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PALLADIUM ON KIESELGUHR (KU)

by

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SRL Record File (4)

January 11, 1988

M E M O R A N D U M

TO: T. L. CAPELETTI, 773-A

FROM: W. C. MOSLEY, 773-A WC Mosley

PALLADIUM ON KIESELGUHR

INTRODUCTION

Palladium supported in kieselguhr (Pd/K) is a candidate material for processing of hydrogen isotopes at SRL and ~~SRP~~. Kieselguhr is a porous, sedimentary rock composed of silicified skeletal remains of single-celled aquatic plants called diatoms. SRL has developed a process for deposition of palladium on kieselguhr particles using immersion in an ammonical palladium chloride solution followed by heating in hydrogen to decompose the chloride to metallic palladium.[1] The goal is to produce Pd/K particles with less than 250 ppm chlorine.

This memorandum describes the characterization of kieselguhr and Pd/K samples prepared during development of the deposition process. Scanning electron microscopy (SEM) and x-ray diffractometry (XRD) were used in these analyses. Samples of Pd/K made by the $PdCl_2/NH_3$ process, a $PdCl_2$ deposition process without ammonia, and a chlorine-free palladium tetraammine dinitrate plating process were examined. Also, several samples of Pd/K that had undergone absorption and desorption of hydrogen were examined.

Recommendations for improving the Pd/K product are presented.

SUMMARY

This work has shown that palladium deposited on kieselguhr by $PdCl_2$ processes developed at SRL is present as submicron particles distributed nonuniformly throughout the kieselguhr rather than as a surface layer. The $PdCl_2$ deposition process with ammonia produces deeper penetration of palladium into the kieselguhr than the process without ammonia. Kieselguhr consists of three components: blocky grains of alpha quartz, skeletal fragments of modified alpha crystobalite, and submicron grains of an amorphous phase. Regions with high concentrations of palladium particles, which are generally near the surface of the kieselguhr, have an open structure because of removal of the submicron granular phase during deposition. Absorption and desorption of hydrogen causes outer regions with high palladium concentrations to become detached.

A chlorine-free process that can produce higher concentrations and more uniform distributions of palladium on kieselguhr is recommended for second generation Pd/K applications although Pd/K used in pilot-scale hydride applications to date has operated satisfactorily.

DISCUSSION

Kieselguhr

Kieselguhr used in development of the palladium deposition process was purchased from Johns-Manville as Chromosorb P (AW). This material had been washed with hydrochloric acid to remove soluble iron. Figure 1 shows SEM photos of material from Lot #202, which consisted of rounded particles. The particle size range of Lot #202 was nominally 30-40 mesh but sieve analysis yielded 70.4 weight percent (w/o) 30-40 mesh (425-600 μm), 28.0 w/o 40-50 mesh (300-425 μm), and 1.6 w/o smaller than 50 mesh. High magnification SEM examination of particle surfaces revealed skeletal fragments of diatoms and clusters of submicron spheroidized grains.

Cross sections of particles from Lot #202 shown in Figures 2 and 3a reveal dense blocky components along with the porous skeletal fragments. Also, regions between these large features are densely packed with the submicron granular material. Energy dispersive x-ray analysis (Figure 3b) detected silicon, aluminum, potassium, iron, and sodium (in order of decreasing x-ray intensity). Figure 3c-g shows elemental maps for the elements in the region of Figure 3a. Silicon is detected throughout the kieselguhr structure with the dense blocky components containing the highest concentrations. Iron appears to be associated with silicon in these dense components. Aluminum appears to be concentrated in the outer surfaces of the skeletal fragments. Potassium and sodium are concentrated in small features, possibly corresponding to the submicron granular material.

X-ray diffractometry suggests that Lot #202 consists of at least three crystallographically distinct phases. One phase is the alpha quartz form of silicon dioxide[2] with its strongest diffraction peak (hexagonal 101) corresponding to an interplanar spacing (d-value) of 3.34 angstroms (Å). A second phase is crystallographically similar to the alpha crystobalite[3] form of silicon dioxide (tetragonal; a = 4.971 Å and c = 6.918 Å) but with a larger unit cell with a = 4.998 Å and c = 6.985 Å, possibly caused by additional elements in the structure. The strongest diffraction peak from this crystobalite-like phase corresponds to d = 4.07 Å. A very broad diffraction band between d = 6.3 Å and 3.2 Å indicates an amorphous component in the kieselguhr.

