-06).

2. Summary of results:

The ORNL DUO_2 kernels sampled from the DUN-500 composite had a measured mean diameter of 519±12 μm with less than 1% measured outside the range 500-545 μm. The sphericity was 1.020±0.008 with less than 0.5% measured greater than 1.05. The envelope density was about 10.6 g/cc and the open porosity was about 1%. SEM showed a rough kernel surface with grains less than 10 μm in size. 0.25 μm closed pores were observed throughout the kernels.

The ORNL DUO_2 kernels sampled from the DUN-482 composite had a measured mean diameter of 497±13 μm with less than 1% measured outside the range 450-530 μm. The sphericity was 1.022±0.010 with 1.6% above 1.05.

The German 10.6% $LEUO_2$ kernels had a similar measured mean diameter (504±7 μm) but the size distribution was narrower and more Gaussian. They were not as spherical as the ORNL DUO_2, with a mean sphericity of 1.05±.02 and over 50% greater than 1.05. The envelope density was the same but the open porosity of the German kernels was lower (less than 0.02%). SEM showed a smoother kernel surface with larger grains up to 50 μm in size. The German kernels also showed evidence for closed porosity but the pores were fewer in number and larger (0.5 – 1.5 μm).

3. Details of characterization

The following sections discuss the results in more detail.

3.1 Size and shape measurement: (Hunn, Kercher, Price)

Shadow images of the perimeter of 1576 kernels (about 1.1 g) riffled from DUN-500-S-1 were obtained for a random kernel orientation. Image analysis software was used to find the center of each kernel and identify 360 points around the perimeter. The uncertainty for this measurement was ±1 μm. This data was then compiled to report sphericity, mean diameter, standard deviation in diameter, maximum diameter, and minimum diameter for each kernel measured. The summary data from each kernel was then compiled to obtain the mean, standard deviation, maximum, and minimum for each of these quantities. Figure 1 contains the compiled data and shows the distributions of the kernel sphericity and mean kernel diameter.

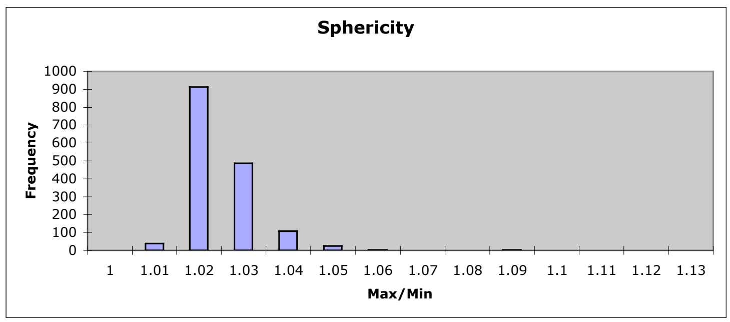
The measured kernels from DUN-500 had an average mean diameter of 519 μm with a standard deviation in the distribution of 12 μm. Based on variable sampling statistics, we expect the average mean diameter of the DUN-500 composite of kernels to be 517 - 522 μm with 95% confidence. Note that the distribution was more rectangular than Gaussian and this was not rigorously accounted for in calculating the expected range in mean diameter. However, the deviation due to the rectangular distribution should be minimal. The DUN-500 composite of kernels was taken from a sieve fraction between ASTM E161 electroformed sieves of 500±2 μm and 534±2 μm. These sieves defined the kernel distribution shown in the table. The non-Gaussian distribution was due to variation from batch to batch as the processing conditions were adjusted. Less than 1% of the kernels measured had mean diameters outside the range 500 - 545 μm. The largest kernel measured had a mean diameter of 545 μm. The smallest kernel had a mean diameter of 445 μm. Kernels with mean diameter ≥ 536 μm were a result of non-spherical particles passing through the sieve.

The average sphericity of the kernels from DUN-500 was 1.020 with a standard deviation of 0.008. Note that the sphericity distribution was skewed toward higher sphericity. Less than 0.5% of the kernels measured had a sphericity greater than 1.05. Sphericities above 1.05 were usually associated with kernels that exhibited flats in the projection image. The flats in the shadow image were probably shallow depressions like those seen in Figure 5. These craters are thought to be the result of kernels being stuck together at some point. The fact that these kernels were not removed during tabling shows that there is room for further improvement in the tabling efficiency.

Note that with this technique we actually measured the radius of the kernel. In the table we simply multiplied the radius by two in order to report the numbers in terms of diameter. This was done because these values are usually specified and reported in terms of diameter. However, there was some error introduced by making this conversion due to the fact that the kernel cross sections were not necessarily symmetrical. The uncertainty this introduced in the reported average mean diameter is small because the average standard deviation in the mean diameter measured for each kernel was only 1.6 μm. However, if the maximum or minimum radii were due to bumps or depressions (which is likely), the values reported as maximum and minimum diameters may be exaggerated. Also note that the sphericity was calculated from the maximum radius over the minimum radius. This ratio may yield a higher sphericity than if the ratio was calculated as the maximum diameter over the diameter perpendicular to the maximum diameter (which may not be the minimum). Because the kernel shape is not always symmetric and given the additional data available using computer automated imaging and analysis, a new definition of sphericity should be considered which would be more descriptive of the average shape and of deviations from the mean. It also might be better to specify and report the radius of the kernel rather than the diameter, for the same reasons. This will be discussed further in a future report.

	Sphericity	Mean Diameter	St. Dev. In Diameter	Maximum Diameter	Minimum Diameter
Mean	1.020	519	1.6	524	513
Standard Deviation	0.008	12	0.6	12	12
Maximum	1.122	545	8.0	555	538
Minimum	1.007	445	0.7	449	434

Sphericity	*Frequency*
1	0
1.01	39
1.02	912
1.03	486
1.04	108
1.05	24
1.06	3
1.07	1
1.08	0
1.09	2
1.1	0
1.11	0
1.12	0
1.13	1
More	0



Mean Diameter	*Frequency*
440	0
445	1
450	0
455	1
460	0
465	0
470	0
475	2
480	1
485	2
490	0
495	6
500	32
505	176
510	190
515	179
520	207
525	231
530	227
535	181
540	134
545	6
550	0
More	0

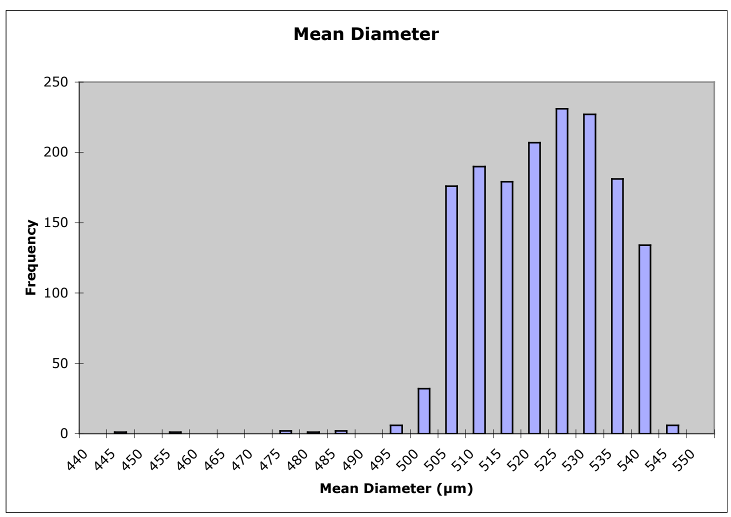


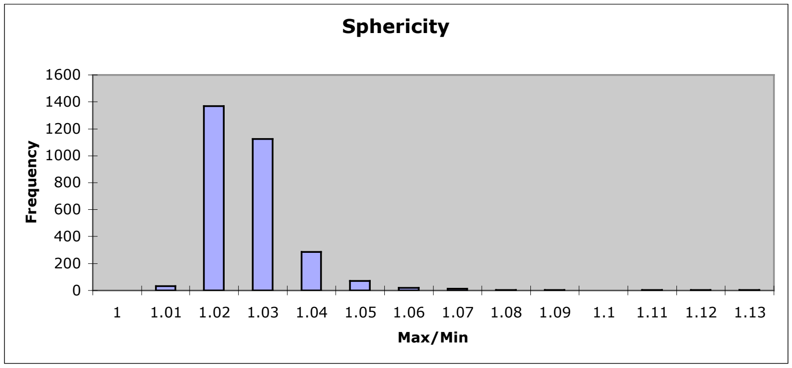
Figure 1: Size and shape summary for kernels riffled from DUN-500-S-1. Reported diameters are actually two times measured radii.

