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September 27, 2005

AGR-1042

Dr. David Petti
Idaho National Laboratory
Engineering Fellow
Fission and Fusion Systems Department
P. O. Box 1625
Idaho Falls, ID 83415-3860

Dear Dr. Petti:

DE-AC05-00OR22725, Notification of Completion of Deliverable Associated with the Generation IV FY05 Work Package

The attached report, ORNL/TM-2005/533 "Effects of Deposition Conditions on the Properties of Pyrolytic Carbon Deposited in a Fluidized Bed," documents work performed at ORNL to develop an improved understanding of coated particle fuel process-product relationships. The inner pyrolytic carbon (IPyC) deposition study conducted at ORNL in early CY05 used a reference set of processing conditions to generate coatings with a range of microstructures for detailed characterization and permeability testing. The results of this study provided the AGR Program with key information needed to establish IPyC acceptance criteria for the baseline fuel and to select the variants to be included in the AGR-1 shakedown irradiation test.

This notification satisfies the ORNL level 3 deliverable listed as Activity #19, "Issue Inner Pyrocarbon Anisotropy versus Permeability Report," due September 30, 2005, in the DOE-NE approved Generation IV Nuclear Energy Systems ORNL FY05 Work Package Form, Revision 0 (27Jan05).

If you have any questions, please contact me at 865-241-4400 or John Hunn at 865-574-2480.

Sincerely,

Gary L. Bell, Manager
Advanced Gas Reactor Program

GLB/kyf

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ORNL/TM-2005/533

Effects of Deposition Conditions on the Properties of Pyrolytic Carbon Deposited in a Fluidized Bed

R.A. Lowden, J.D. Hunn, S.D. Nunn, A.K. Kercher, J.R. Price, P.A. Menchhofer and G.E. Jellison, Jr.

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UT-BATTELLE
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R.A. Lowden, J.D. Hunn, S.D. Nunn, A.K. Kercher, J.R. Price, P.A. Menchhofer and G.E. Jellison, Jr.

Oak Ridge National Laboratory

Background

The high-density, isotropic pyrolytic carbon layer beneath the silicon carbide (IPyC) plays a key role in the irradiation performance of coated particle fuel. The IPyC layer protects the kernel from reactions with chlorine during deposition of the SiC layer, provides structural support for the SiC layer, and protects the SiC from fission products and carbon monoxide during operation. The process conditions used by the Germans to deposit the IPyC coating produced a highly isotropic, but somewhat permeable IPyC coating. The permeability of the IPyC coating was acceptable for use with the dense German UO_2 kernels, but may not be suitable when coating UCO kernels. The UCO kernels are typically more porous and thus have a larger surface area than UO_2 kernels. The lower density and the higher surface area of UCO kernels could make them more susceptible to attack by HCl gas during the silicon carbide (SiC) coating process, which could result in heavy metal dispersion into the buffer and IPyC coatings and a higher level of as-manufactured SiC defects.

The relationship between IPyC deposition conditions, permeability, and anisotropy must be understood and the appropriate combination of anisotropy and permeability for particle fuel containing UCO kernels selected. A reference set of processing conditions have been determined from review of historical information and results of earlier coating experiments employing 350 and 500 μm UO_2 kernels. It was decided that a limited study would be conducted, in which only coating gas fraction (CGF) and temperature would be varied. Coatings would be deposited at different rates and with a range of microstructures. Thickness, density, porosity and anisotropy would be measured and permeability evaluated using a chlorine leach test. The results would be used to select the best IPyC coating conditions for use with the available natural enrichment uranium carbide/uranium oxide (NUCO) kernels.

Deposition Conditions

The coating experiments for the IPyC study are summarized in Table 1 and Figure 1. Based upon a kernel diameter of 346 - 347 μm and a density of 10.78 g/cm^3, a batch size of 62.25 g was selected for the IPyC study using the NUCO kernels. The batch had a volume of ~ 9.5 cm^3 and a surface area of ~ 1000 cm^2. The batch size was slightly smaller than used in previous experiments to provide more flexibility if process adjustments were required.

The deposition conditions for the buffer layer were held constant while CGF and temperature were varied during IPyC coating. Deposition time was also varied to accommodate differences in efficiency caused by changes in temperature and reactant gas concentration. Efficiencies were calculated from earlier experiments using similar deposition conditions and coater configurations.

Summary of Deposition Parameters

Batch:

Kernel = 346 – 347 μm NUCO with a density of 10.78 g/cm^3
Weight = 62.25 g
Surface area = 1000 cm^2
Volume = 9.5 cm^3

Buffer:

Temperature = 1275°C
Coating gas fraction = 0.60
Total gas flow = 7,500 sccm
Argon flow = 3,000 sccm
Acetylene flow = 4,500 sccm
Time = 5 min

IPyC:

Temperature = 1275 ± 50°C
Coating gas fraction = 0.30 ± 0.15
Propylene/acetylene ratio = 0.85
Total gas flow = 8,500 sccm
Time adjusted based upon efficiency.

Table 1. Summary of Coating Experiments for the IPyC Study

Run no.	Temperature (°C)	CGF	Argon (sccm)	C_2H_2 (sccm)	C_3H_6 (sccm)	Predicted Rate (μm/min)	Time (min)
6	1225	0.15	7225	690	585	1.5	26.7
3	1225	0.30	5950	1375	1175	3.0	13.3
8	1225	0.45	4675	2065	1760	4.5	8.9
4	1275	0.15	7225	690	585	1.8	22.2
10	1275	0.30	5950	1375	1175	3.6	11.1
7	1275	0.45	4675	2065	1760	5.4	7.4
5	1325	0.15	7225	690	585	2.3	17.8
2	1325	0.30	5950	1375	1175	4.5	8.9
9	1325	0.45	4675	2065	1760	6.8	5.9
1	1275	0.30	5950	1375	1175	3.6	11.1
12	1275	0.30	5950	1375	1175	3.6	11.1
11	1300	0.30	5950	1375	1175	4.1	9.9
13	1170	0.30	5950	1375	1175	2.6	15.5
16	1250	0.30	5950	1375	1175	2.5	16.0
17	1250	0.15	7225	690	585	1.3	30.0
18	1250	0.45	4675	2065	1760	4.3	9.0
20	1250	0.30	5950	1375	1175	3.0	13.0

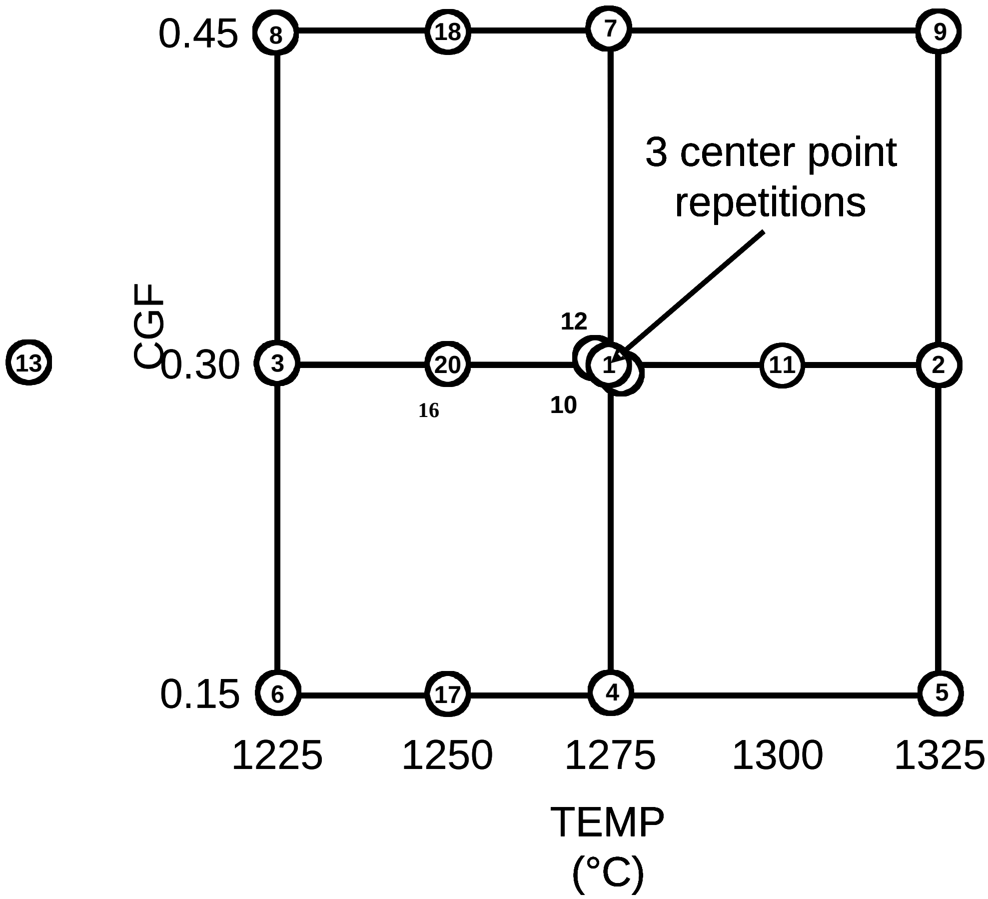

Figure 1. “Schematic” of the IPyC deposition study.

Coating Properties

Results for the initial IPyC study experiments using the NUCO kernels are highlighted in Figures 2 through 32 and Table 2. Temperatures have been adjusted 25°C to reflect results of recent calibrations of the sight glass and prism. From initial observations and measurements, the coatings appeared to be uniform and have similar thicknesses. Some variation in thickness was expected for deposition time was varied for each coating run to control thickness. Times were based upon predicted efficiencies and thus deposition rates. Many of the experiments fell outside of the ranges explored in earlier experiments thus some “error” in the predicted deposition rate was expected.

The polished cross sections of particles were characterized using light and scanning electron microscopy. Representative images are given in Figures 2 through 17. The images were used to gather information about coating thickness and uniformity as well as particle sphericity. The individual images are also assembled in grids that resemble the schematic of the study in Figures 18 through 21 to better shown trends and correlations between processing and coating properties.

The factors (processing conditions) and responses (coating properties) for the coatings produced in the IPyC study were examined employing design of experiments software. Coating gas fraction and temperature were the factors that were varied in the study. The effect of these factors on efficiency, deposition rate, coating density, permeability, open porosity, and anisotropy were investigated. The results are shown in the response plots in Figures 22 through 27 and Figures 31 and 32.

IPyC density was measured by placing IPyC fragments into a liquid density gradient column. Pieces of IPyC were gathered by cracking off the coatings and each fragment was carefully examined to avoid pieces with remnants of the buffer layer. However, some residual buffer could still be attached which may effect the measurement. The results are summarized in Table 2 and in Figure 24.

Diattentuation, retardation, and the preferred direction of the fast axis were measured on the IPyC layers from the study using the two-modulator generalized ellipsometry microscope (2-MGEM). Ten particles from each variant were examined. The results are given in Table 2 and shown graphically in Figures 25 through 27.

The IPyC/buffer-coated NUCO was heated in chlorine for 18 hours at 1500°C. After chlorination, the uranium dispersion in the buffer and IPyC layers was imaged by x-ray absorption. For each IPyC variant, an x-ray transmission image was obtained on a single layer of particles sandwiched in Kapton tape containing both chlorinated and un-chlorinated particles. An increase in x-ray absorption due to uranium dispersion was seen as a net darkening of the image in the carbon layers. Clear trends in the degree of permeability to chlorine can be seen in figures 28 through 30. To allow this comparison, the images in these arrays were adjusted for brightness and contrast to roughly normalize to the un-chlorinated particles from each variant. This normalization was not ideal due to variations in the particle geometry, as well as subjective error. A more thorough quantification of the uranium dispersion was performed using automated image analysis which measured the intensity increase in each particle coating and used the particle radius to take into account the x-ray path length and volume analyzed. The permeability data in Table 2 is in arbitrary units proportional to the density of the uranium dispersed into the carbon layers. Figure 31 graphs the permeability trend versus CGF and temperature.

Open porosity was measured employing a mercury porosimeter. Table 2 and Figure 32 show the results in terms of the volume of mercury intruded into the open pores (in ml) per surface area (in m^2). Values are given in Table 2 for two different ranges of intrusion pressure.

<u>Summary</u>

The response plots from the investigation of the deposition of pyrolytic carbon in a fluidized bed graphically depict the relationships between processing parameters and coating properties. The additional figures present optical, scanning electron microscopy, and other images to highlight microstructural details. For the study, only two parameters (factors), coating gas fraction and deposition temperature, were varied. The plots reveal obvious trends and links between factors and responses. The dominant relationships determined by this study for this range of coating conditions are:

- Rate is dependent upon coating gas fraction or in other terms, reactant concentration.
- Density is controlled by deposition temperature.
- Efficiency is influenced by both CGF and temperature.
- Anisotropy is affected by CGF and temperature, however, the relationship is more complex than for other properties.
- Permeability is dependent upon deposition temperature (thus density).
- Open porosity is affected by CGF thus is influenced by coating rate.

The response plots can be used as “maps” for the deposition process and are thus valuable for selecting coating conditions necessary to produce desired combinations of properties. The information is useful in predicting the effects of changes to processing on properties and is beneficial in optimizing the process and product properties. Although the study was limited to only two parameters, the information provides a foundation from which other aspects of the coating process can be more easily investigated.

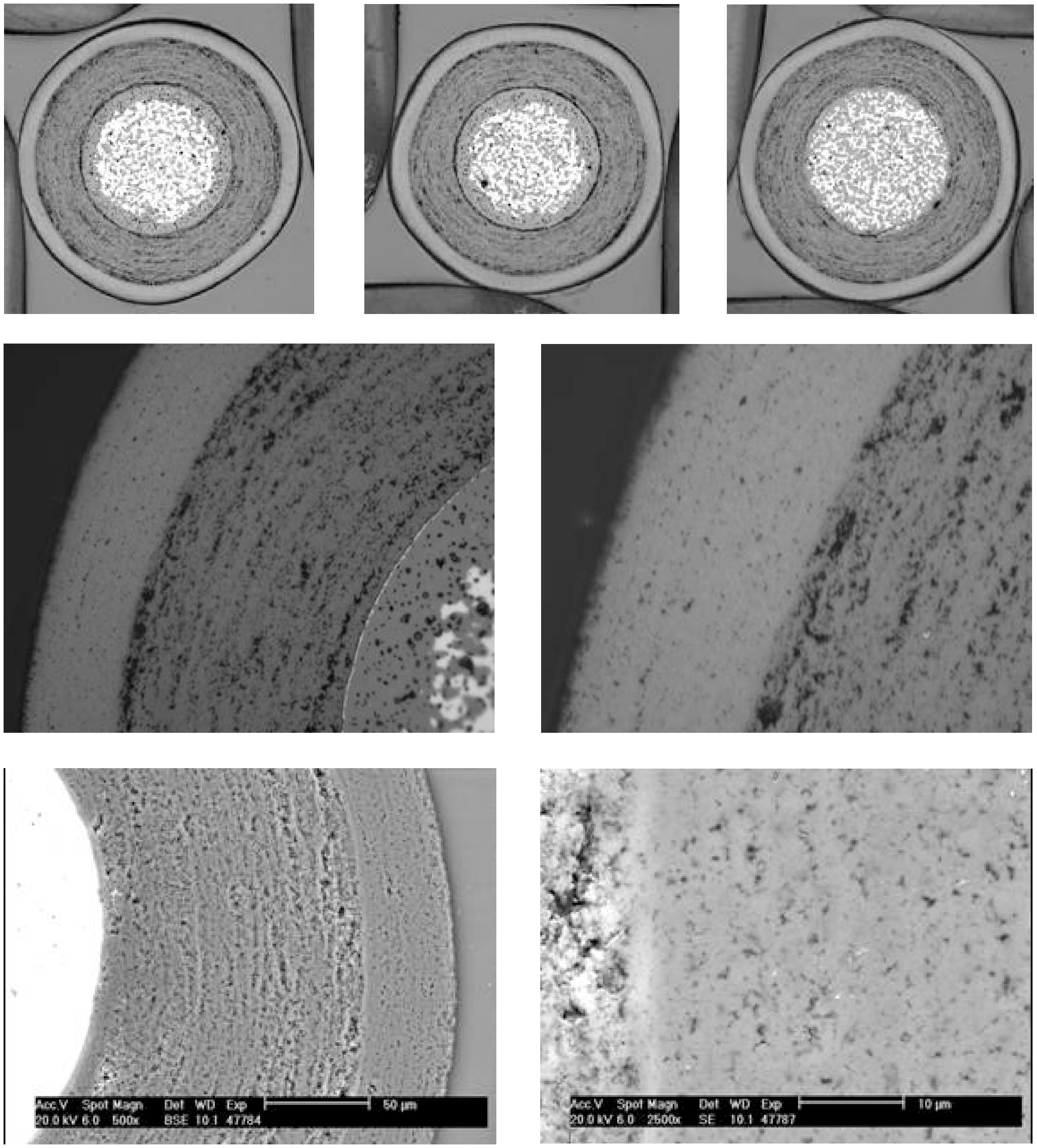

Figure 2. IPyC-1 deposited at center point conditions; 1275°C and CGF = 0.30.