Pd/K Made by the $PdCl_2/NH_3$ Process

51.2 Pd/K

Figure 4 shows particles of 51.2 Pd/K (51.2 w/o palladium on kieselguhr) prepared using eight cycles of $PdCl_2/NH_3$ deposition on kieselguhr from Chromosorb P Lot #202.[1] The particles retained their rounded shapes during processing but the surfaces were changed by the palladium deposition. The palladium is present as a lace-like network of interconnected submicron particles rather than as a thin coating layer.

Cross sections of the Pd/K particles (Figure 5) reveal the nonuniform distribution of the palladium (bright phase) throughout the particles. Outer regions of the particles contained high concentrations of palladium to depths up to 100 µm with channels containing moderate concentrations extending into the particle interiors. Except for a few dense spots, the palladium deposits in the kieselguhr are in the form of submicron particles. In regions of high palladium deposition, the kieselguhr structure has been altered by removal of the submicron granular material between the

skeletal fragments. Some granular material remains in the regions with low palladium deposition, but it is not as dense as in the original kieselguhr. The palladium deposition process appears to selectively remove the granular material from the kieselguhr.

X-ray diffractometry of 51.2 Pd/K detected palladium along with the three phases in the kieselguhr.[4] Ratios of characteristic diffraction peak heights of the phases with respect to that of the alpha quartz in the kieselguhr are given in Table 1.

Figure 6 shows an agglomerate of small particles removed from 51.2 Pd/K with a 50 mesh (300 μm) sieve. Comparison with Figure 5 reveals a much higher palladium content on the smaller particles. This fact is confirmed by x-ray diffractometry which yielded a high Pd peak height to alpha-quartz peak height ratio (Table 1). Irregular shaped particles are probably palladium-bearing outer portions of large particles that became detached during deposition or subsequent handling. Rounded particles are probably fines in Lot #202 that were more thoroughly penetrated by palladium during deposition. These indications of higher palladium content on fine particles contrast with results of earlier tests on other Pd/K samples that showed the same percentages of palladium on fines as on material that did not pass through the sieve.[5]

Figure 7 shows cross sections through 51.2 Pd/K particles that have undergone five cycles of hydrogen absorption and desorption. Comparison with Figure 5 suggests that some of the outer regions containing high palladium concentrations have become detached as a result of the cycling in hydrogen. The lower palladium-to-alpha quartz x-ray peak height ratio (Table 1) is caused by broadening of the palladium peak during cycling in hydrogen.

73 Pd/K

Figure 8 shows cross sections of particles of 73 Pd/K prepared by the $PdCl_2/NH_3$ process. Comparison with Figure 5 indicates higher palladium deposition in the interior of the kieselguhr particles for 73 Pd/K than for 51.2 Pd/K. Thus, 73 Pd/K has a more uniform palladium distribution than 51.2 Pd/K. Also, the palladium particles in 73 Pd/K are larger than those in 51.2 Pd/K. These differences are probably related to variations in the $PdCl_2/NH_3$ deposition process.

XRD detected palladium oxide[6] along with palladium, alpha quartz, and the amorphous phase. The detection of PdO suggests that 73 Pd/K may have been heated in impure hydrogen to remove chlorine. Also, the absence of XRD peaks for modified crystobalite suggests that the kieselguhr in 73 Pd/K came from a lot significantly different from Lot #202.

outer layer appears to be in the process of becoming detached. This observation suggests that, in Pd/K prepared by the $PdCl_2$ process, detachment can occur during the first few cycles of absorption and desorption of hydrogen.

Pd/K Made with Palladium Tetraammine Dinitrate

Several attempts were made to prepare Pd/K using a chlorine-free chemical plating process developed at SRL for making palladium-californium oxide cermet.[7] The kieselguhr was suspended in a solution of palladium tetraamine dinitrate (PTDN) and hydrazine hydrate was added to reduce the palladium to metal. Figure 13 shows cross sections of Pd/K made by this process. Since this is a plating process rather than a deposition process, much of the palladium is present as a thin layer of interconnected micron-sized particles on the surface of the kieselguhr. Individual submicron particles of palladium are sparsely distributed near the surface of the kieselguhr and practically none are present near the center. X-ray diffractometry suggests an overall palladium loading of 25-30 weight percent. High magnification photos of Pd/K-PTDN shows the kieselguhr structure to be fairly open because the coating process has removed much of the submicron granular material between the skeletal fragments.