Size and shape were also measured on 2925 kernels (about 2 g) riffled from DUN-482-S-1. The measured kernels had an average mean diameter of 497 μm with a standard deviation in the distribution of 13 μm. Based on variable sampling statistics, we expect the average mean diameter of the DUN-482 composite of kernels to be 495 - 499 μm with 95% confidence. Note, however, that the distribution was irregular. This irregular distribution may effect the calculated range for mean diameter and has not been taken into account. The irregular distribution in the mean diameter comes from variation from batch to batch as the processing conditions were adjusted and from the fact that the composite was the result of combining 113.5 g from a sieve fraction between ASTM E161 electroformed sieves of 500±2 μm and 518±2 μm with 272 g from a sieve fraction between ASTM E161 electroformed sieves of 482±2 μm and 500±2 μm. Less than 1% of the kernels measured had mean diameters outside a range of 450 - 530 μm. The largest kernel measured had a mean diameter of 558 μm. This was unusually large and turned out to be a broken kernel that had passed through the sieve. The next largest kernel had a mean diameter of 525 μm. The smallest kernel had a mean diameter of 422 μm.

The average sphericity was 1.022 with a standard deviation of 0.010. The sphericity of this composite was not as good as the other. 1.6% of the kernels measured had a sphericity greater than 1.05. The highest sphericities were often associated with kernels that had very irregular profiles suggesting they had chunks broken out of them. It appears that the shape separation tabling was not as thorough for this composite.

	Sphericity	Mean Diameter	St. Dev. In Diameter	Maximum Diameter	Minimum Diameter
Mean	1.022	497	1.7	502	491
Standard Deviation	0.010	13	0.9	13	13
Maximum	1.129	558	13.7	575	520
Minimum	1.007	422	0.6	423	419

Sphericity	*Frequency*
1	0
1.01	31
1.02	1368
1.03	1124
1.04	284
1.05	69
1.06	20
1.07	14
1.08	4
1.09	2
1.1	1
1.11	2
1.12	2
1.13	3
More	0



Mean Diameter	*Frequency*
420	0
425	2
430	0
435	3
440	10
445	8
450	11
455	12
460	13
465	9
470	18
475	17
480	41
485	172
490	341
495	581
500	722
505	311
510	198
515	187
520	222
525	44
530	1
535	0
540	0
545	0
550	0
555	0
560	1
More	0

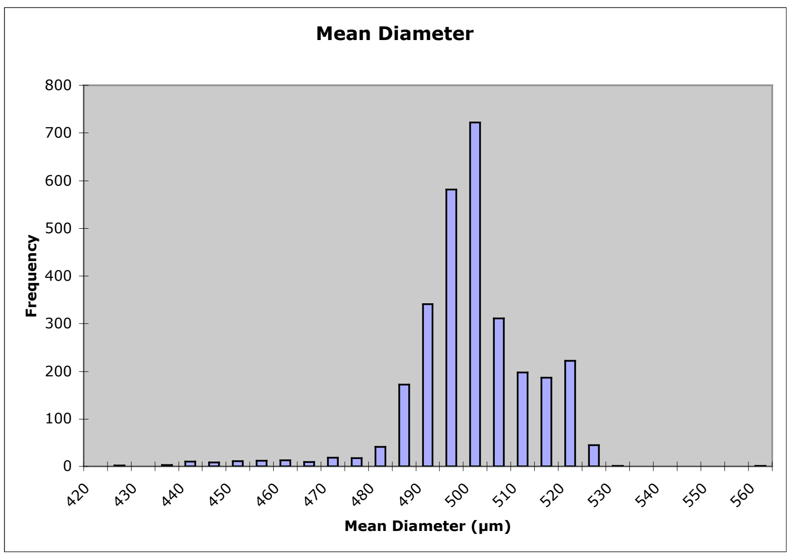


Figure 2: Size and shape summary for kernels riffled from DUN-482-S-1. Reported diameters are actually two times measured radii.

3.2 Density measurement: (Hunn, Pappano, Barker)

Using the ASTM D3766 standard terminology, we define three different types of density: the *theoretical density* is based solely on the solid material volume, the *skeletal density* includes the closed pore volume, and the *envelope density* includes the open and closed pore volume. The theoretical density of UO_2 is 10.96 g/cc.

Envelope density was measured with a Hg porosimeter. A 1.7 g sample was riffled from the 100 g sublot. The envelope density was 10.6 g/cc with a 1% open porosity. This result is preliminary in that the uncertainty and repeatability of the porosimetry measurement has not yet been fully analyzed. The envelope density was measured by weighing the sample and measuring the volume of mercury displaced after sufficient pressure was applied to cause the mercury to envelop each individual kernel in the sample. Open porosity information was obtained by continuing to increase the pressure and measuring the amount of mercury penetrating into the pores.

Skeletal density was measured with a helium pycnometer. A 13.3 g sample was riffled from the 100 g sublot. The skeletal density of the sample was 10.82±0.16 g/cc. The skeletal density was measured by weighing the sample and measuring the volume of helium displaced by the kernel. In this technique, the helium freely enters any open porosity in the kernels. Without knowledge of the open porosity, this measurement is of no value relative to the kernel density specification which refers to the envelope density. Given the 1% open porosity measured by the porosimeter, the measured skeletal density and envelope density are in agreement to within the uncertainty of the measurement.

An average bulk tap density of about 6.6 g/cc was obtained from preliminary measurements during kernel production. Using a packing fraction of 0.62 yielded an expected envelope density of about 10.6 g/cc for the sintered kernels.

3.3 Impurity analysis: (Williams, Collins, DelCul)

A 1.023 g sample of kernels was sent to Analytical Chemistry for analysis. The sample was microwave digested in ultra pure nitric acid to completely dissolve the sample. The uranium was then separated from the solution by using TRU resin obtained from Eichrome Technology, Inc and the collected column effluent was subsequently analyzed by ICP-MS. The only cations reported that were above the detection limit were as follows: 33.6 ± 3.4 μg/g Ni, 11.6 ± 1.2 μg/g Al, 10.7 ± 1.1 μg/g Ca, 10.6 ± 1.1 μg/g Cu, 11.6 ± 1.2 μg/g Al, and 5.6 ± 0.6 μg/g Cr.

ORNL delivered to Materials and Chemistry Laboratory, Inc. (MCLinc) a sample for chlorine analysis. The sample was prepared by pyrohydrolysis and analyzed by MCLinc SOP MCL-7759 Anions by Ion Chromatography. Two runs resulted in <19 and <13 chloride μg/g (ppm).

3.4 Optical micrographs taken during production: (Williams, Collins, Del Cul)

The photographs in Figure 3 and Figure 4 show a sample of yellow air-dried ~1000 μm-diameter UO_3 $2H_2O$ microspheres and a sample of calcined and sintered >500<534 μm sieved UO_2 kernels.

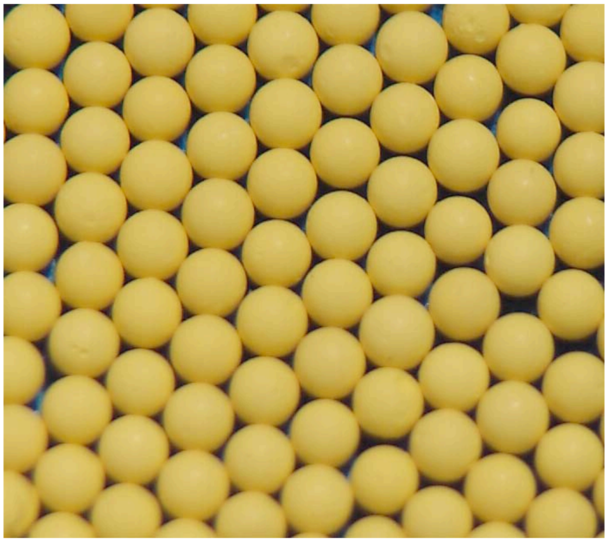


Figure 3: Air dried gel spheres

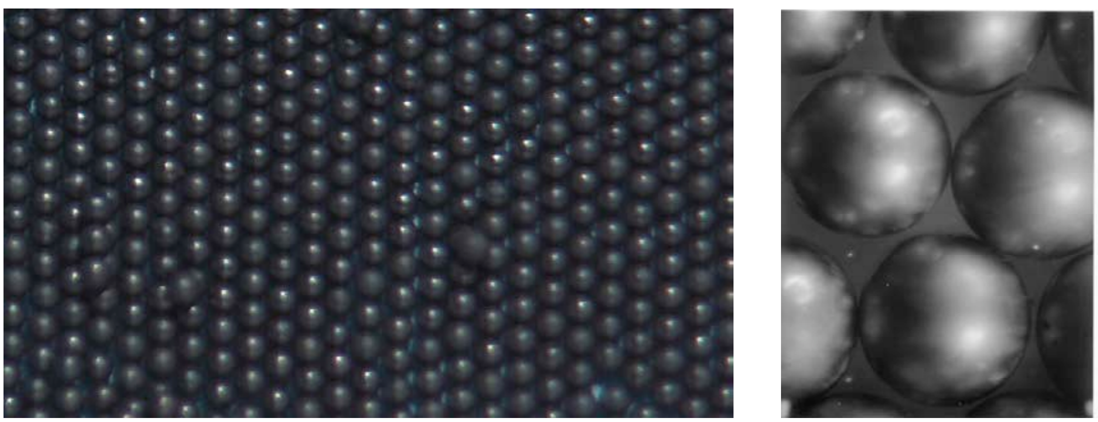


Figure 4: Calcined and sintered DUO_2 kernels

3.5 SEM analysis of kernel surface: (Hunn, Menchhofer)

A single kernel was selected at random and the surface was imaged by SEM. This was done for quick analysis and informational purposes and is not expected to be a statistically adequate analysis of the average microstructure of the whole batch. Figure 5 through Figure 8 show the kernel surface at various magnifications. The surface shows some roughness. The size of the grains exposed at the surface was from 1 - 5 μm. Two large, shallow craters could be seen on the surface in Figure 5.