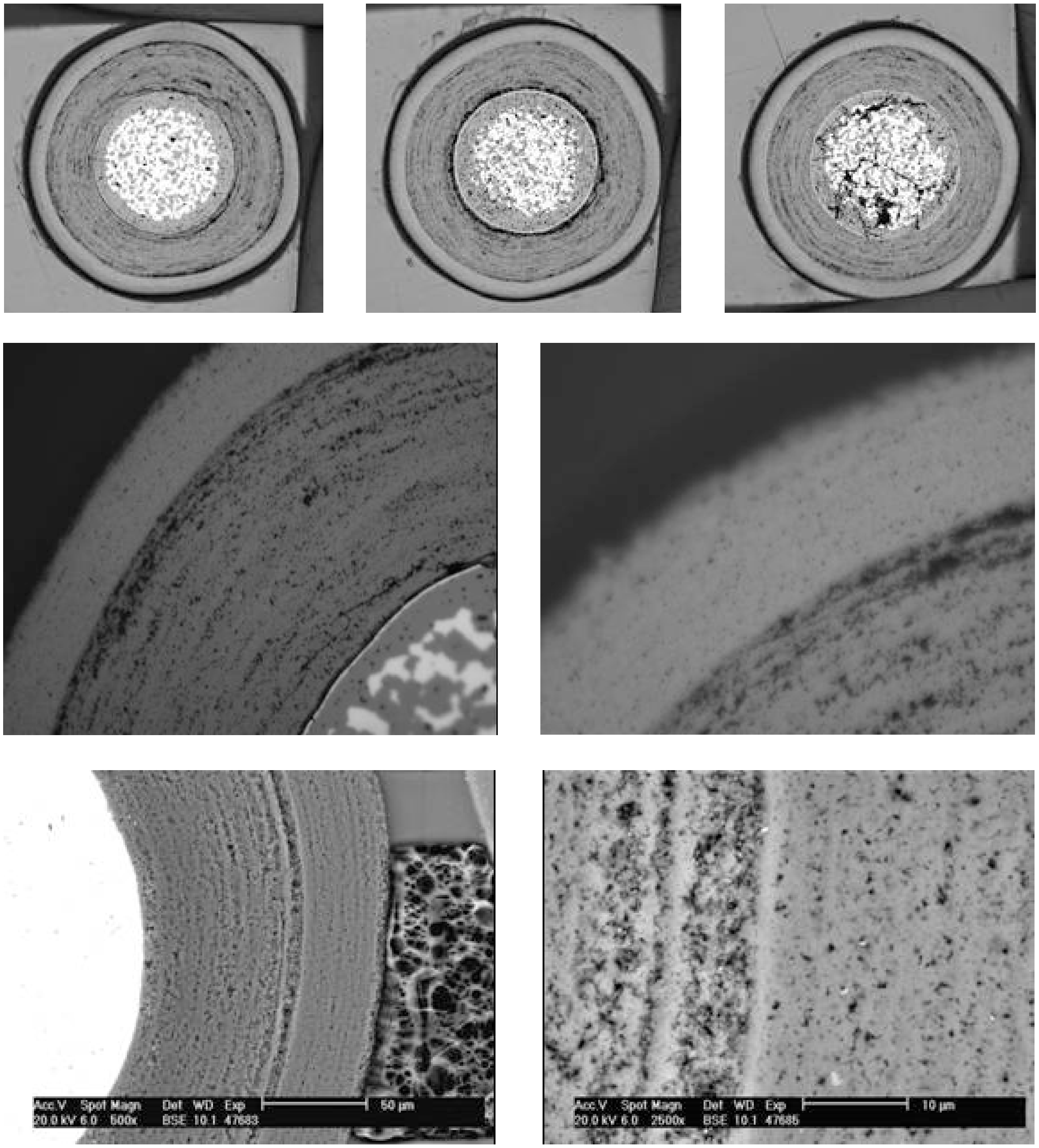

Figure 3. IPyC-2 deposited at 1325°C and CGF = 0.30.

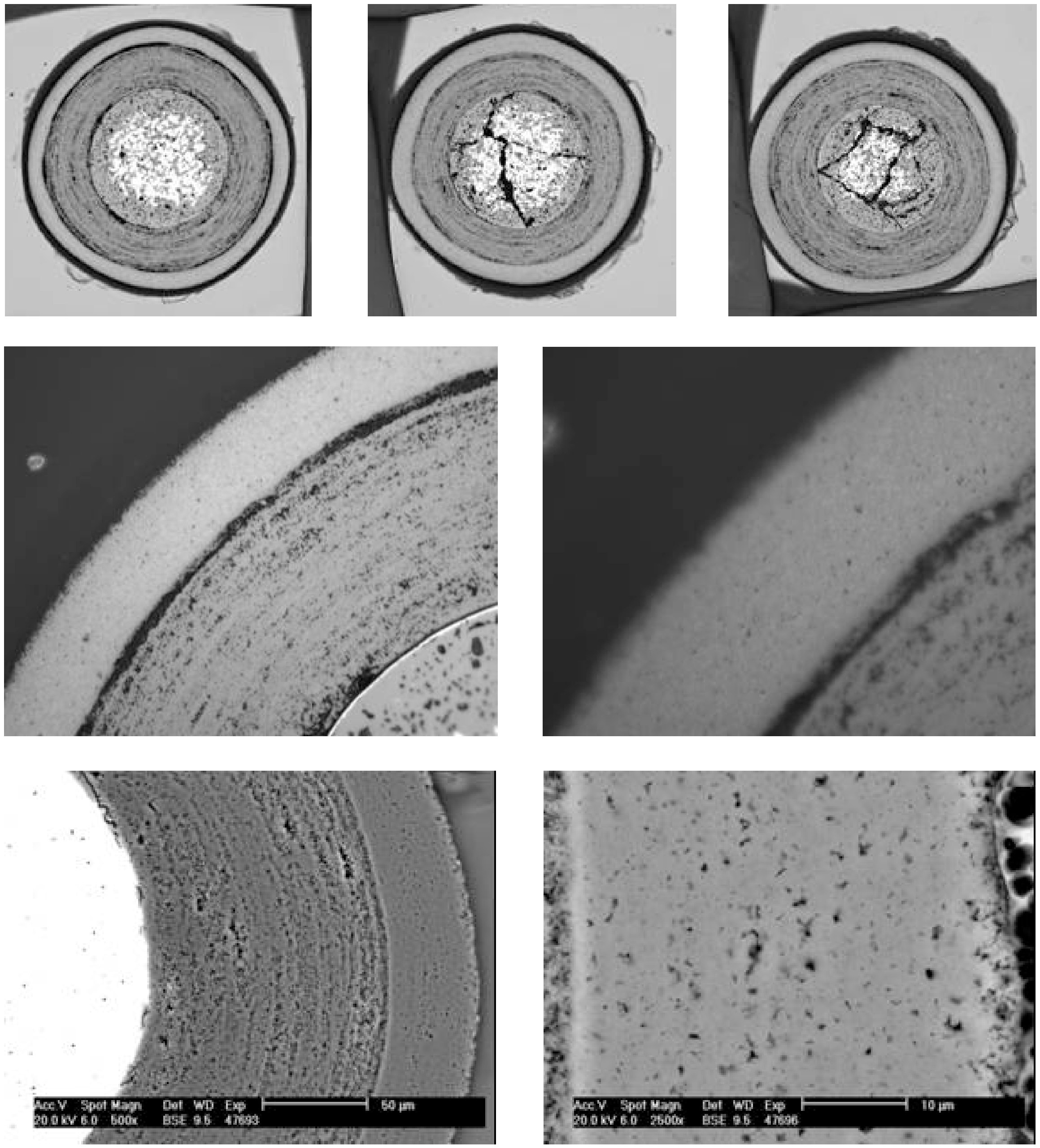

Figure 4. IPyC-3 deposited at 1225°C and CGF = 0.30.

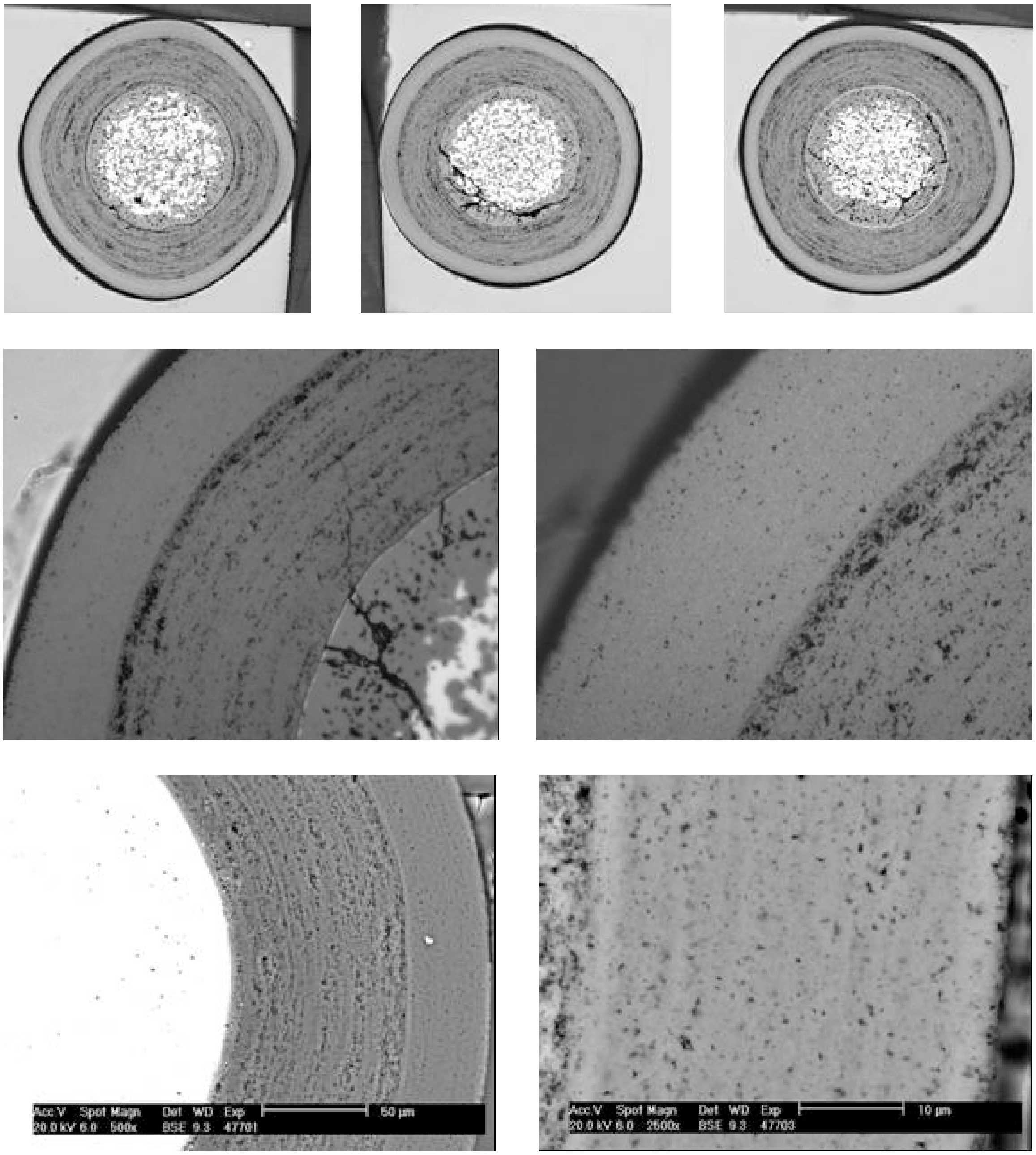

Figure 5. IPyC-4 deposited at 1275°C and CGF = 0.15.

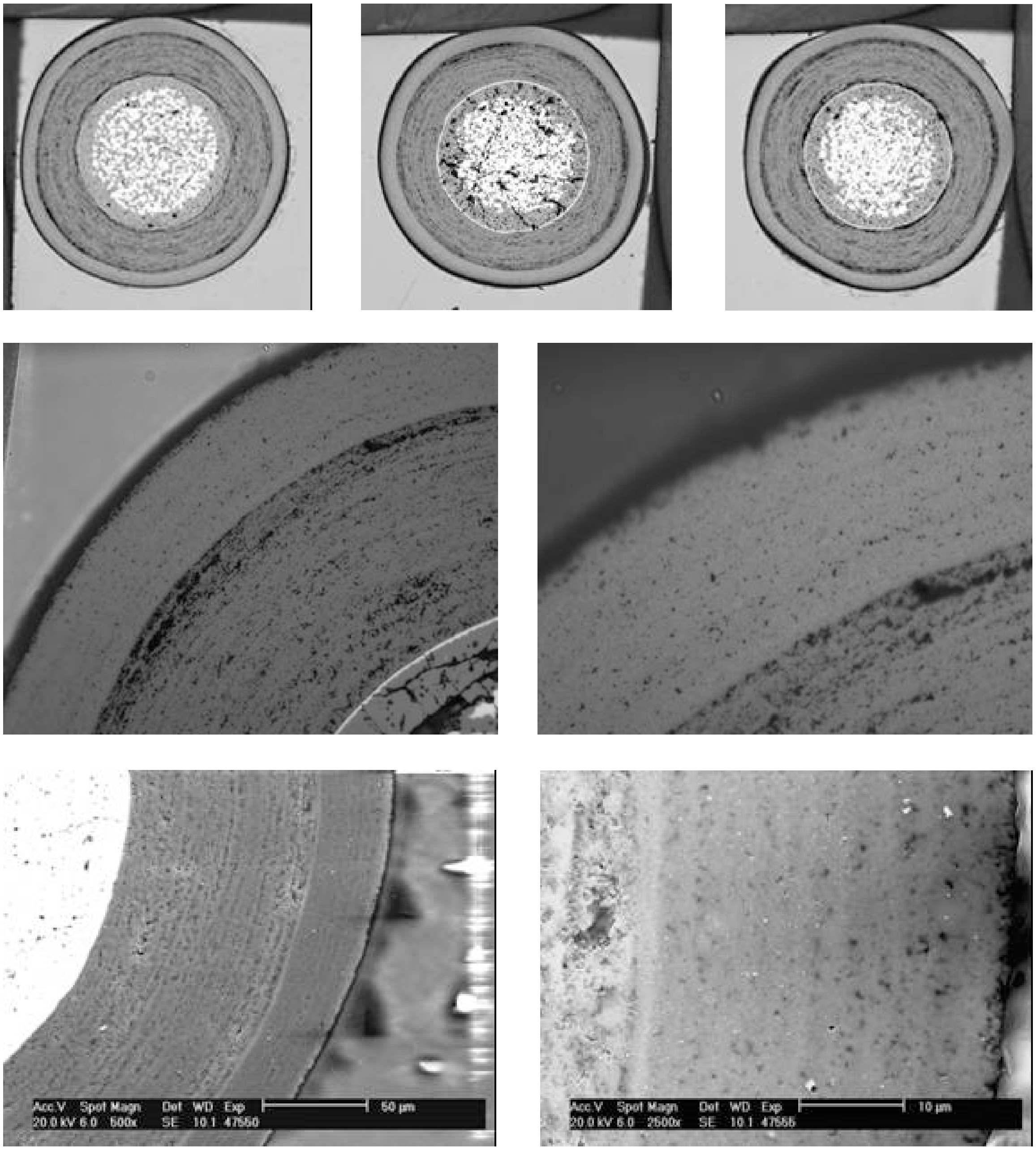

Figure 6. IPyC-5 deposited at 1325°C and CGF = 0.15.

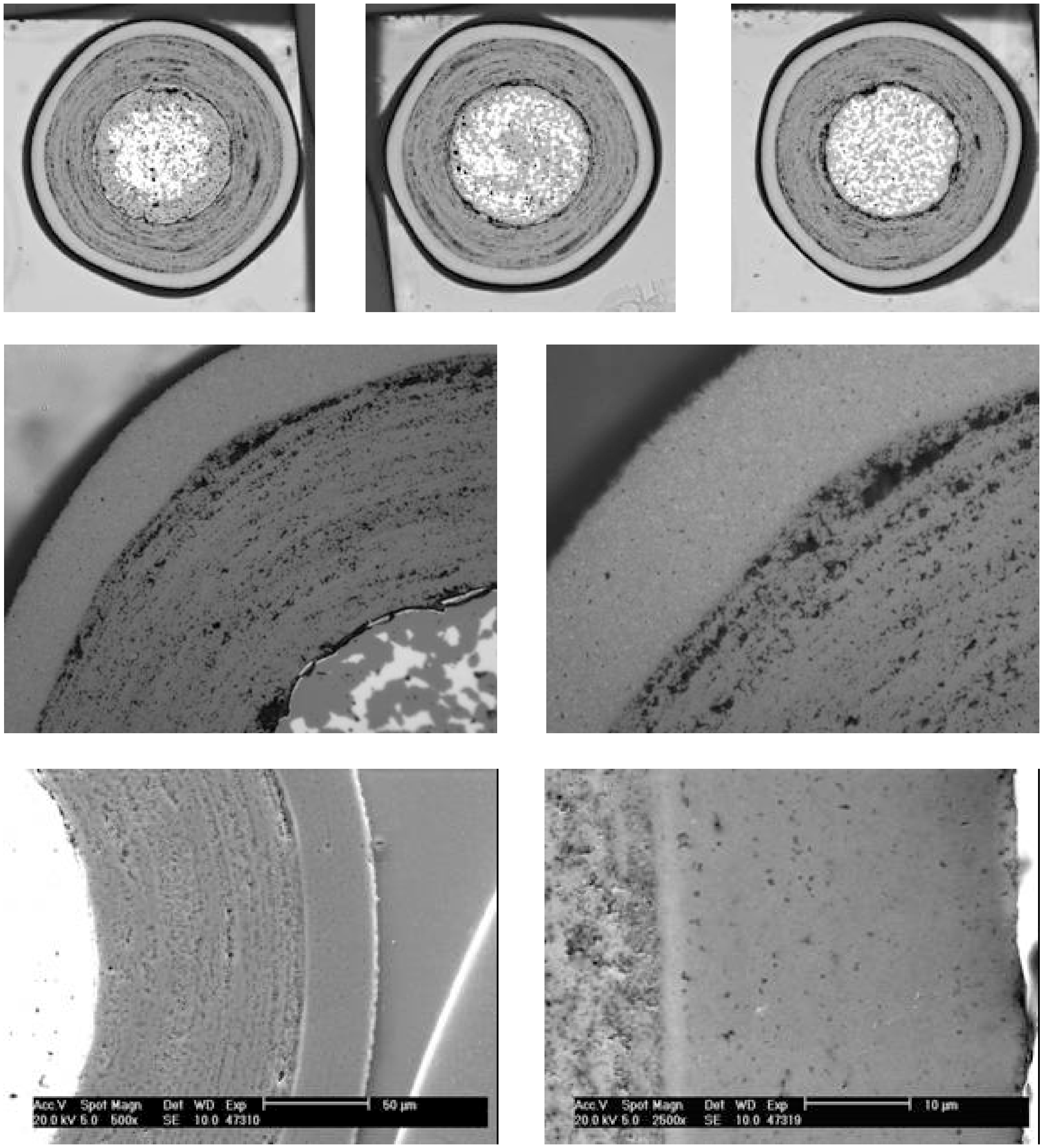

Figure 7. IPyC-6 deposited at 1225°C and CGF = 0.15.

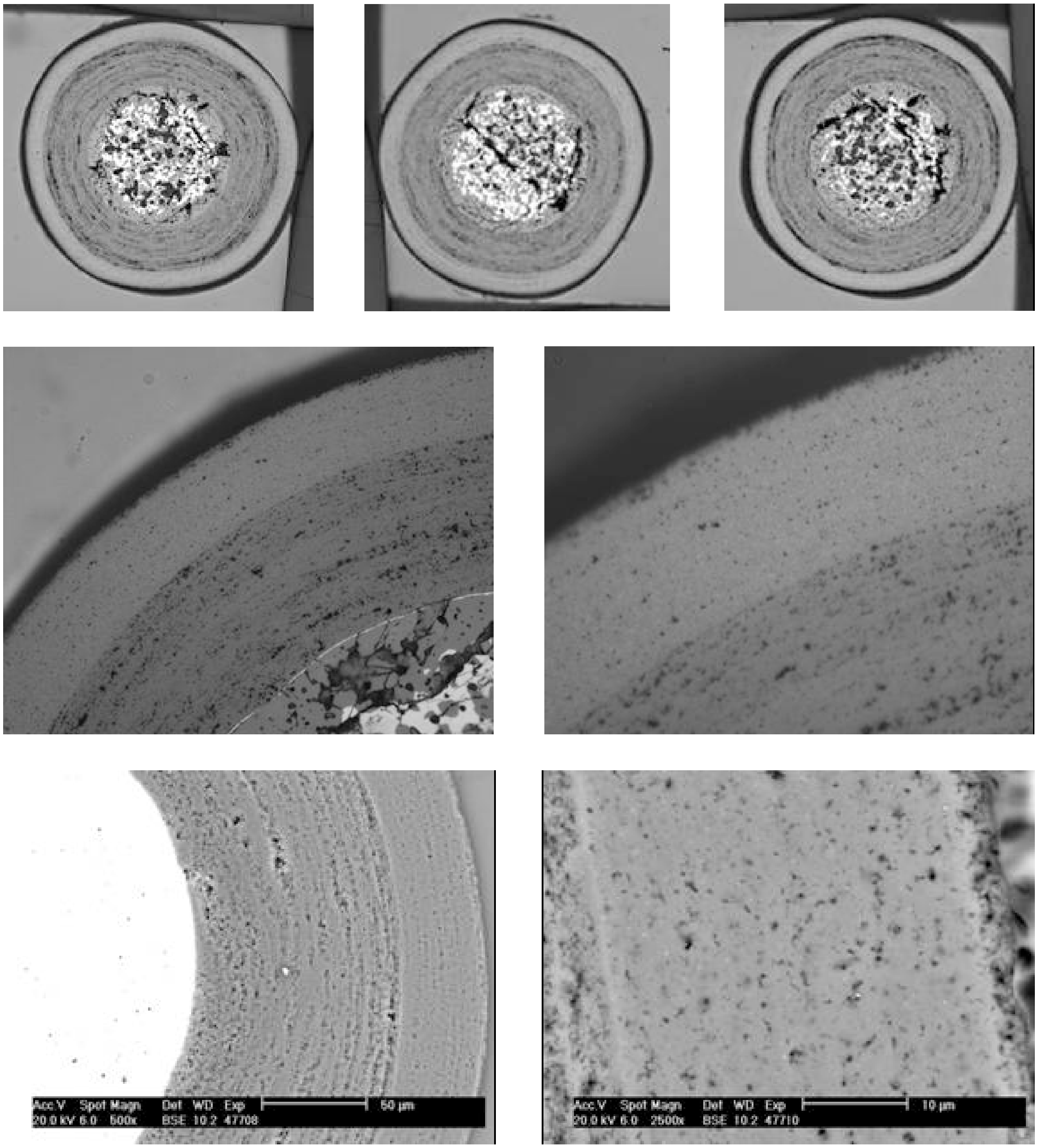

Figure 8. IPyC-7 deposited at 1275°C and CGF = 0.45.

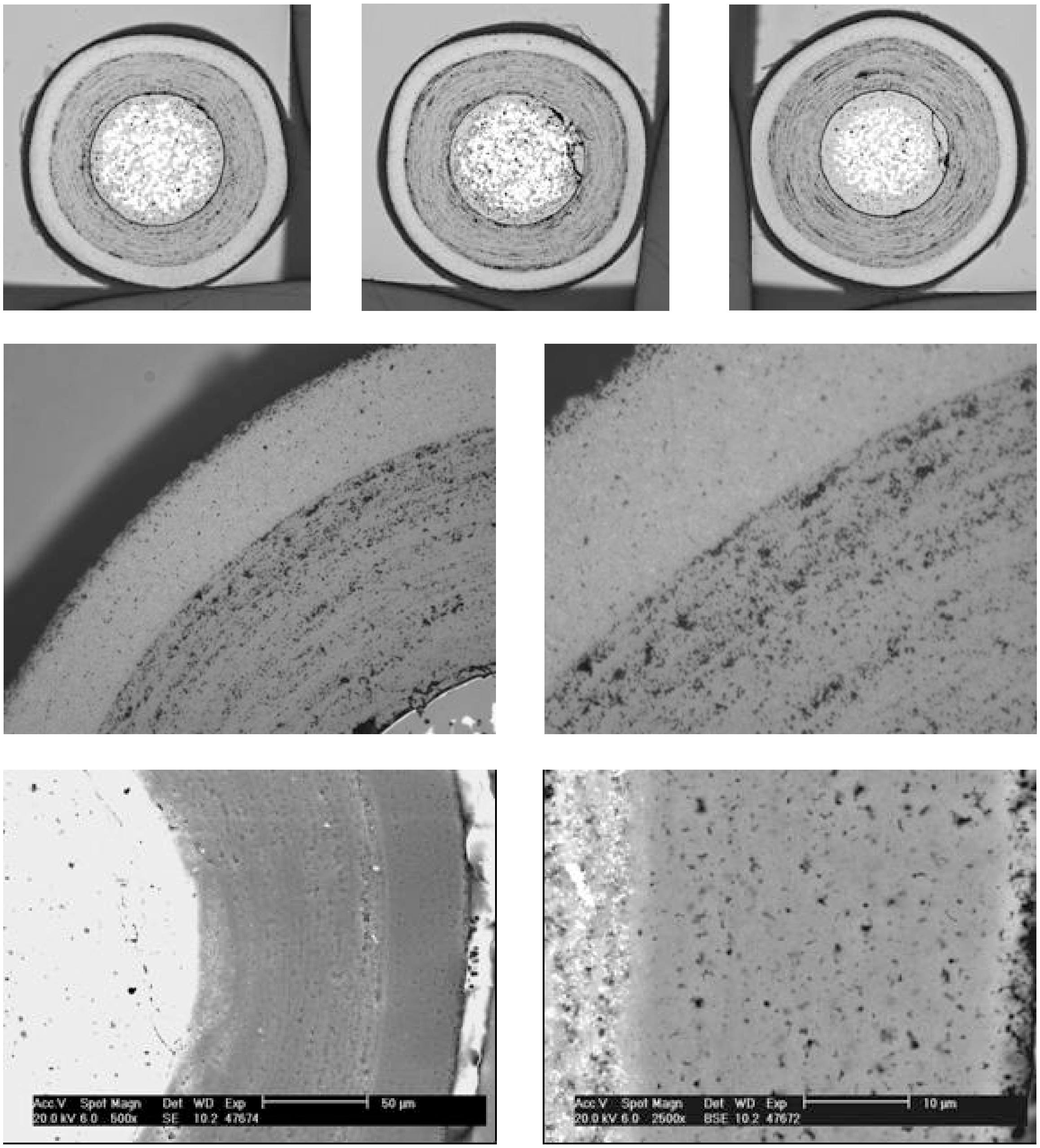

Figure 9. IPyC-8 deposited at 1225°C and CGF = 0.45.

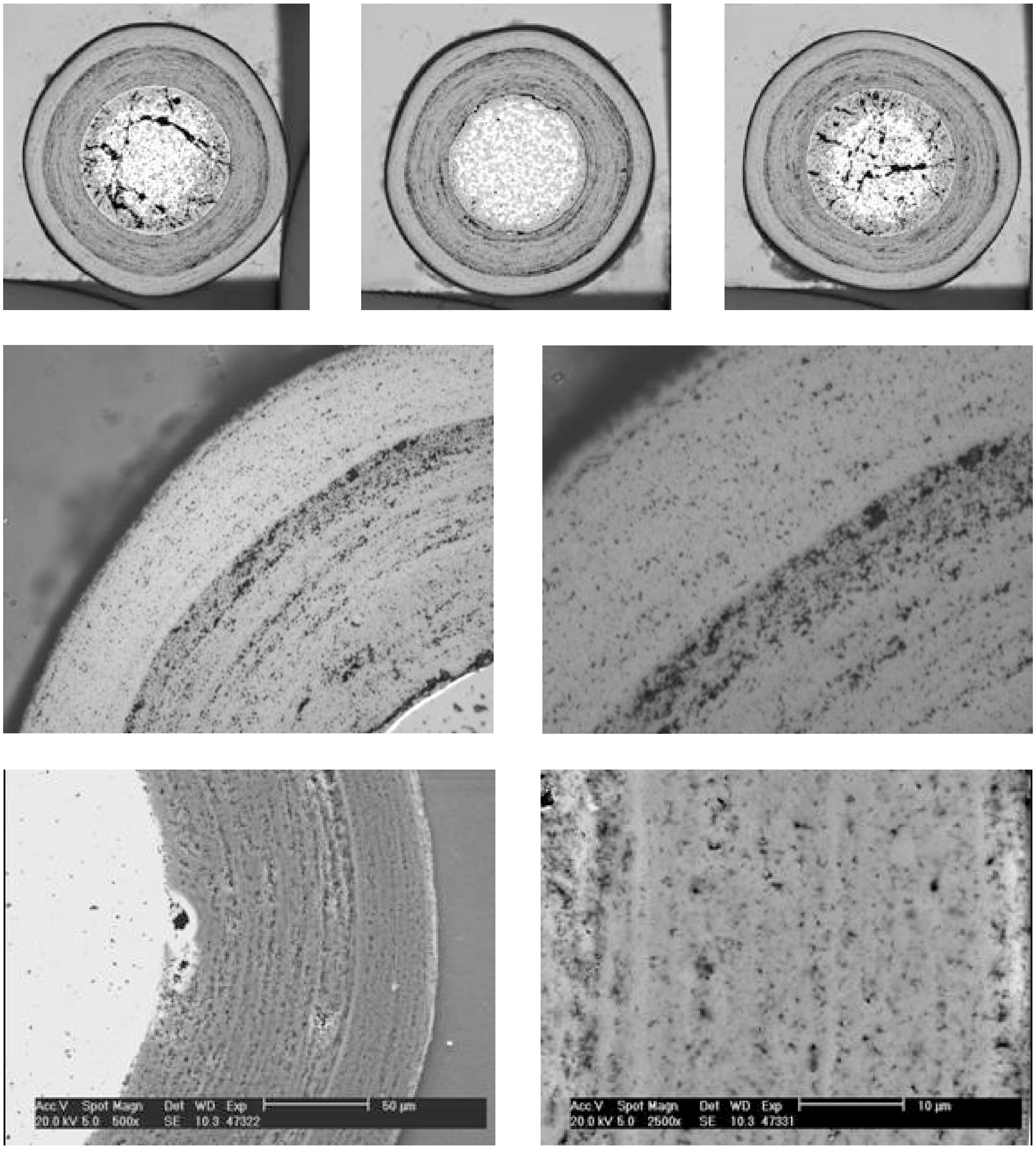

Figure 10. IPyC-9 deposited at 1325°C and CGF = 0.45.