3.6 SEM analysis of kernel polished cross section: (Hunn, Menchhofer, Comings)

19 kernels were mounted in a conducting epoxy for imaging by SEM (mount ID# M040227.1). Again, an attempt was not made to obtain sufficient images and measurements to produce statistically sound quantitative measurements of grain size for this qualitative analysis. However, it was observed that most of the polished kernels had a similar microstructure. Figure 9 and Figure 10 show a typical kernel cross section. Pits could be seen over the entire polished surface and exhibited a bi-modal size distribution. A high density of pits smaller than 0.25 μm appeared to be due to closed porosity exposed by the cross sectioning. The larger, irregularly shaped pits from 1-5 μm in size may be a different type of closed pore but it was more likely that they were due to pull-out during polishing, suggested by the shape and the fact that they were often located along residual scratches caused by the polishing.

Imaging with back scattered electrons gave good contrast for viewing the grain structure. Figure 11 and Figure 12 show grains up to about 10 μm across in the plane of the cross section. Also visible in Figure 11 was a 6 μm pit that looked like a large exposed void.

Some variation in microstructure was observed in one kernel that was believed to be from one of the early batches in the run. Figure 13 and Figure 14 show this kernel, which exhibited higher porosity than was typical. The grain size was also atypical, with the largest grains smaller than 5 μm and most of the grains less than 2 μm across in the plane of the cross section.

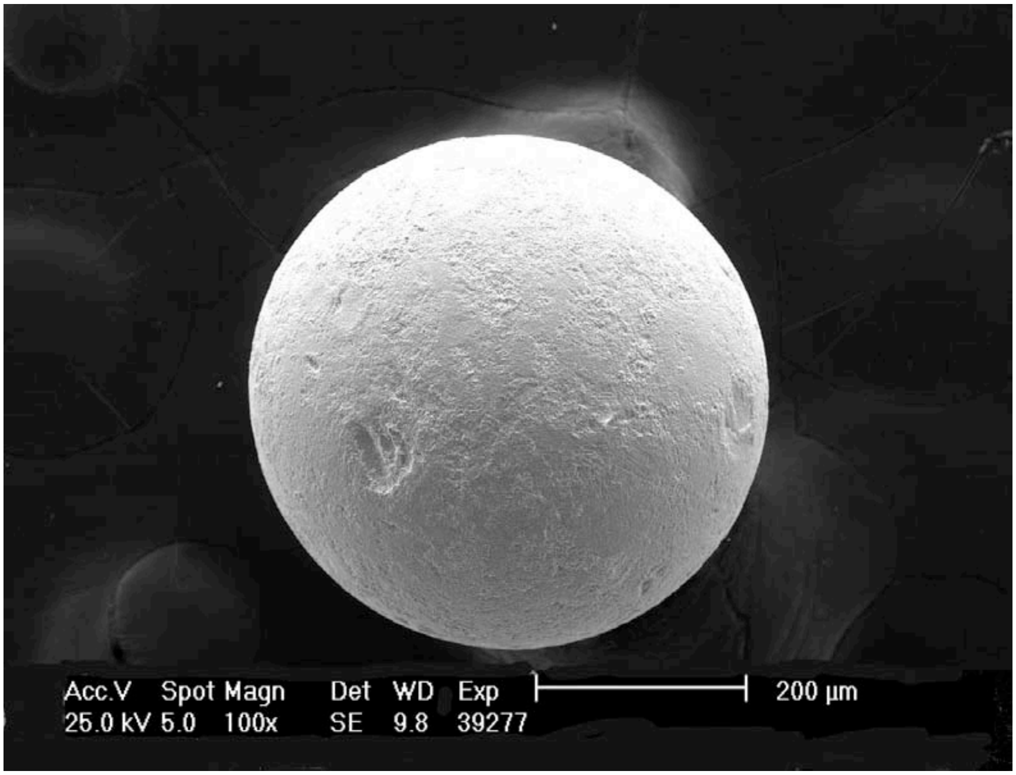


Figure 5: DUO_2 kernel

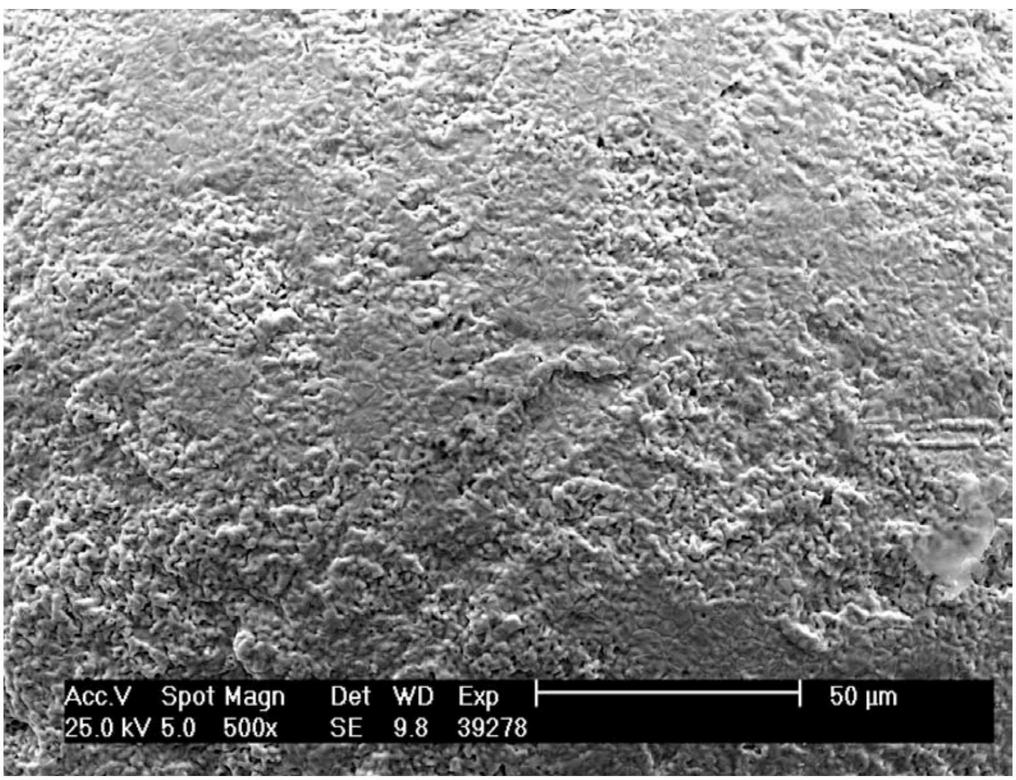


Figure 6: DUO_2 kernel

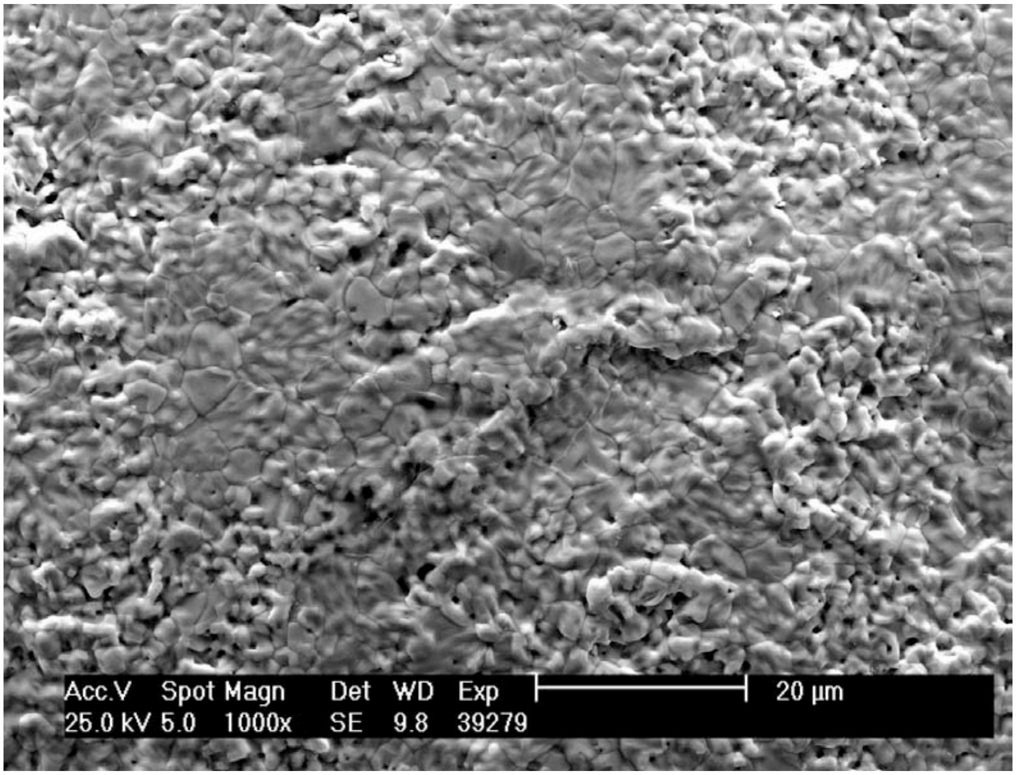


Figure 7: DUO_2 kernel

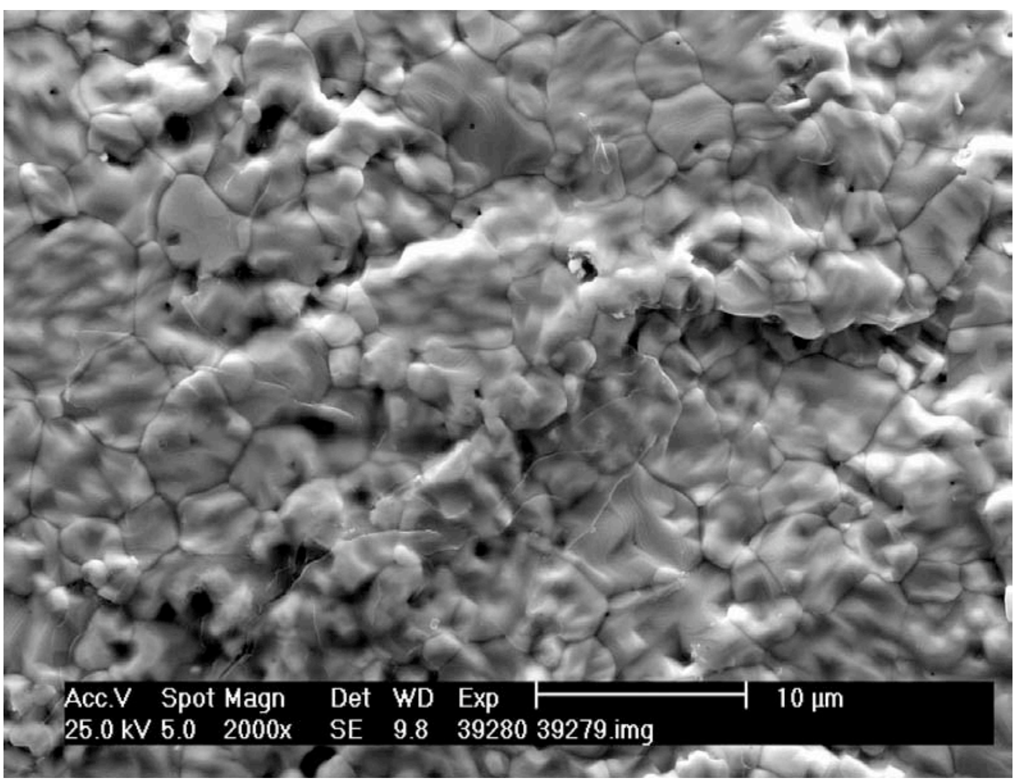


Figure 8: DUO_2 kernel

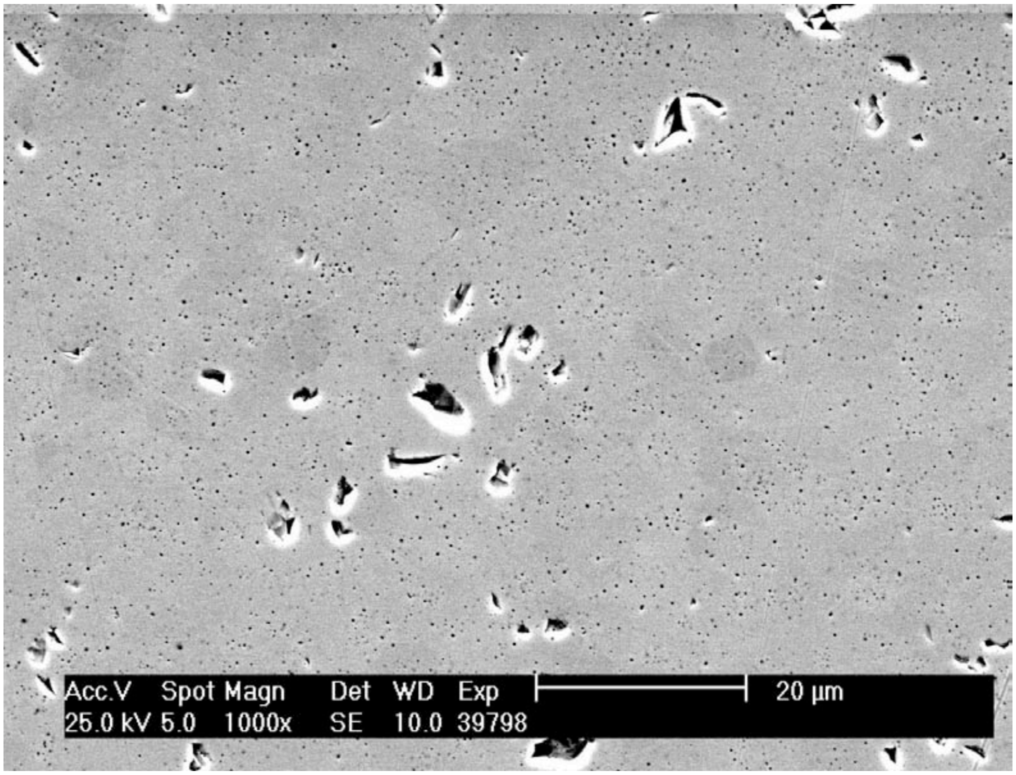


Figure 9: Typical DUO_2 kernel cross section