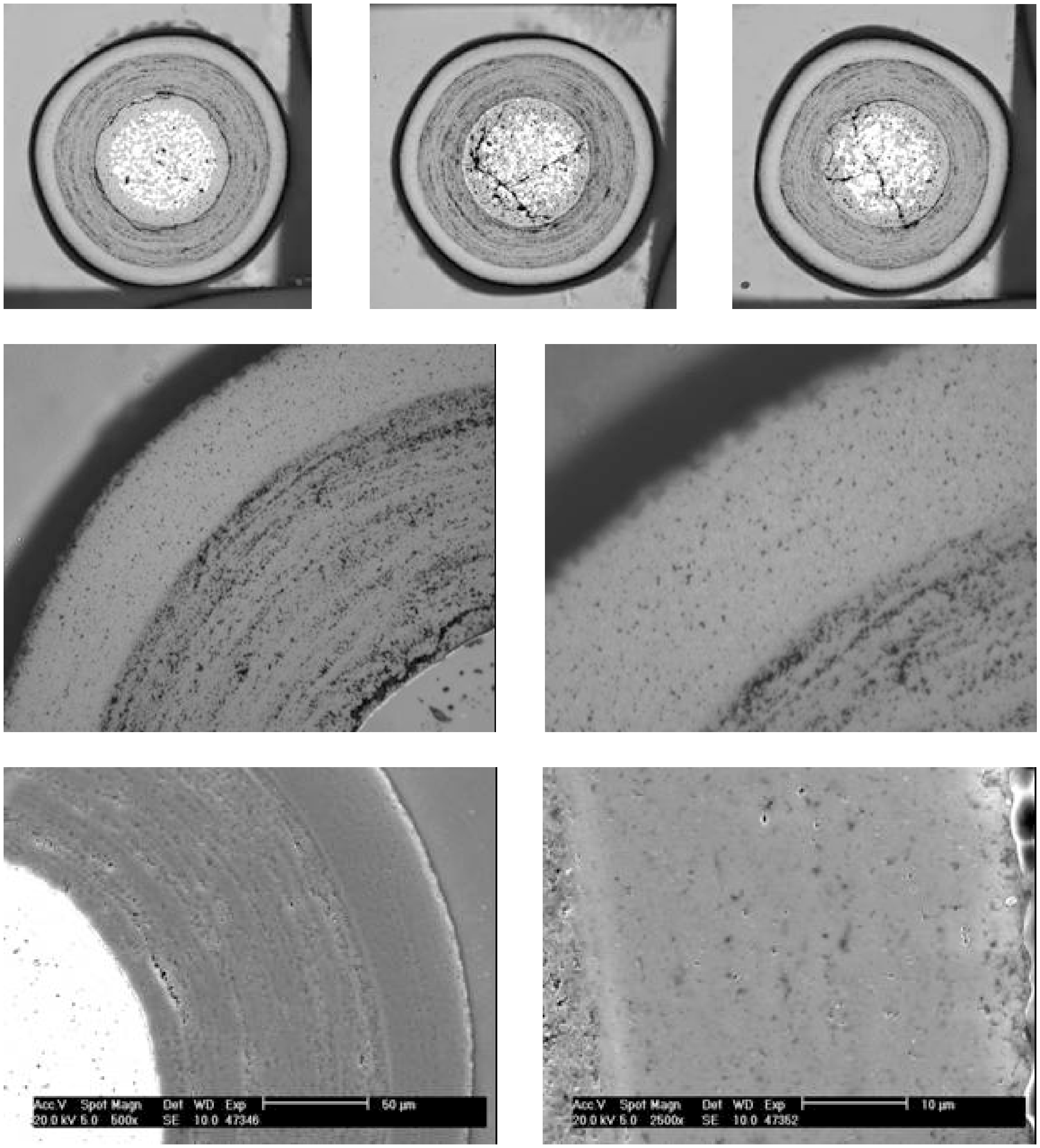

Figure 11. IPyC-10 deposited at 1275°C and CGF = 0.30.

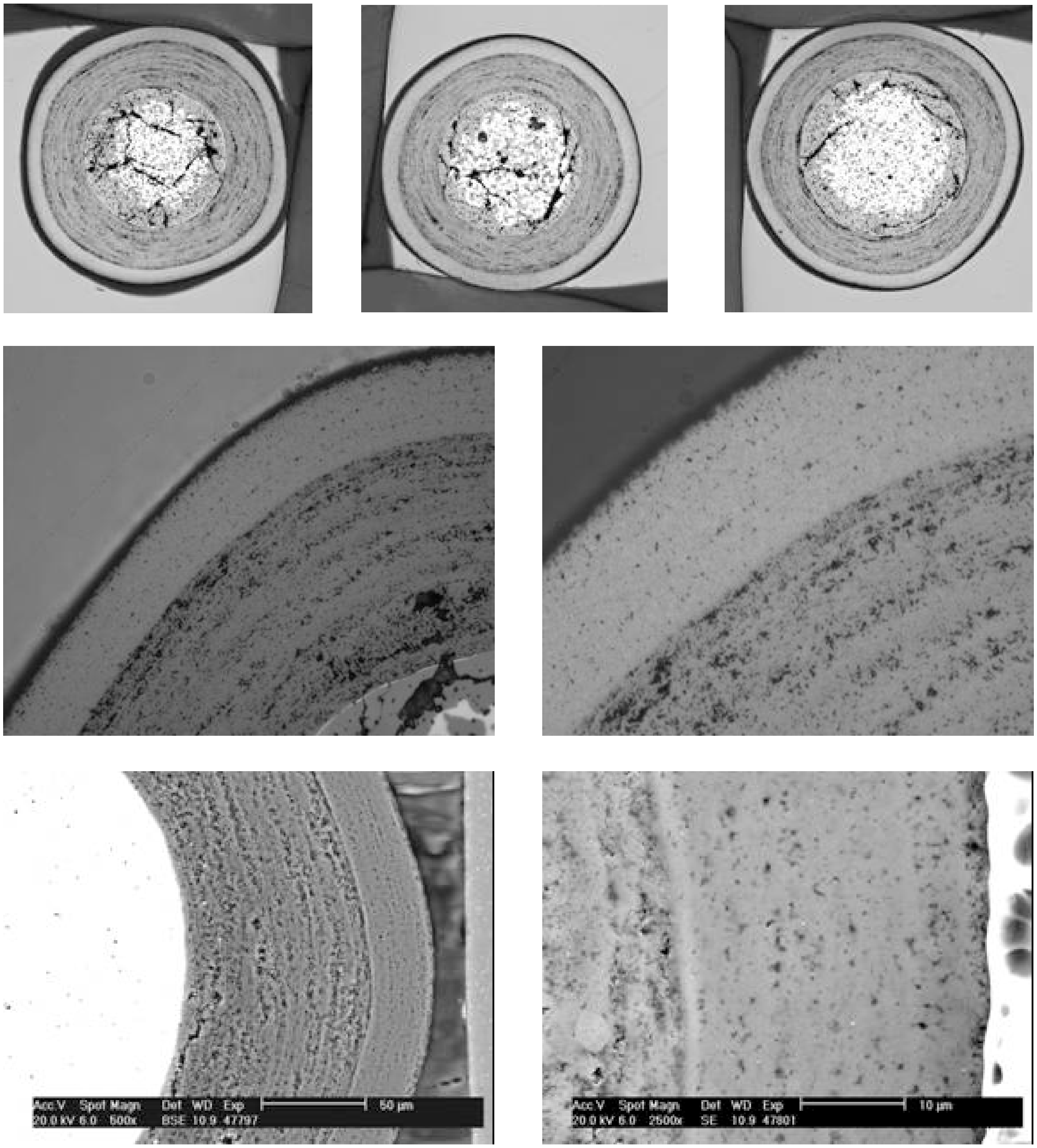

Figure 12. IPyC-11 deposited at 1300°C and CGF = 0.30.

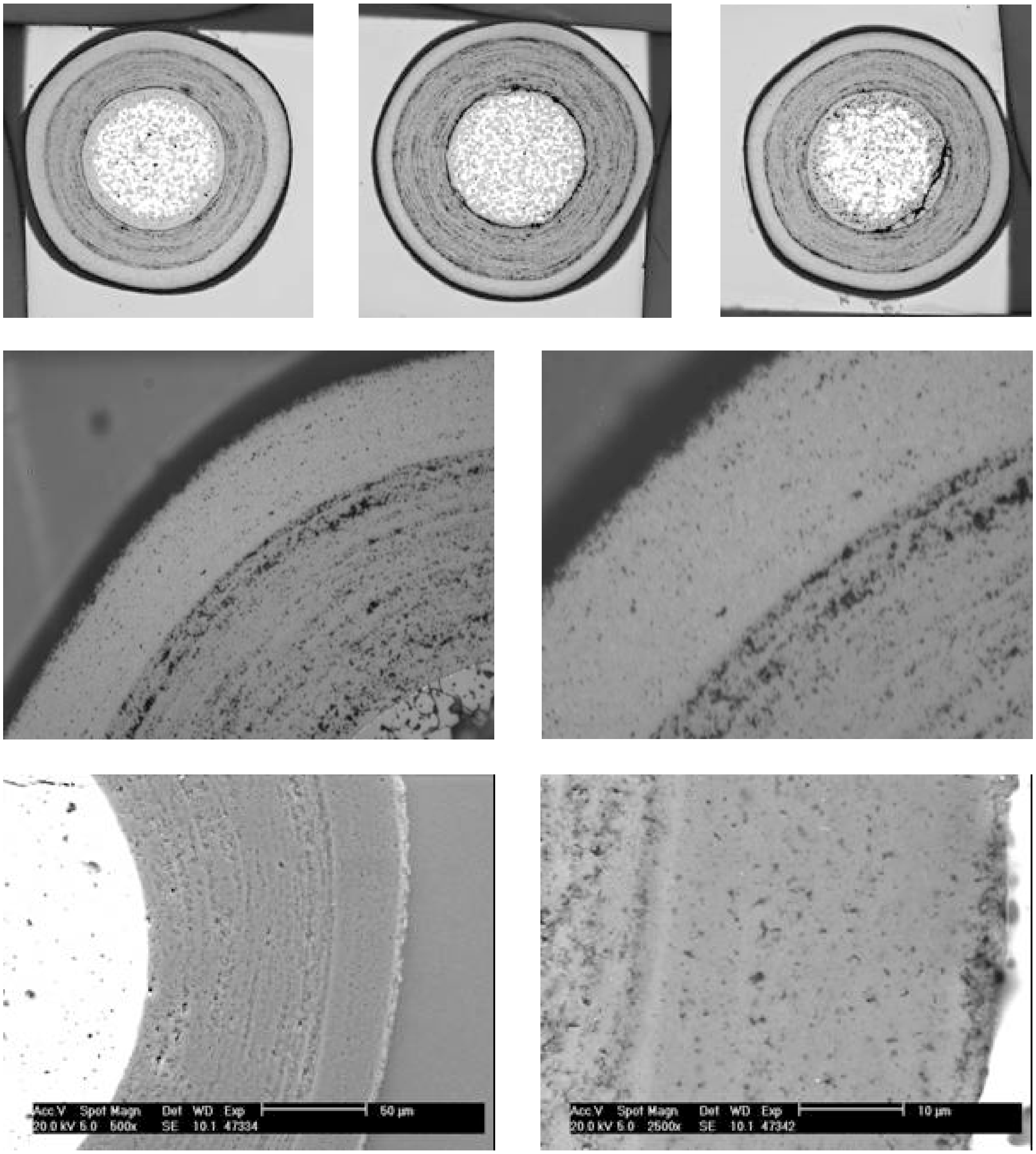

Figure 13. IPyC-12 deposited at 1275°C and CGF = 0.30.

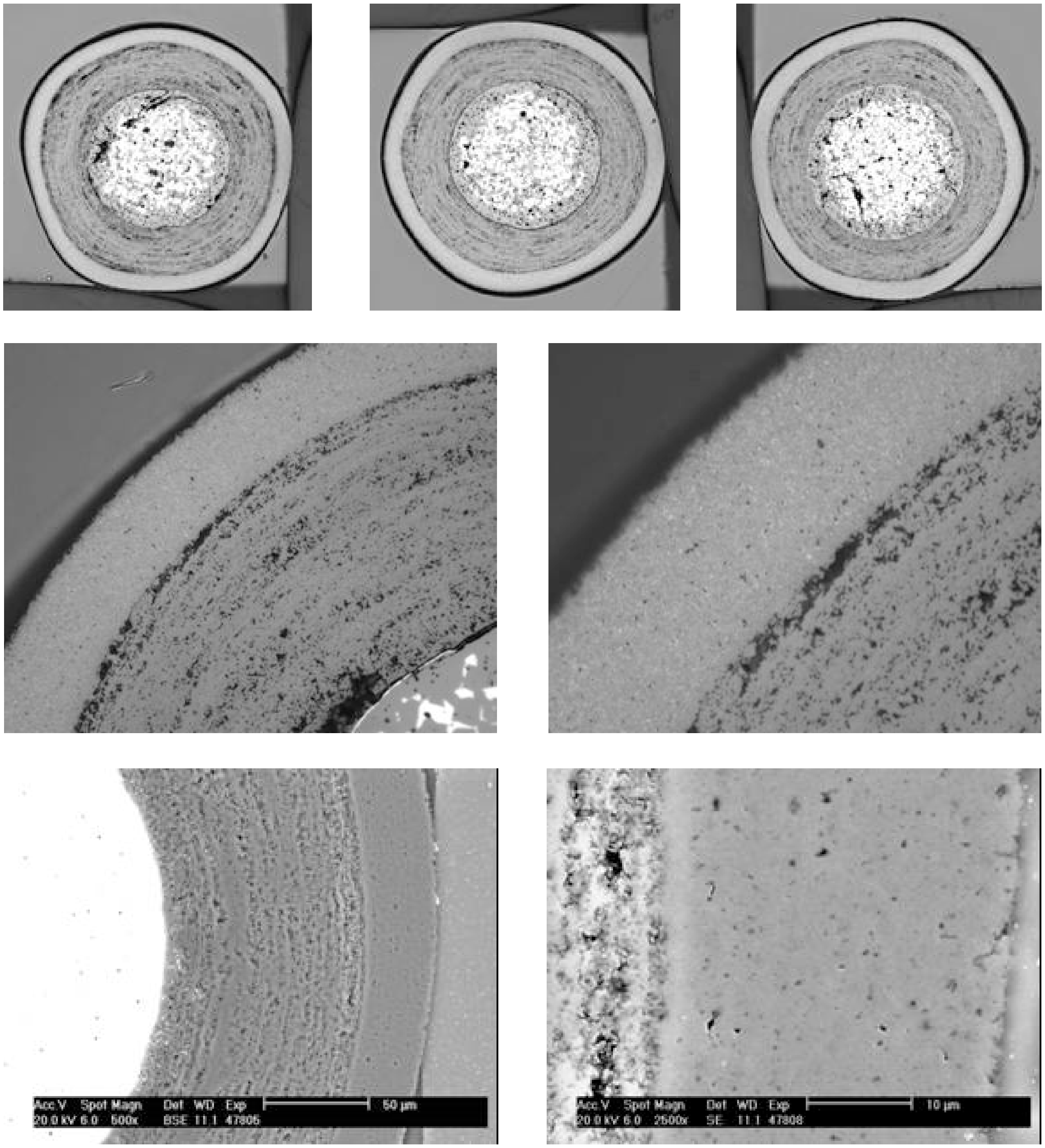

Figure 14. IPyC-13 deposited at 1170°C and CGF = 0.30.