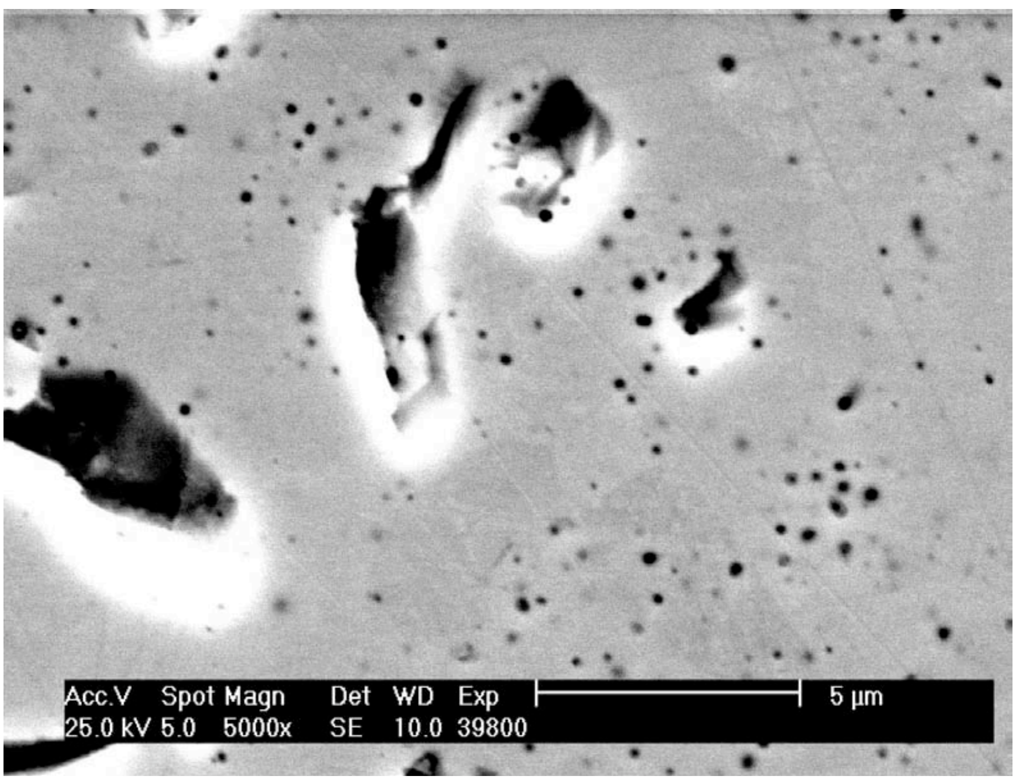


Figure 10: Typical DUO_2 kernel cross section

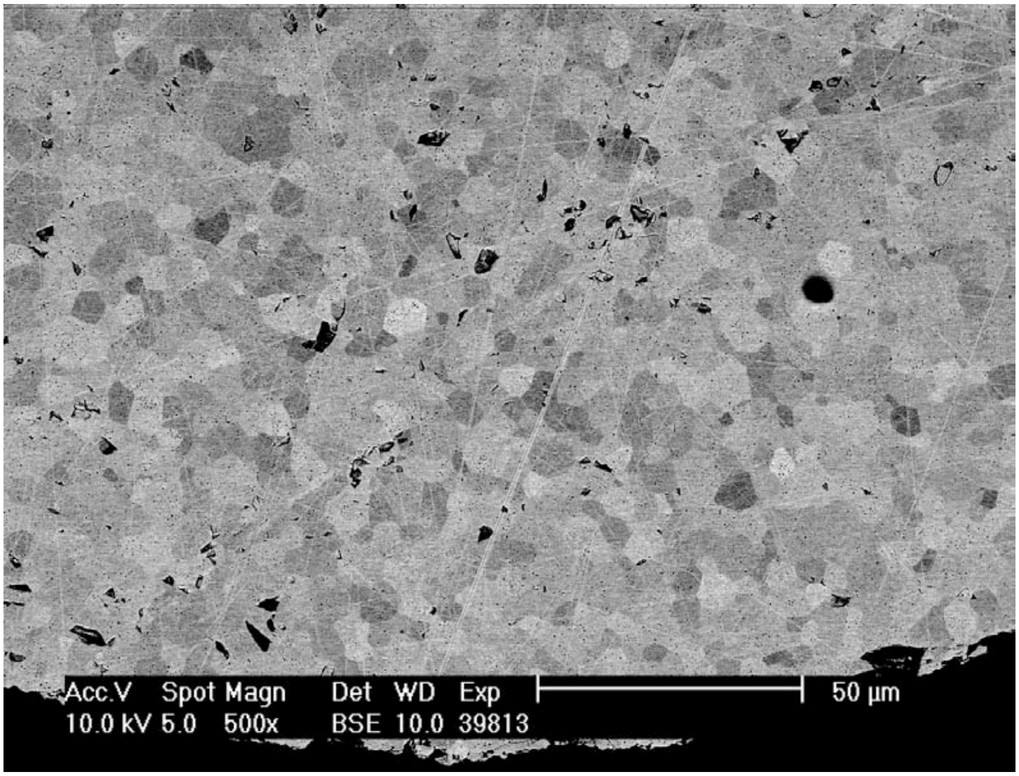


Figure 11: DUO_2 kernel cross section imaged with backscattered electrons.

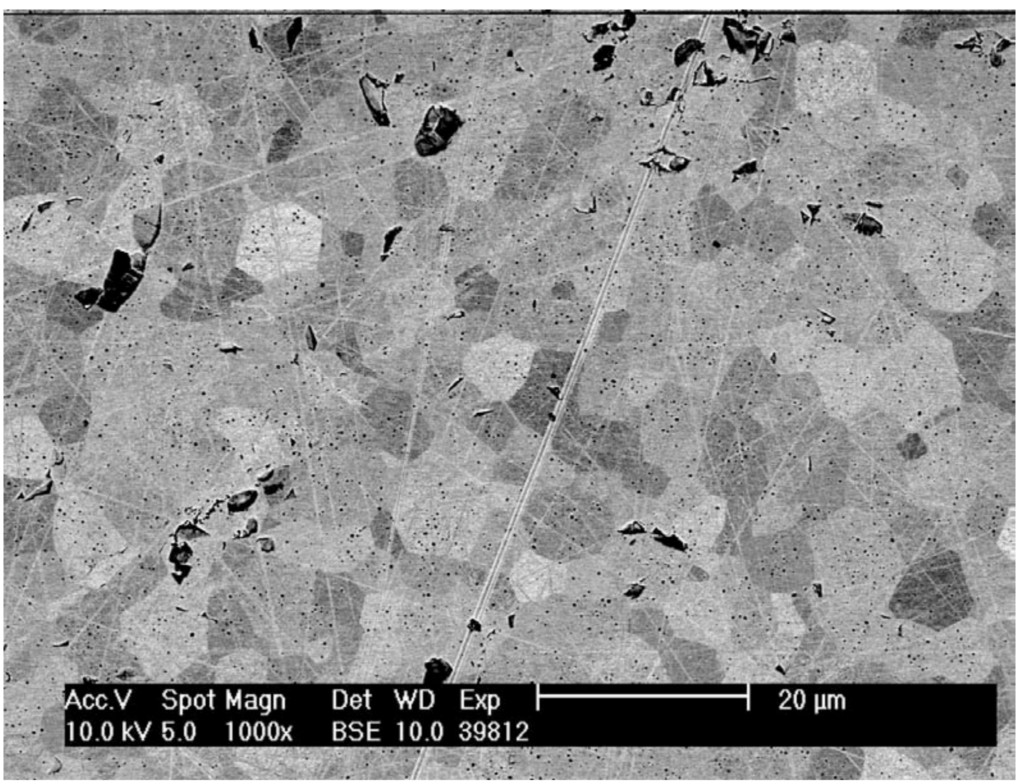


Figure 12: DUO_2 kernel cross section imaged with backscattered electrons.

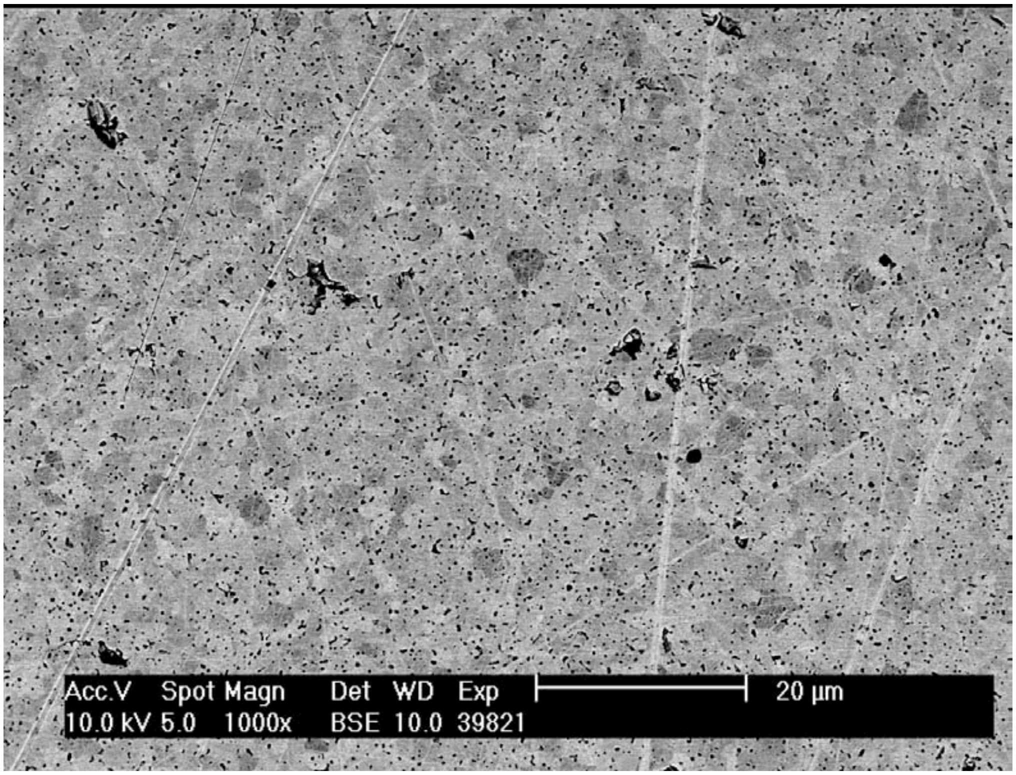


Figure 13: Atypical DUO_2 kernel cross section

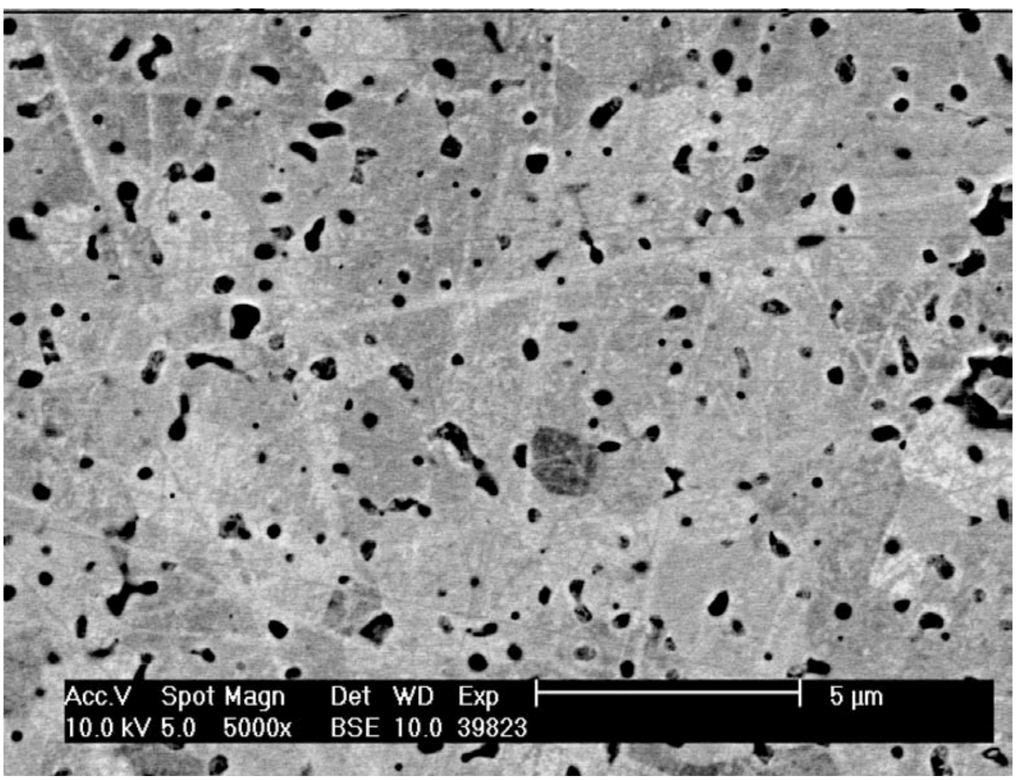


Figure 14: Atypical DUO_2 kernel cross section

4. Comparison to kernels from German reference fuel

It was interesting to compare the DUN-500 DUO_2 kernels produced at ORNL to 500 μm kernels extracted from the German reference fuel EUO 2358-2365. Some of the data for the German kernels is presented below. A more detailed report on the German reference fuel characterization with comparison to previously reported characterization by HOBEG and GA is being prepared.

4.1 Size and shape of German kernels: (Hunn, Kercher, Price)

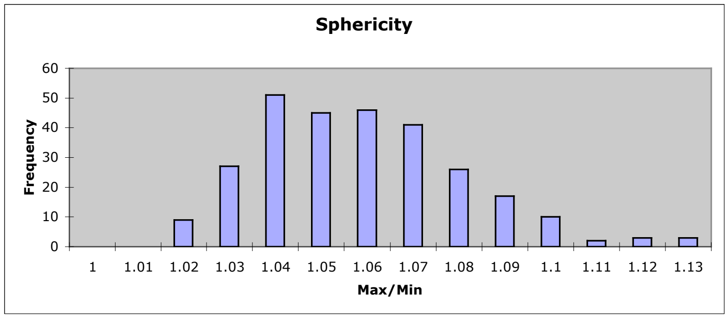
Size and shape was measured for 280 kernels (about 0.2 g) as described for the DUO_2 measurement. Results are shown in Figure 15.

The measured kernels had an average mean diameter of 504 μm with a standard deviation in the distribution of 7 μm. Based on variable sampling statistics, we expect the average mean diameter of the German kernels to be 502 - 506 μm with 95% confidence. The largest kernel measured had a mean diameter of 531 μm. The smallest kernel had a mean diameter of 485 μm. The size distribution of the German kernels was Gaussian and narrower than the ORNL DUO_2 kernels.

The ORNL DUO_2 kernels were, in general, more spherical than the German kernels. The average sphericity of the German kernels was 1.05 with a standard deviation of 0.02. Over 50% of the kernels measured had a sphericity greater than 1.05 compared to less than 0.5% for the ORNL DUO_2. Sphericities above 1.05 for the ORNL DUO_2 kernels were usually due to depressions (imaged as flats). High sphericity values in the German kernels were usually associated with oval shaped cross sections.

	Sphericity	Mean Diameter	St. Dev. In Diameter	Maximum Diameter	Minimum Diameter
Mean	1.05	504	7	517	490
Standard Deviation	0.02	7	3	7	10
Maximum	1.13	531	15	546	515
Minimum	1.01	485	1	497	462

Sphericity	*Frequency*
1	0
1.01	0
1.02	9
1.03	27
1.04	51
1.05	45
1.06	46
1.07	41
1.08	26
1.09	17
1.1	10
1.11	2
1.12	3
1.13	3
More	0



Mean Diameter	*Frequency*
480	0
485	1
490	3
495	23
500	57
505	70
510	74
515	40
520	10
525	1
530	0
535	1
540	0
More	0

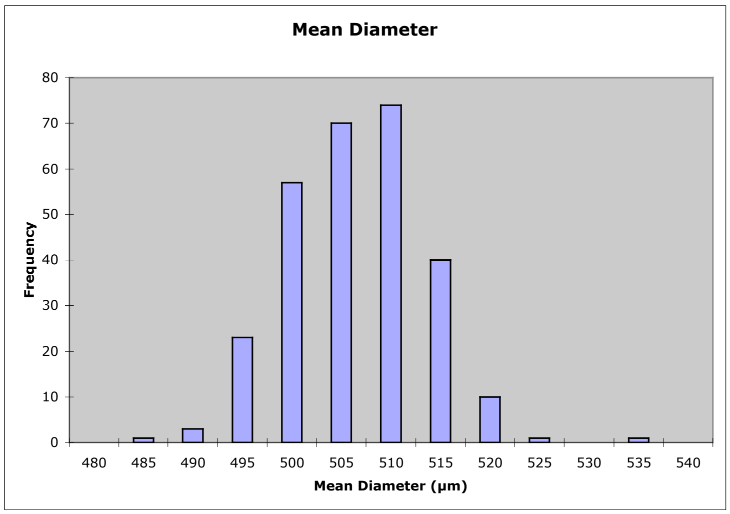


Figure 15: Size and shape data for 280 German kernels. Reported diameters are actually two times measured radii.

4.2 Density of German kernels: (Hunn, Pappano, Barker)

The density of the German fuel was similar to the ORNL DUO2 but the open porosity of the German fuel was lower. Envelope density was measured with a Hg porosimeter. A 7 g sample was riffled from the 100 g sublot. The envelope density was 10.6 g/cc with less than 0.02% open porosity. This result is preliminary in that the uncertainty and repeatability of the porosimetry measurement has not yet been fully analyzed. Skeletal density was measured with a helium pycnometer on the same 7 g sample. The skeletal density of the sample was measured to be 10.97±0.16 g/cc.

4.3 SEM of German kernels: (Hunn, Menchhofer, Comings)

A single kernel was selected at random and the surface was imaged by SEM. This was done to make a quick qualitative comparison with the ORNL DUO_2 kernel previously imaged and should not be considered a statistically adequate measure of the average microstructure. The surfaces of the German kernel was smoother and the grain size was much larger. Figure 16 through Figure 19 show the surface of the German kernel. The size of the grains at the surface was from 10 – 40 μm. This was about a factor of 10 larger than observed in the ORNL DUO_2 kernel. There was some open porosity within the grains, but overall the surface was much smoother than the DUO_2 kernels. One might expect the ORNL DUO_2 kernel surface to be more reactive because of the increased surface area.

38 kernels were mounted in a conducting epoxy for imaging by SEM (mount ID# M040127.1 and M040127.2). Again, an attempt was not made to obtain sufficient images and measurements to produce statistically sound quantitative measurements of grain size for this qualitative comparison. However, it was observed that most of the polished kernels had a similar microstructure. Figure 20 through Figure 22 show a German kernel in cross section. Scratches were deeper and more prevalent due to a different polishing procedure. The grain size in the plane of the cross section for the German kernels was larger at the surface (30 - 50 μm) then in the interior of the kernel (5 - 20 μm). The ORNL DUO_2 grain size (2 – 10 μm) in the plane of the cross section was more uniform throughout and smaller than the German grains. Comparison of Figure 9 and Figure 22 show that the German fuel also exhibited intergranular porosity but the pores were larger and fewer in number. Pit size was 0.5 – 1.5 μm compared to the less than 0.25 μm pits observed in the ORNL DUO_2 cross section . The irregular pitting observed in the ORNL DUO_2 and attributed to pull out was not seen in the German kernel. This may be due to the larger grain size, if these pits were indeed pull out.