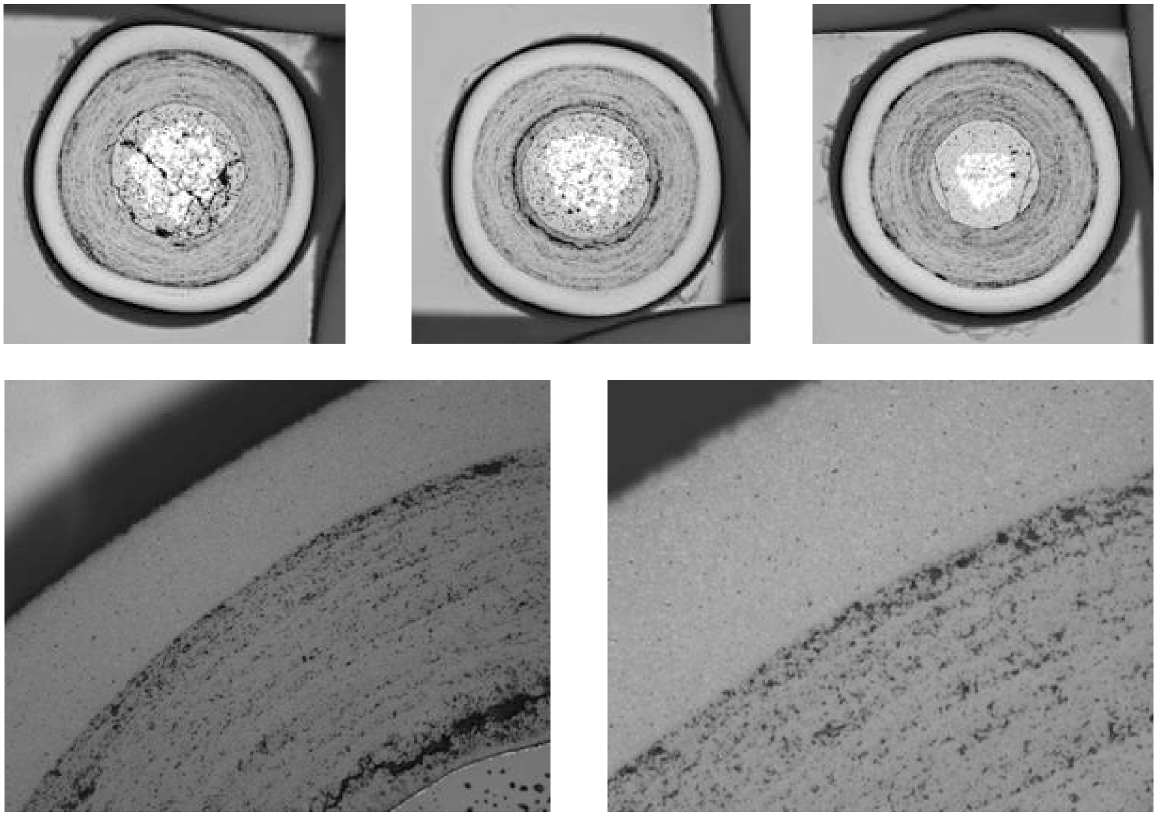

Figure 15. IPyC-17 deposited at 1250°C and CGF = 0.15.

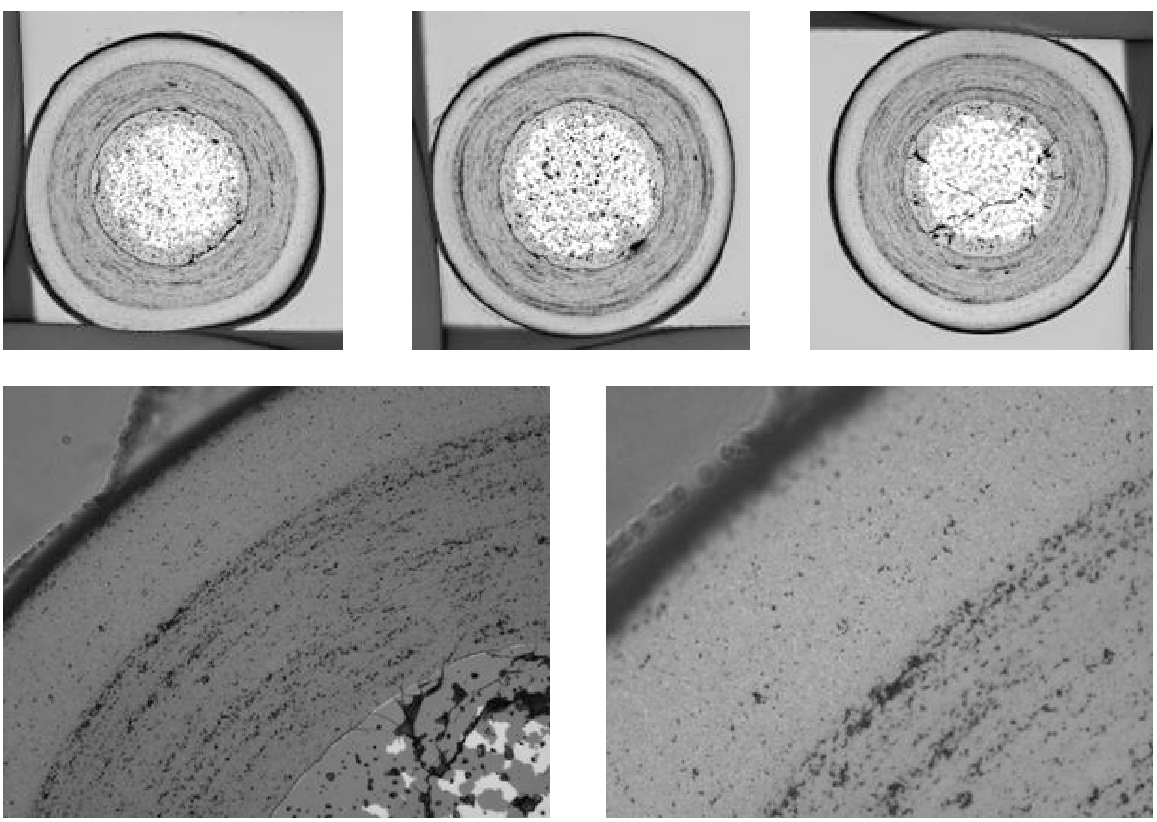

Figure 16. IPyC-18 deposited at 1250°C and CGF = 0.45.

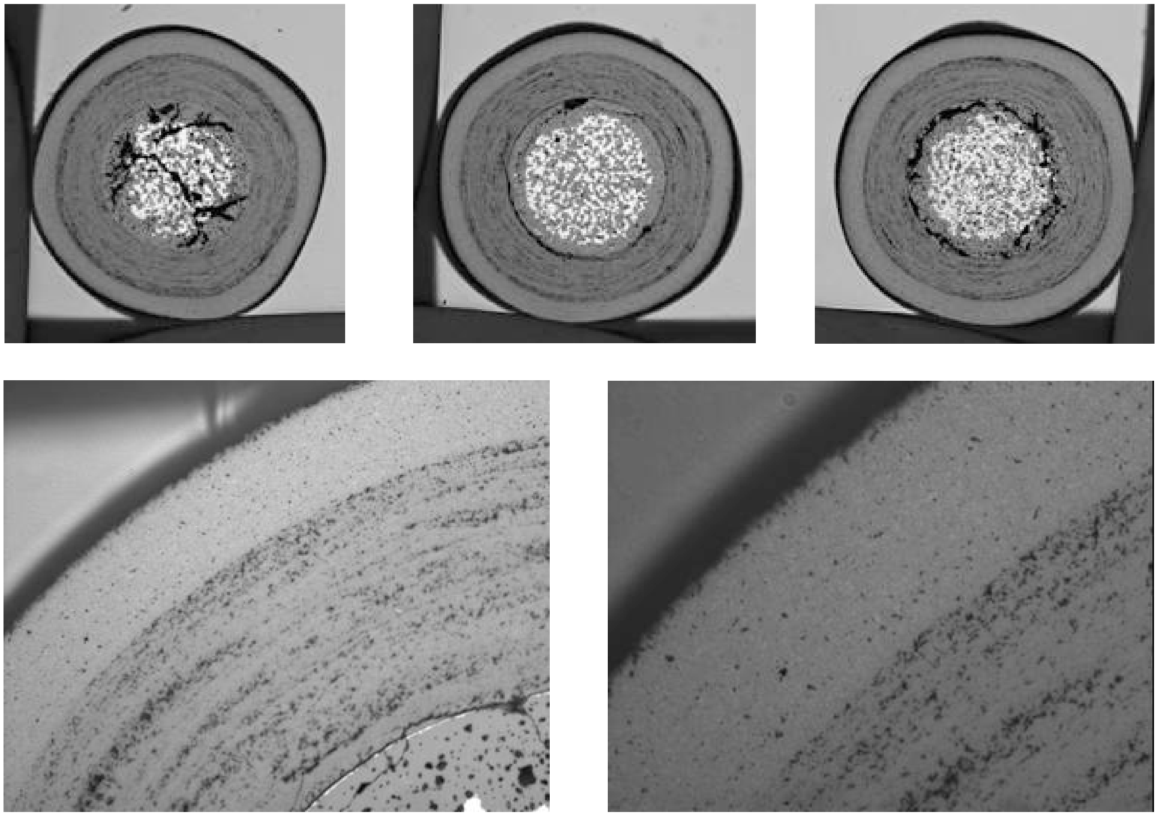

Figure 17. IPyC-20 deposited at 1250°C and CGF = 0.30.

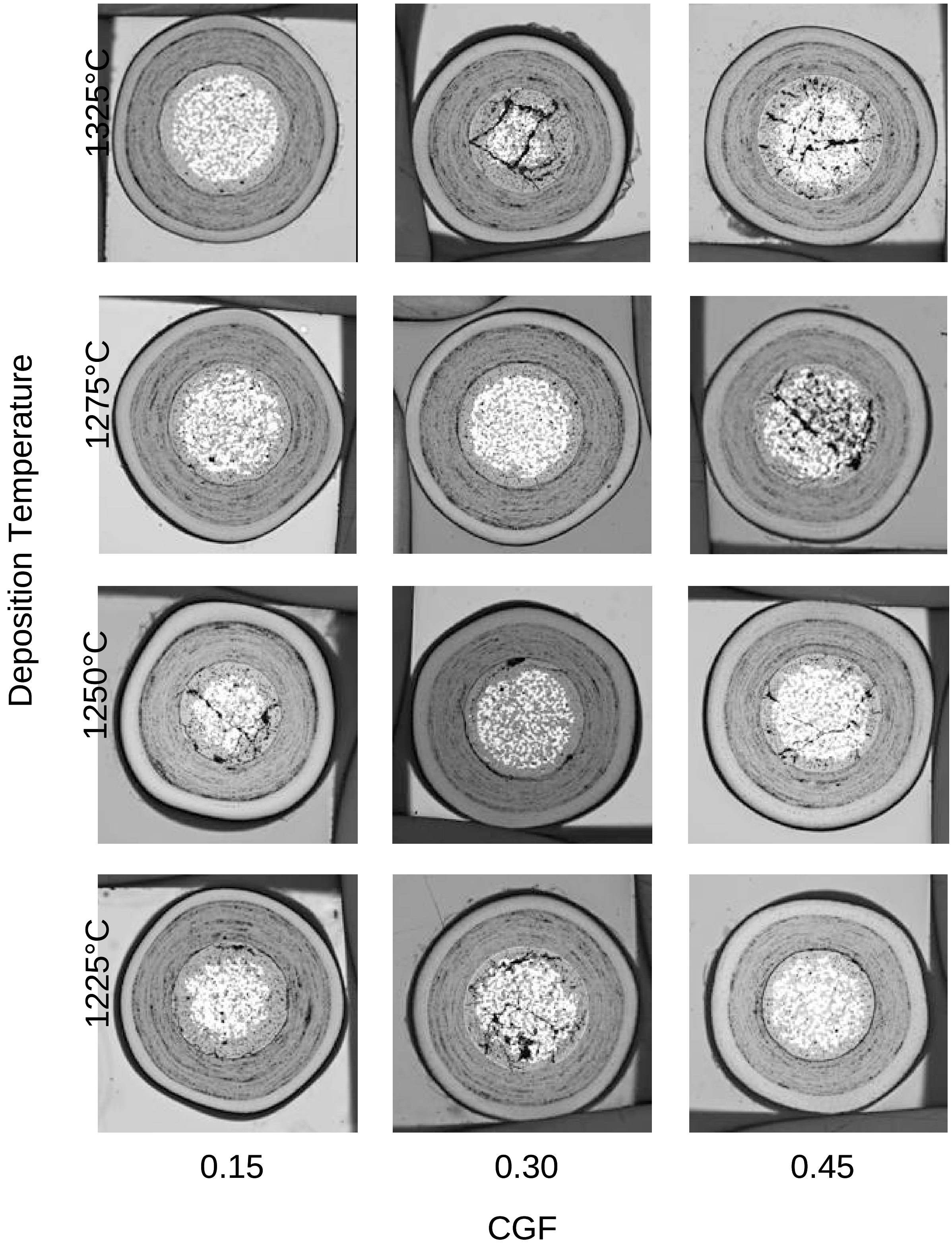

Figure 18. Images of particles from IPyC study coated using the various conditions.