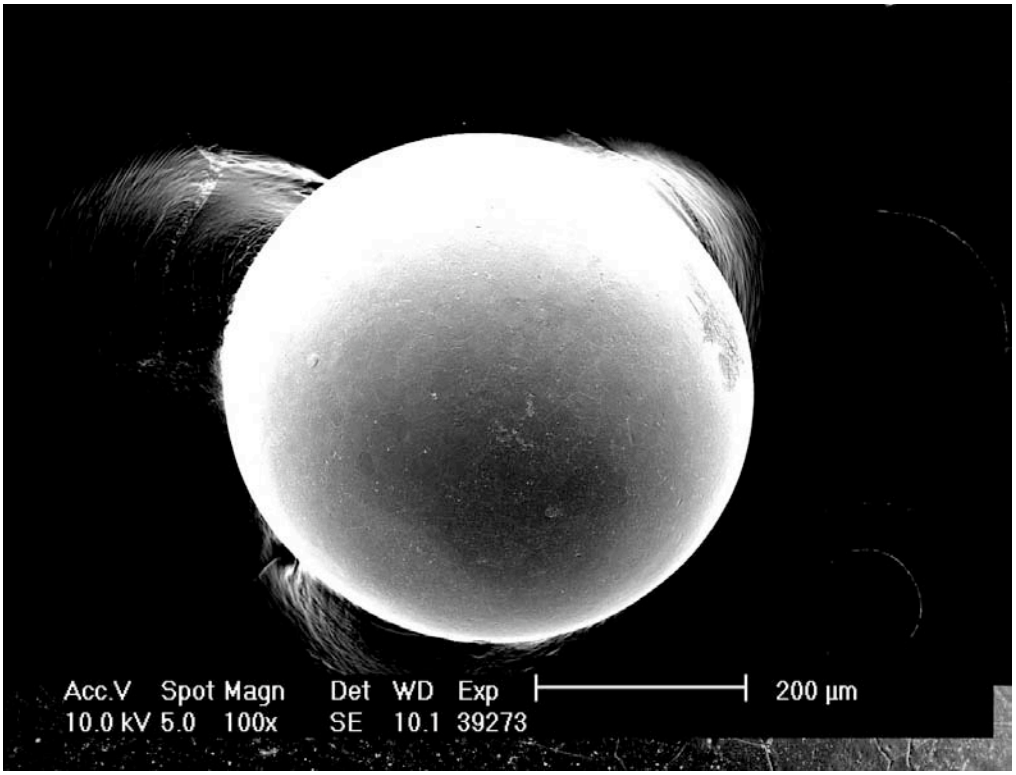


Figure 16: German kernel

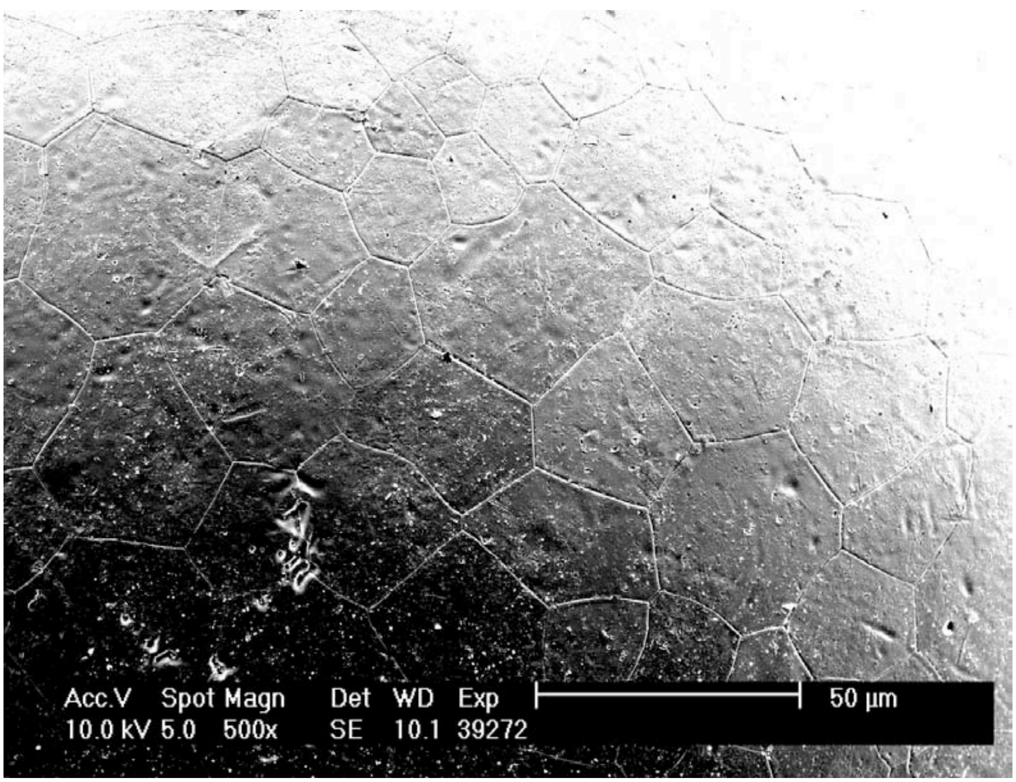


Figure 17: German kernel

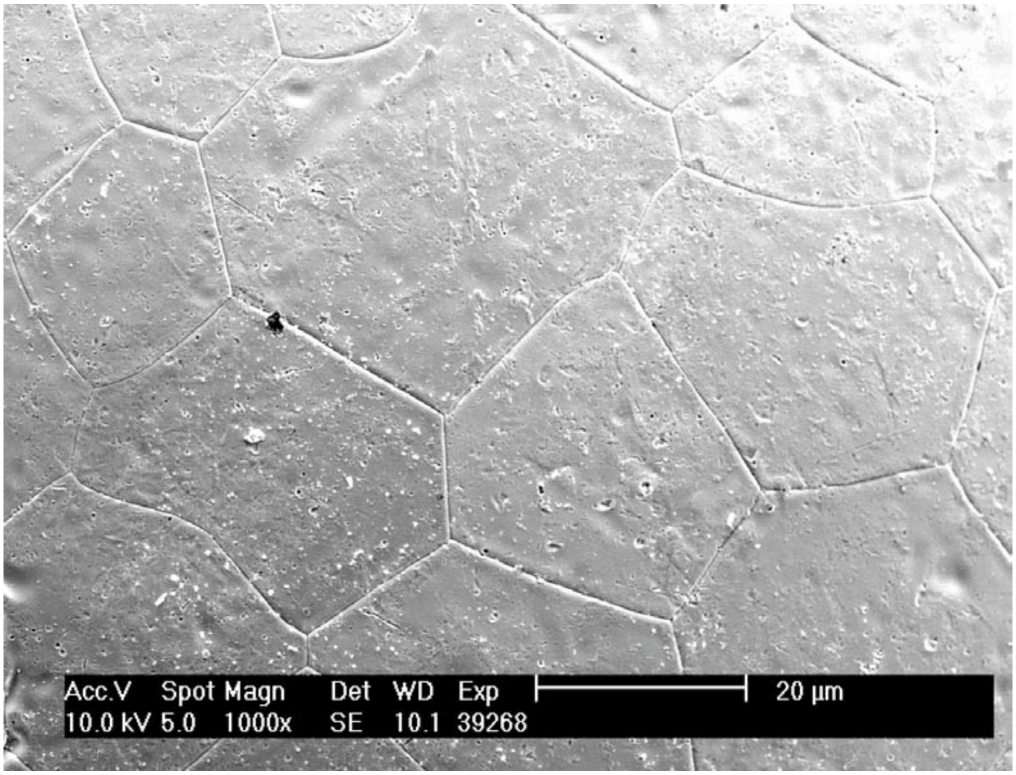


Figure 18: German kernel

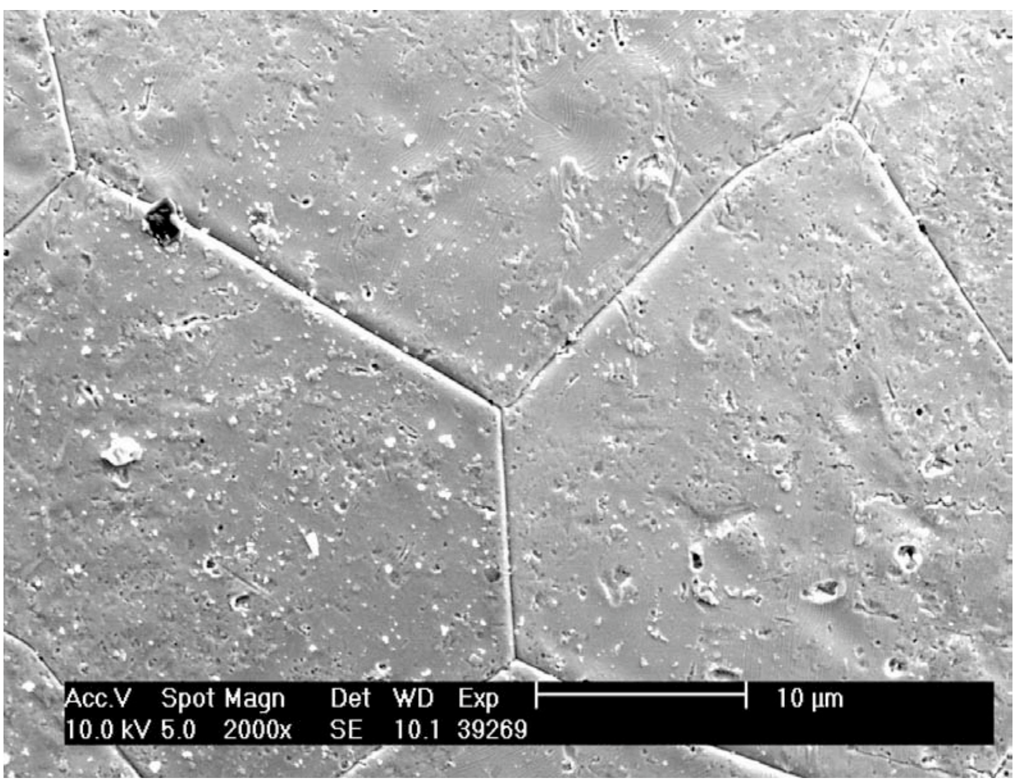