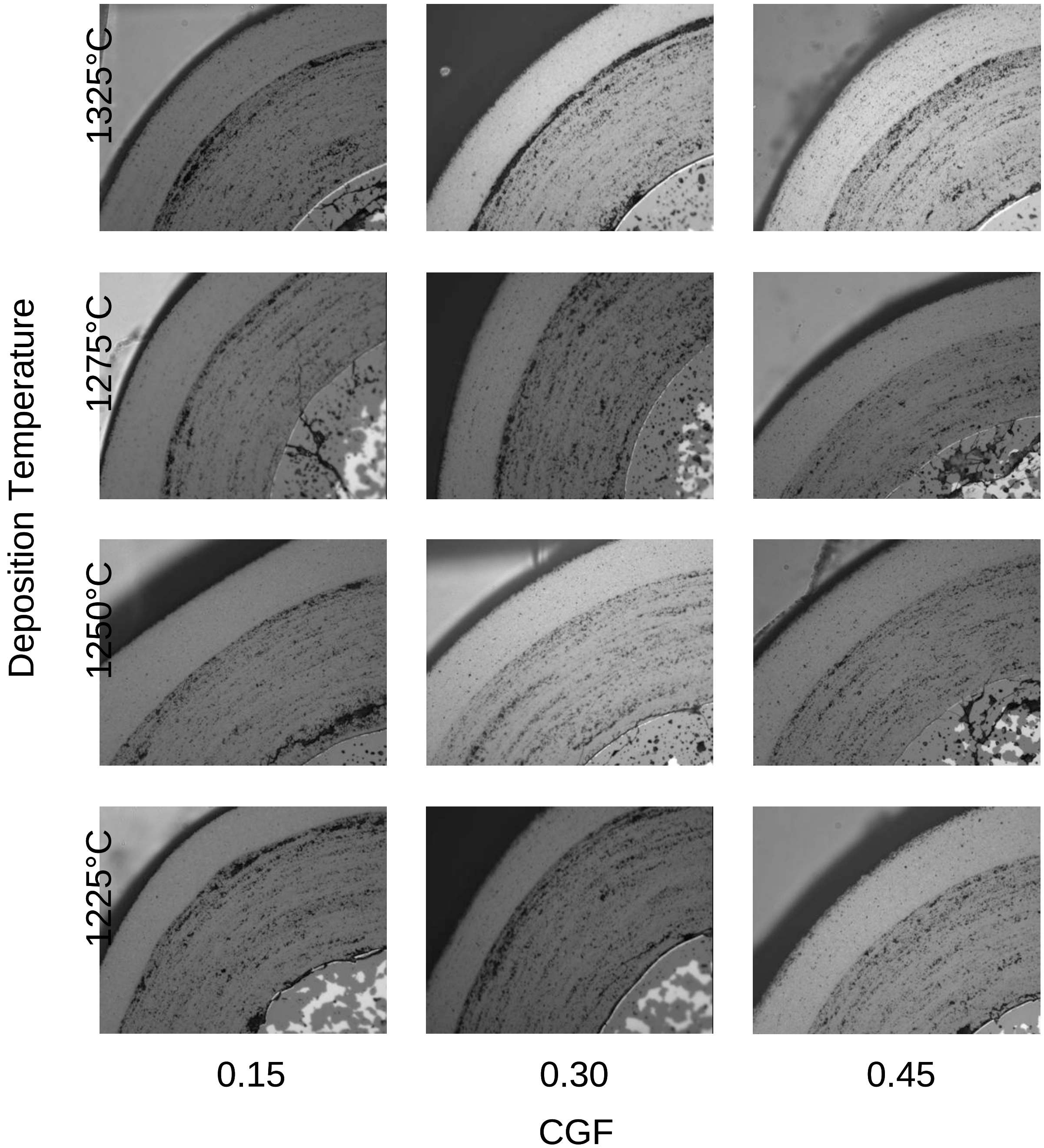

Figure 19. Low magnification images of buffer and IPyC layers on 350 μm NUCO kernels.

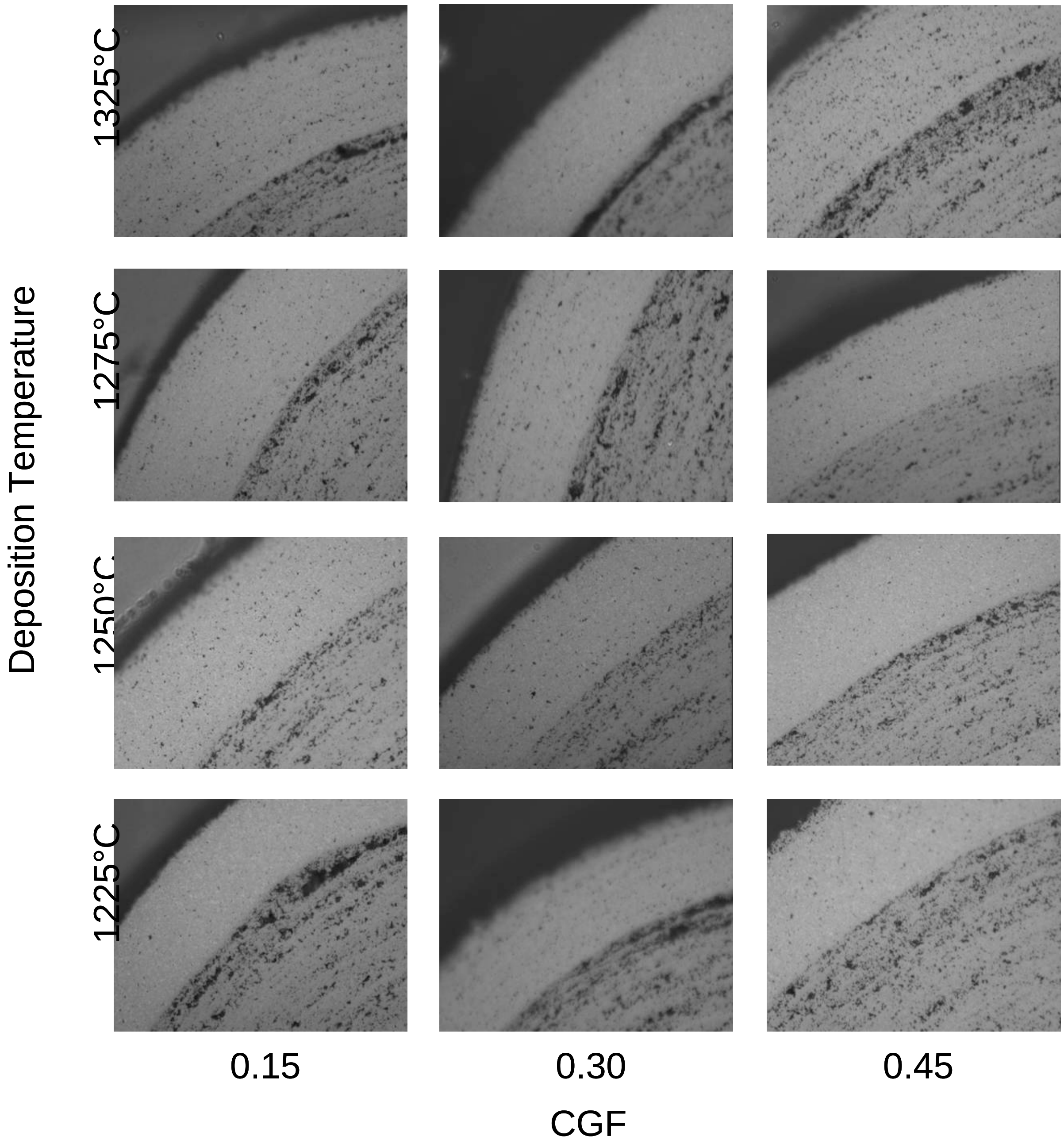

Figure 20. High magnification images of buffer and IPyC layers on 350 μm NUCO kernels.

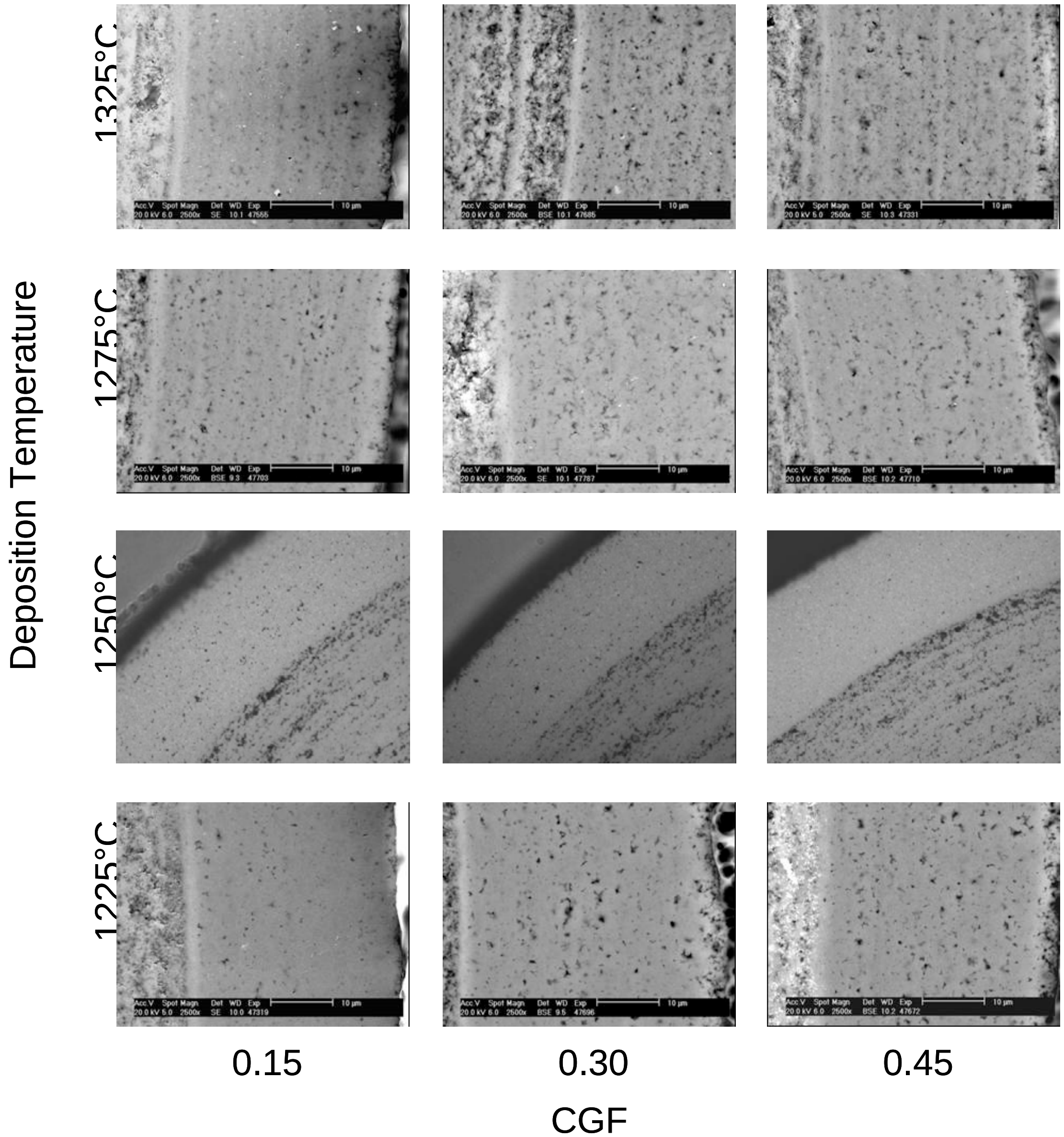

Figure 21. SEM images of buffer and IPyC layers on 350 μm NUCO kernels.

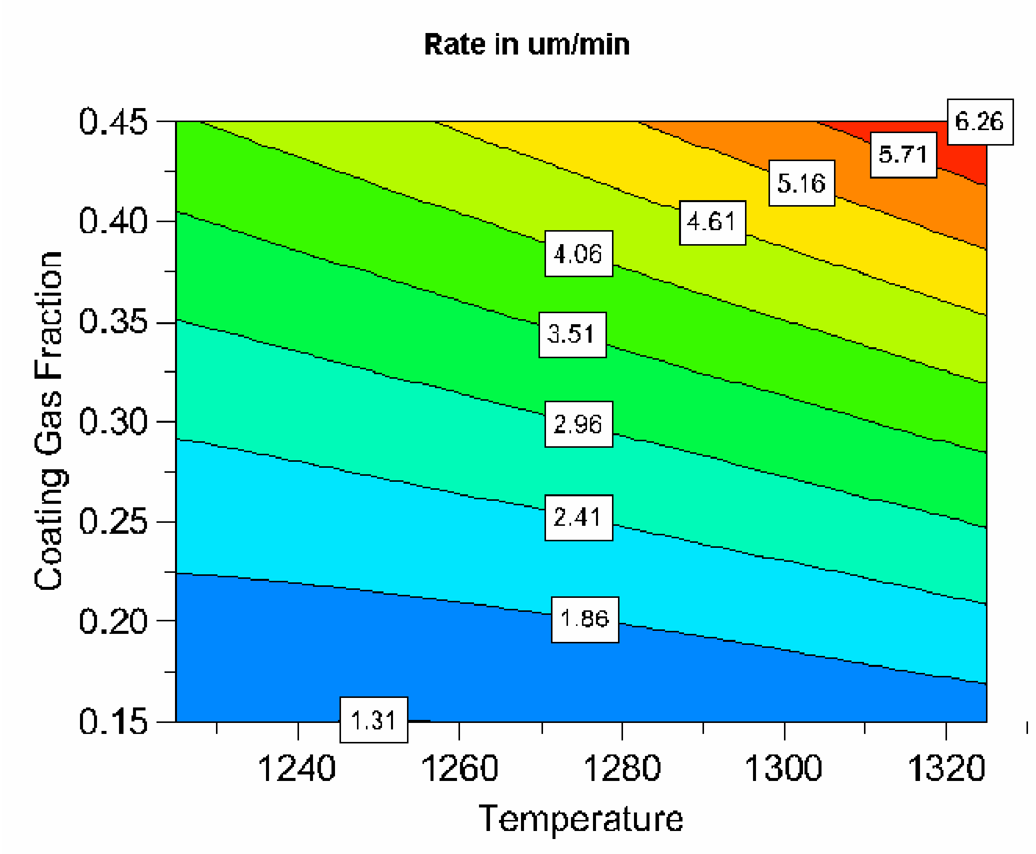

Figure 22. Response plot for deposition rate (rate in μm/min).

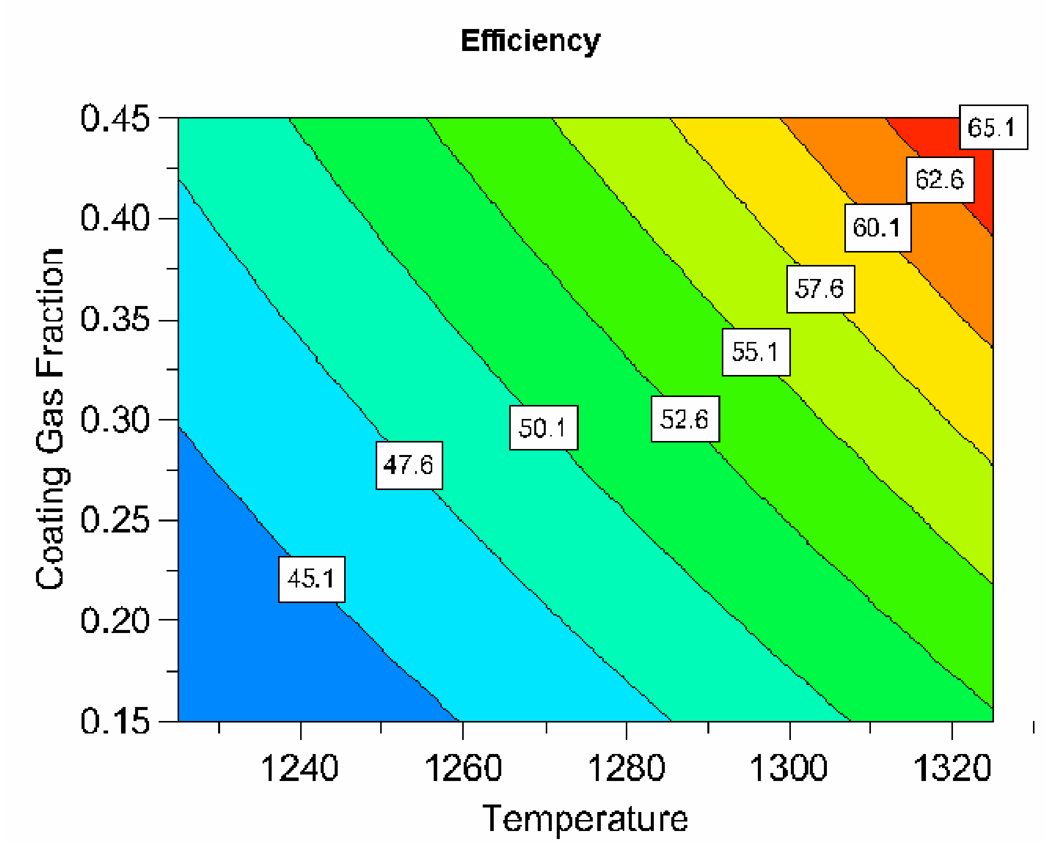

Figure 23. Response plot for deposition efficiency (efficiency in %).