Figure 19: German kernel

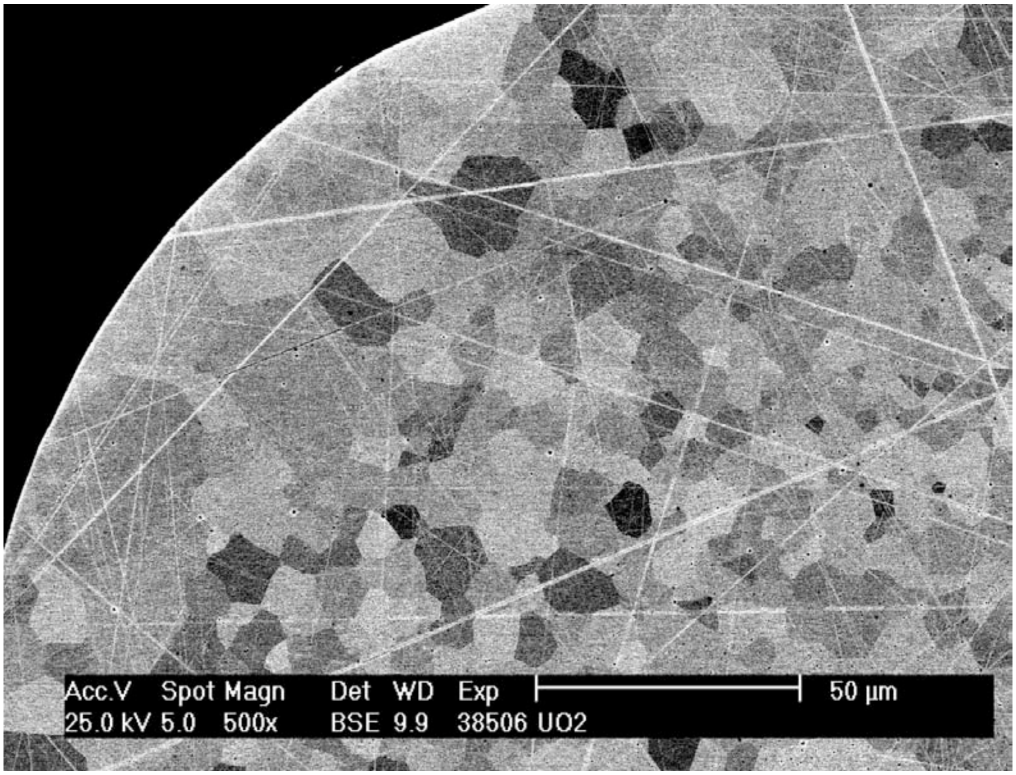


Figure 20: German kernel cross section

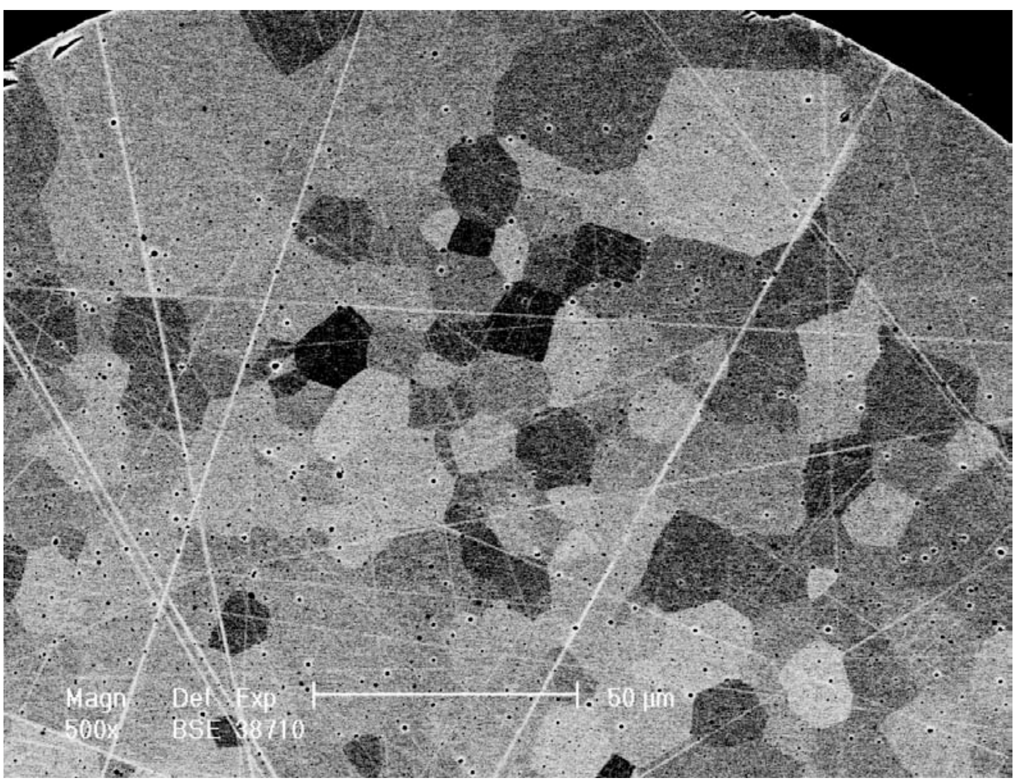


Figure 21: German kernel cross section

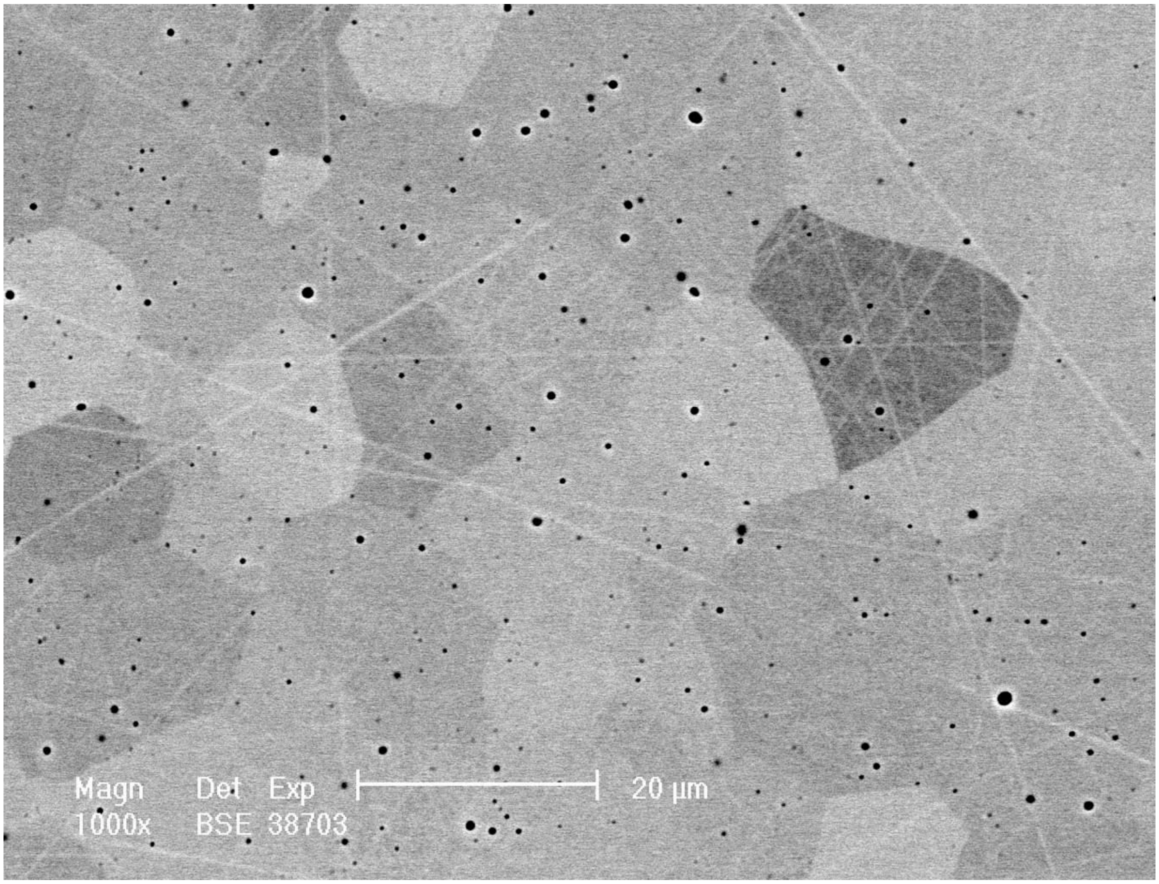


Figure 22: German kernel cross section