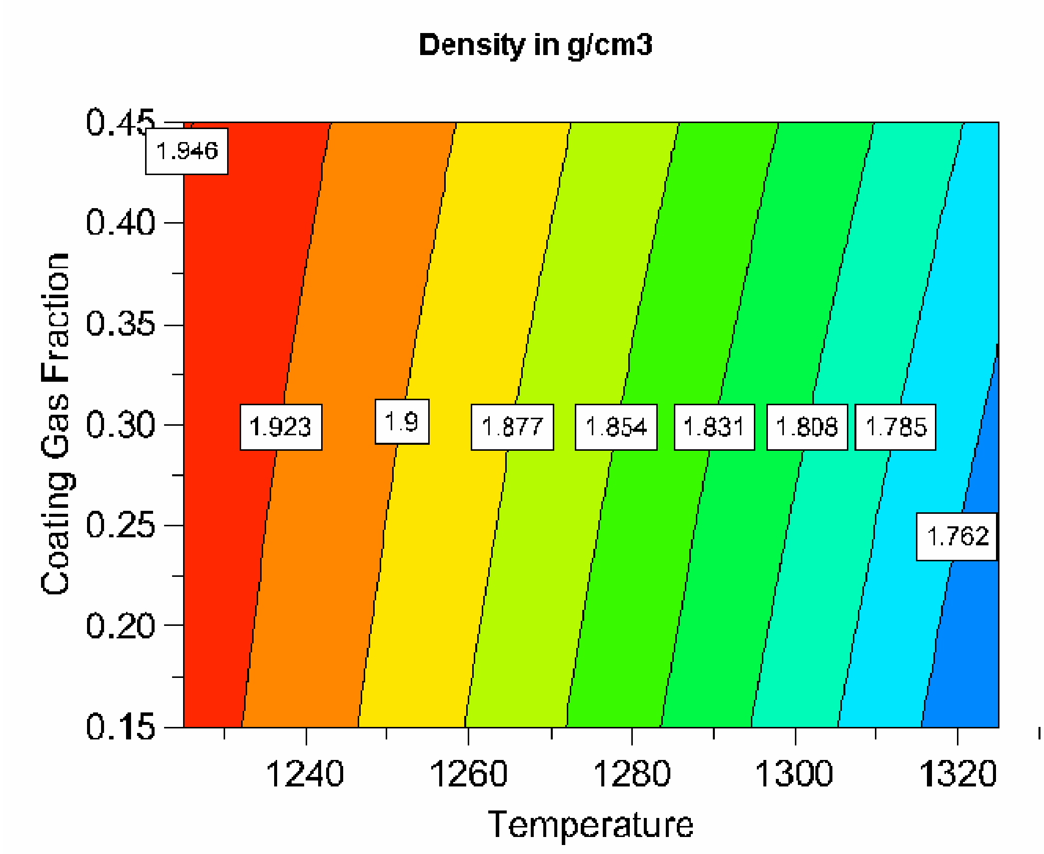

Figure 24. Response plot for coating density (density in g/cm^3).

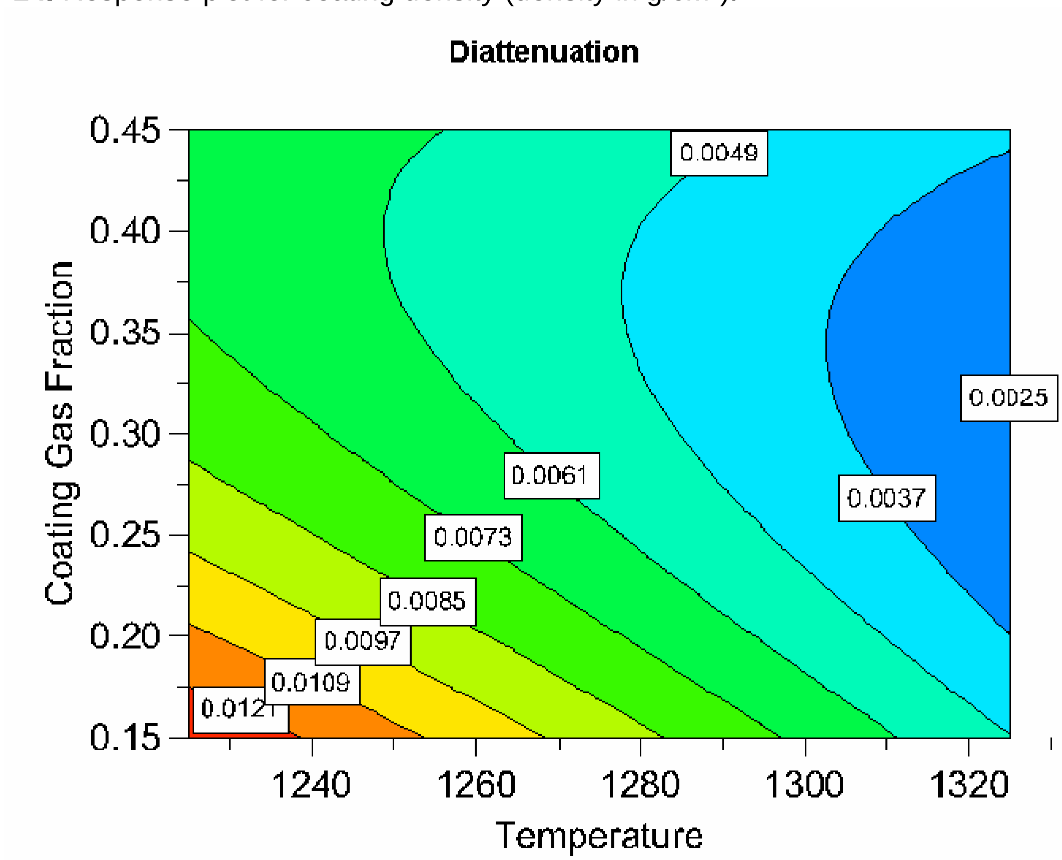

Figure 25. Response plot for diattenuation, N.

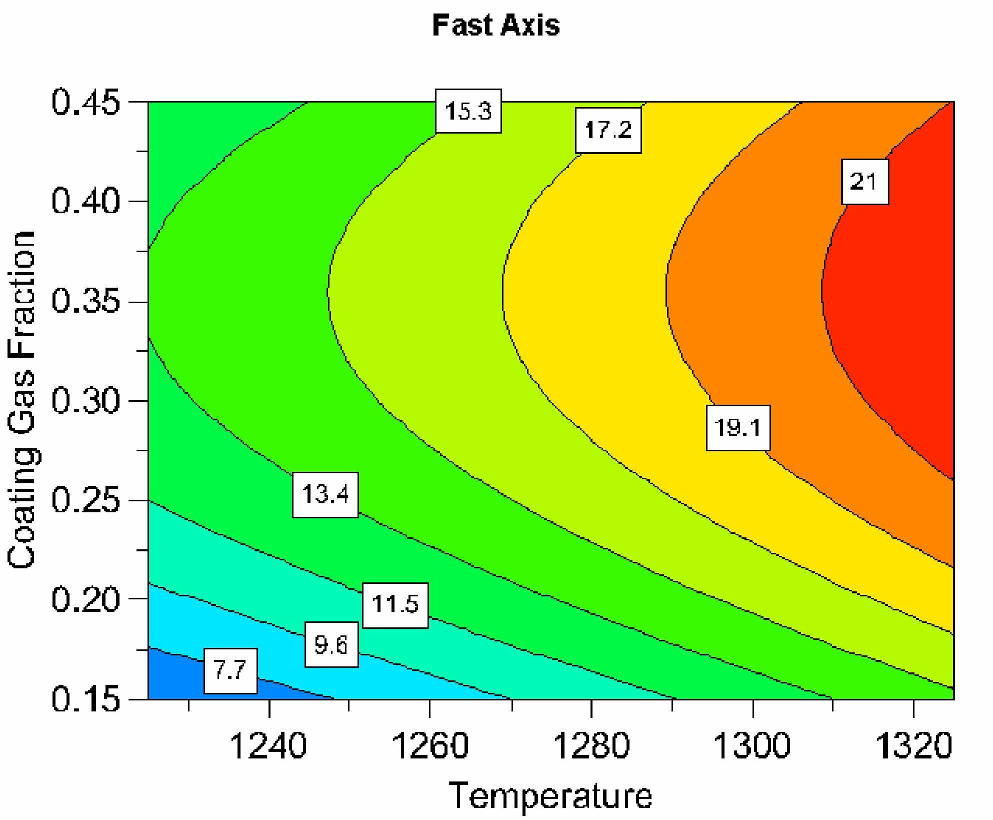

Figure 26. Response plot for preferred fast axis standard deviation in degrees.

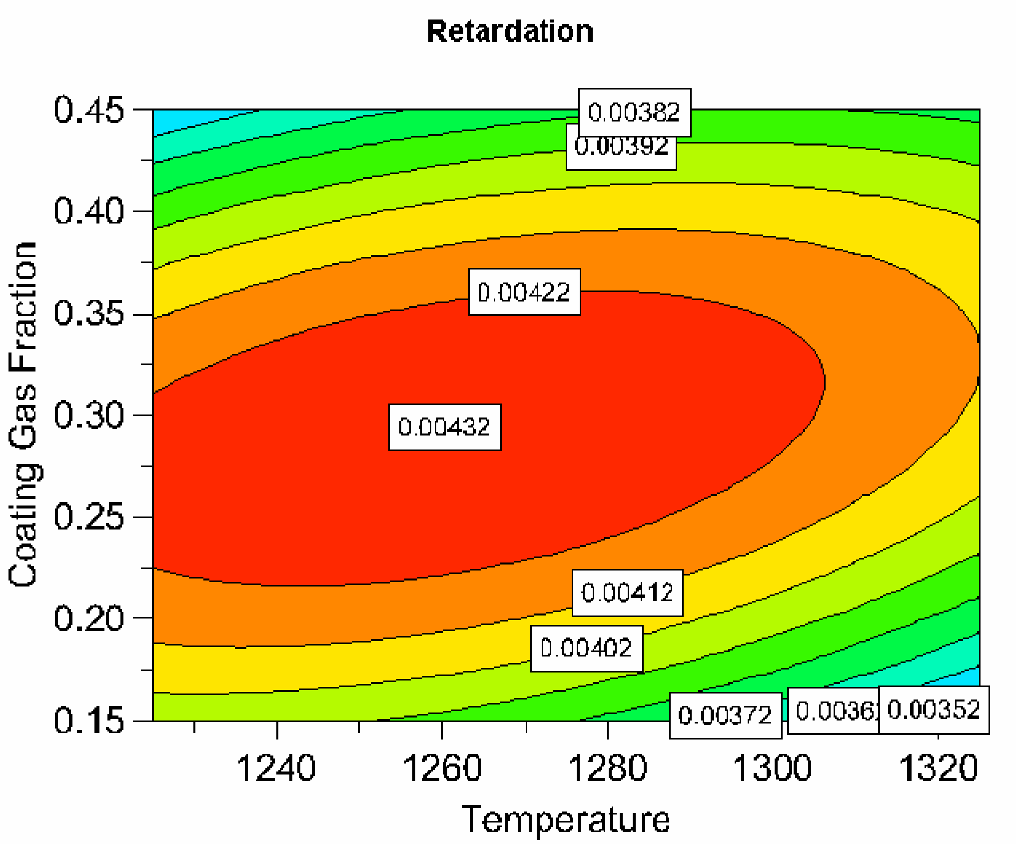

Figure 27. Response plot for retardation.

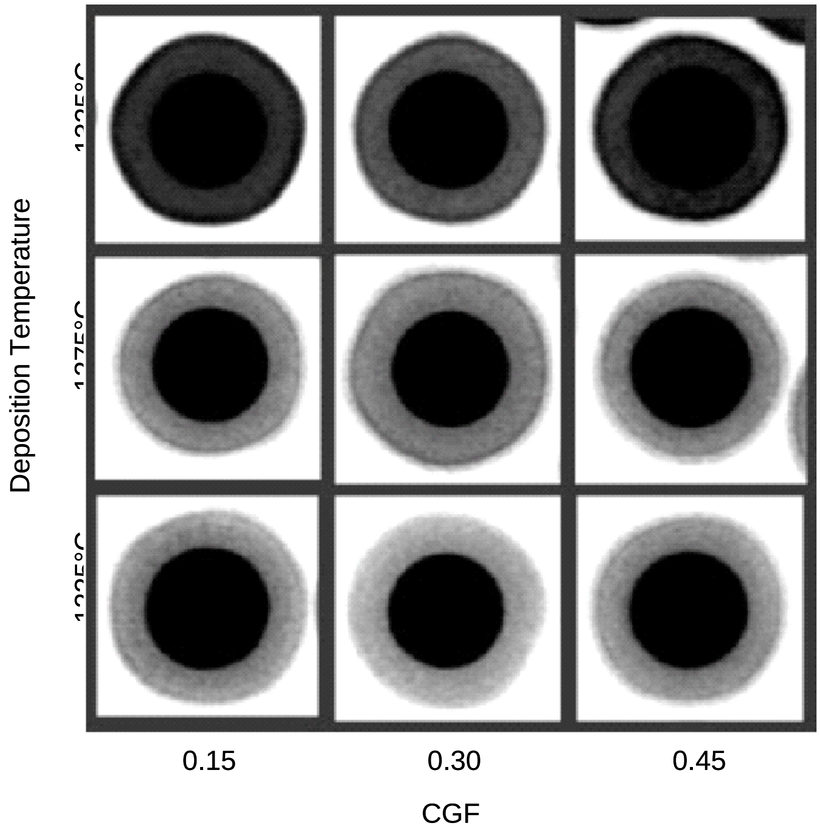

Figure 28. Normalized images of uranium dispersion after 18 hour chlorination at 1500°C for IPyC coatings deposited using various coating gas fractions and temperatures.

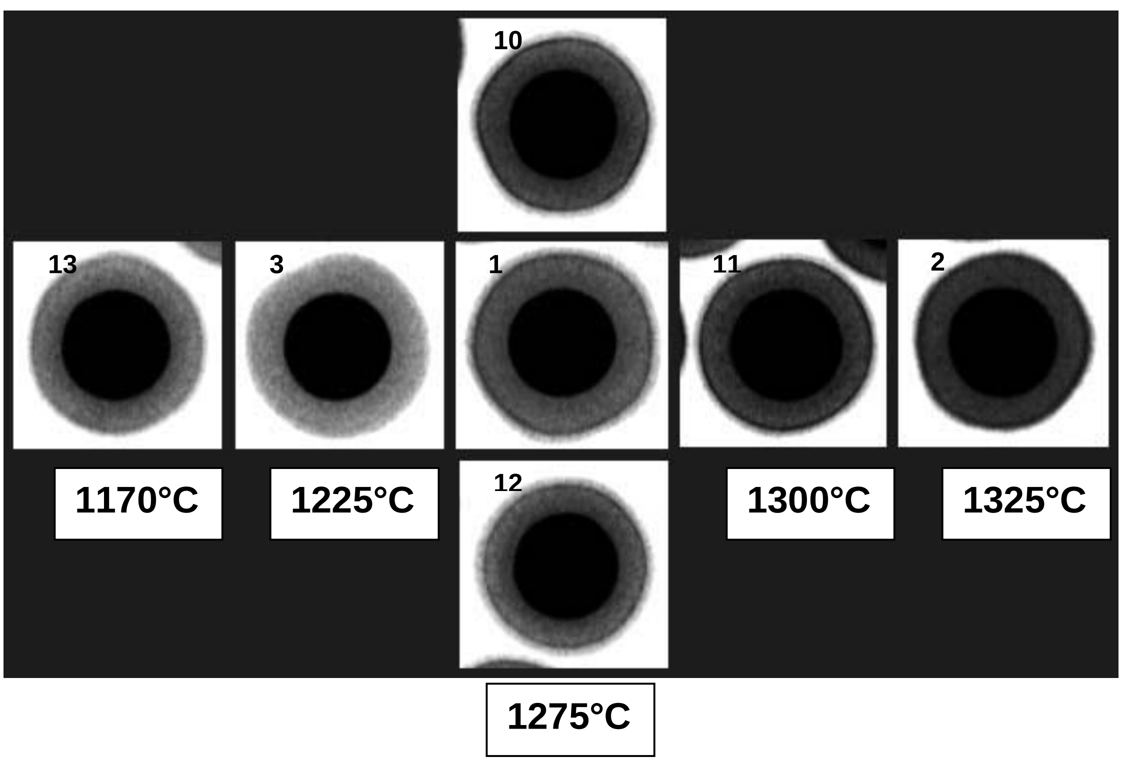

Figure 29. Normalized images of uranium dispersion after 18 hour chlorination at 1500°C for IPyC layers deposited at different temperatures and a coating gas fraction of 0.30 (IPyC coating run number included for each image).

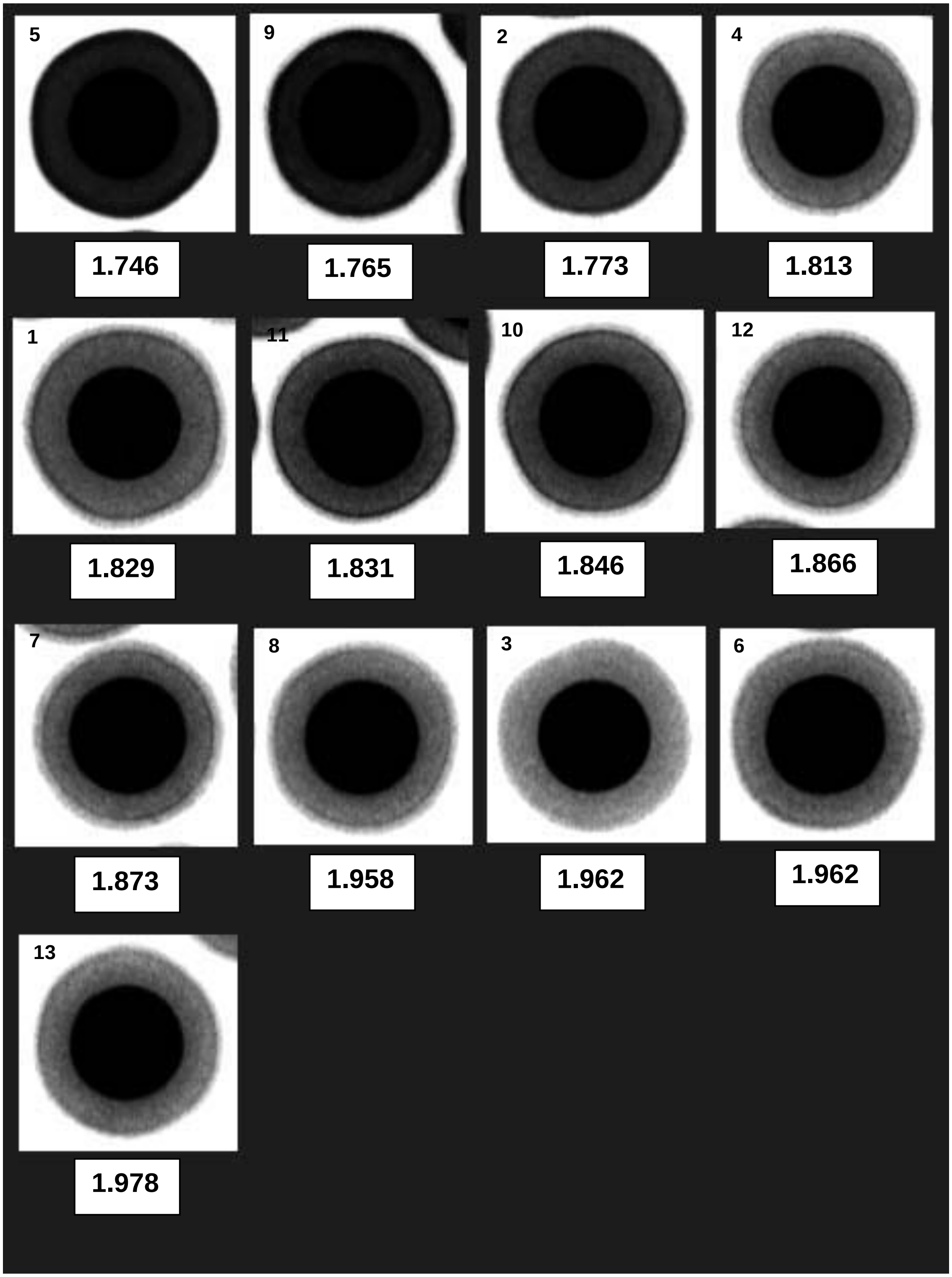

Figure 30. Normalized images of uranium dispersion after 18 hour chlorination at 1500°C organized with respect to IPyC density (IPyC coating run number included for each image).

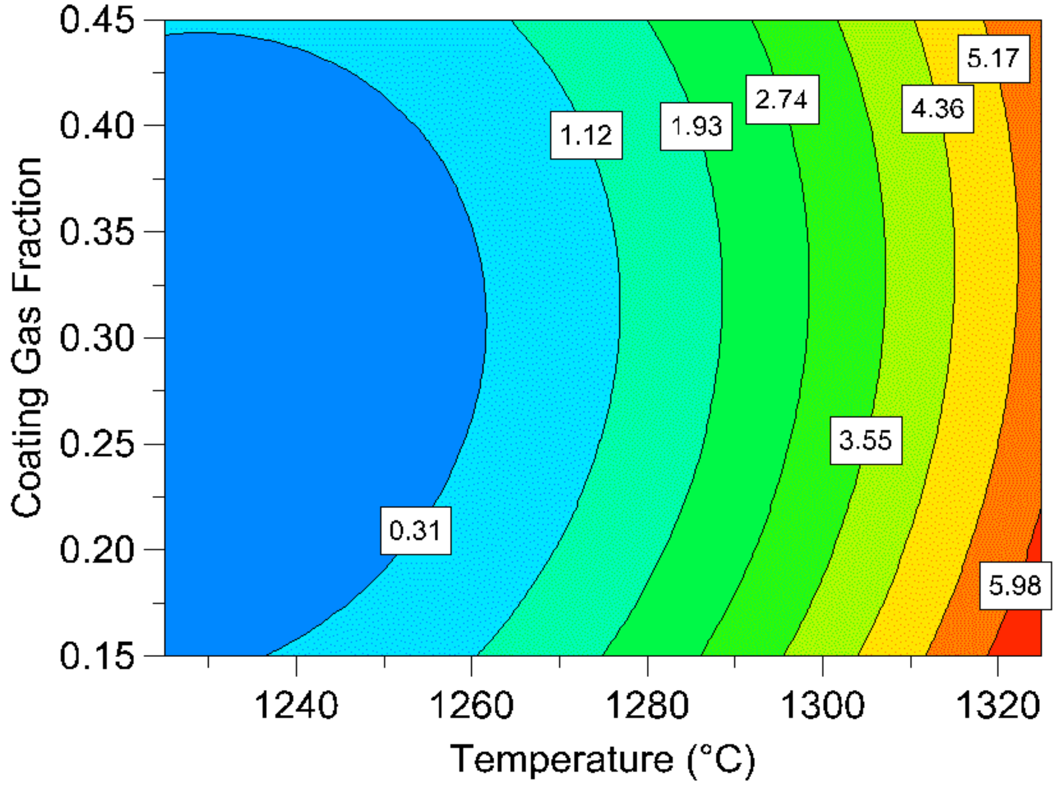

Figure 31. Response plot for permeability (in arbitrary units proportional to U dispersion).

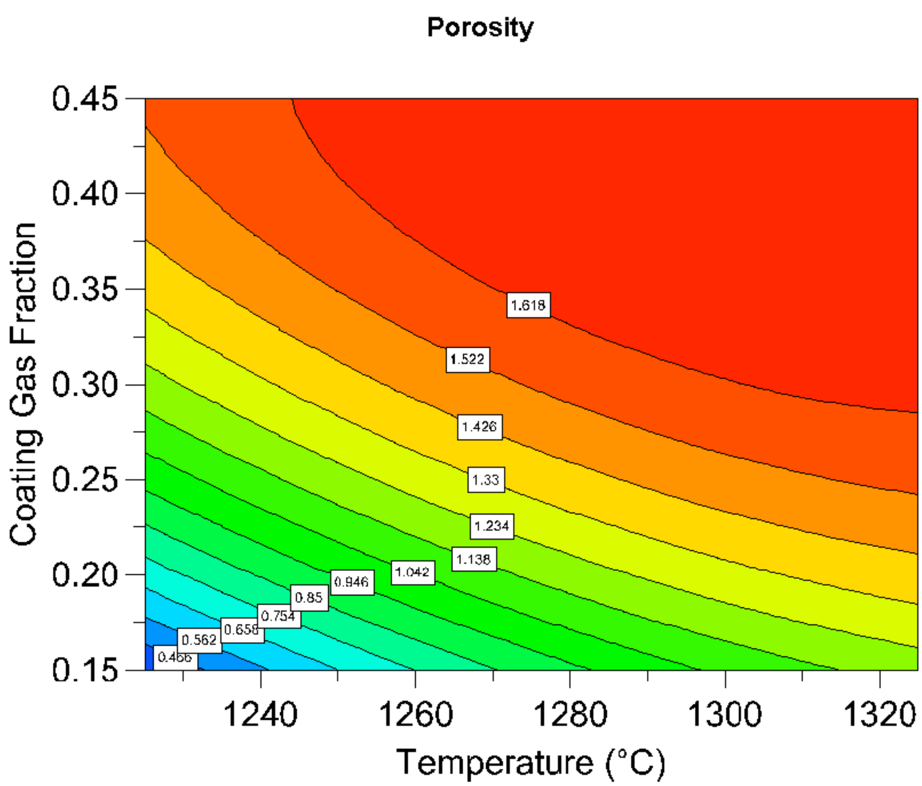

Figure 32. Response plot for open porosity (in mL/m^2).

Table 2. Measurements for Particles from the IPyC Study

Run No. NUCO350-IPYC-	Dep. Temp. (°C)	CGF	Deposition Time (min)	Buffer Thickness (μm)	IPyC Thickness (μm)	Dep. Rate (μm/min)	Density (g/cm^3)	Diattenuation N	Fast Axis SD	Perm. X 10^{-2}	Porosity[a] (ml/m^2)
1	1275	0.30	11.1	102 ± 7	36 ± 2	3.2	1.829 ± 0.011	0.0038 ± 0.0005	25.2	0.932 ± 0.190	NM
2	1325	0.30	8.9	85 ± 7	31 ± 2	3.5	1.773 ± 0.006	0.0040 ± 0.0005	17.8	4.48 ± 2.72	NM
3	1225	0.30	13.3	89 ± 8	35 ± 2	2.6	1.962 ± 0.005	0.0078 ± 0.0012	11.8	0.342 ± 0.175	1.10 (1.05)
4	1275	0.15	22.2	85 ± 6	34 ± 2	1.5	1.813 ± 0.010	0.0075 ± 0.0005	8.2	0.760 ± 0.244	0.83 (0.70)
5	1325	0.15	17.8	90 ± 6	31 ± 2	1.7	1.746 ± 0.015	0.0047 ± 0.0006	16.7	7.52 ± 2.70	1.28 (0.97)
6	1225	0.15	26.7	93 ± 4	29 ± 2	1.1	1.962 ± 0.008	0.0151 ± 0.0017	5.9	0.588 ± 0.151	NM
7	1275	0.45	7.4	84 ± 6	35 ± 2	4.7	1.873 ± 0.010	0.0050 ± 0.0004	13.9	0.727 ± 0.289	1.85 (1.75)
8	1225	0.45	8.9	88 ± 5	36 ± 2	4.0	1.958 ± 0.011	0.0083 ± 0.0011	12.0	0.661 ± 0.308	1.45 (1.50)
9	1325	0.45	5.9	88 ± 6	39 ± 3	6.6	1.765 ± 0.010	0.0031 ± 0.0002	23.0	6.56 ± 2.11	NM
10	1275	0.30	11.1	89 ± 9	36 ± 3	3.2	1.846 ± 0.010	0.0051 ± 0.0004	20.2	1.46 ± 0.876	NM
11	1300	0.30	9.9	85 ± 5	29 ± 2	2.9	1.831 ± 0.014	0.0052 ± 0.0006	20.4	3.32 ± 2.77	NM
12	1275	0.30	11.1	89 ± 8	34 ± 3	3.1	1.866 ± 0.006	0.0061 ± 0.0005	10.6	0.960 ± 0.307	1.55 (1.43)
13	1170	0.30	15.5	95 ± 7	35 ± 2	2.3	1.978 ± 0.007	0.0099 ± 0.0035	9.7	0.540 ± 0.122	0.71 (0.69)
16	1250	0.30	16.0	89 ± 6	48 ± 2	3.0	1.914 ± 0.006	NM	NM	NM	NM
17	1250	0.15	30.0	87 ± 8	43 ± 3	1.4	1.902 ± 0.007	0.0103 ± 0.0029	NM	0.453 ± 0.156	0.61 (0.58)
18	1250	0.45	9.0	84 ± 5	41 ± 4	4.6	1.922 ± 0.006	0.0047 ± 0.0021	13.2	0.689 ± 0.150	1.56 (1.46)
20	1250	0.30	13.0	85 ± 4	38 ± 3	2.9	1.909 ± 0.005	0.0048 ± 0.0022	18.6	0.555 ± 0.124	1.32 (1.19)

CGF = coating gas fraction
SD = standard deviation
NM = not measured

a. 250 – 10,000 psi and (40 – 3,000 psi)

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