CONCLUSIONS

Conclusions derived from these characterizations of Pd/K samples are as follows:

1. Kieselguhr consists of at least three components: alpha quartz, modified crystobalite, and an amorphous phase. Fragments of silicified diatom skeletons are probably the modified crystobalite. The amorphous phase is probably the submicron granular material between the fragments that is removed by deposition and coating processes. The large blocky features are probably the alpha quartz.

2. The $PdCl_2$ deposition process, with or without ammonia, produces palladium as submicron particles distributed nonuniformly throughout the kieselguhr rather than as a surface layer. The $PdCl_2$ deposition process with ammonia produces deeper penetration of palladium into the kieselguhr than the process without ammonia.

Pd/K Made by the $PdCl_2$ Proces (No NH_3)

10 x Pd/K

Figure 9 shows cross sections of particles from a Pd/K sample prepared with ten deposition-drying cycles using $PdCl_2$ solution followed by heating at 700°C for ten hours in hydrogen to reduce the chloride to metal. The palladium is present as submicron particles mostly concentrated within 5-20 µm of the kieselguhr surface. XRD results (Table 1) suggest that this Pd/K contains ~4 weight percent palladium. Correlation of the high proportion of modified crystobalite detected by XRD (Table 1) with the observance of more skeletal fragments by SEM suggests that the skeletal fragments correspond to the modified crystobalite.

2 x Pd/K

Cross sections of particles of a sample of Pd/K prepared with two $PdCl_2$ deposition-drying cycles and reduction heating at 350-450°C for two hours are shown in Figure 10. Submicron palladium particles are sparsely distributed near the kieselguhr surface with a few being detected within the kieselguhr. X-ray diffractometry (Table 1) suggests a palladium content of about 0.5 weight percent. SEM photos and x-ray diffractometry suggest that the kieselguhr in this material is the same as in 10 x Pd/K.

48.4 Pd/K

Preparation of this material involved about thirty $PdCl_2$ deposition-drying cycles. Figure 11 shows cross sections of 48.4 Pd/K particles that had been cycled in hydrogen 250 times. Palladium is deposited generally as submicron particles non-uniformly throughout the kieselguhr but the outer 5-20 µm of the kieselguhr surface contains very high concentrations of palladium in the form of interconnected 1-2 µm particles. As Figure 11 shows, this outer portion of the surface tends to become detached, supposedly during cyclic absorption and desorption of hydrogen.

55 Pd/K

Details of the preparation of this material by the $PdCl_2$ process are not available. It had been cycled in hydrogen to collect pressure-composition-temperature (isotherm) data at 80°C. As shown in Figure 12, palladium particles are distributed non-uniformly throughout the kieselguhr. Some kieselguhr particles exhibit high surface concentrations of palladium while others do not. In some particles, this 5-20 µm thick, palladium-bearing

3. Absorption and desorption of hydrogen causes outer portions of the Pd/K particles containing high concentrations of palladium to become detached. Detachment during cycling in hydrogen was extensive in Pd/K prepared by the $PdCl_2$ deposition process without ammonia. Stresses at the interface between the interior and the palladium-bearing outer region during cycling probably cause cracking and detachment.

RECOMMENDATIONS

Although the Pd/K used in pilot-scale hydride apoplications to date has operated satisfactorily, a material in which palladium is distributed more uniformly throughout the support structure would be desirable. Detachment of palladium-rich surface regions might be avoided. Higher palladium loading might be achievable that would reduce the size of process vessels. Deposition of palladium from a chloride-free solution would eliminate the need for lengthy heatings to remove chlorine. These improvements could probably be made with slight changes in the present deposition process.

The following deposition process changes are recommended:

1. Pretreat the kieselguhr to remove the amorphous, submicron granular material and produce a more open structure that allows the palladium solution to penetrate the particles more thoroughly. Testing is needed to determine the correct pretreatment.

2. Use a palladium deposition process like the one developed using $PdCl_2$ except use a palladium salt-like PTDN to eliminate chlorine from the process.

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3. ASTM Powder Diffraction File #11-0695.

4. ASTM Powder Diffraction File #5-0681.

5. M. S. Ortman, Private Communication.

6. ASTM Powder Diffraction File #6-0515.

7. W. S. Mosley, P. K. Smith, and P. E. McBeath. Neutron Sources of Palladium-^{252}Cf Oxide Cermet Wire, DP-MS-72-40.

TABLE 1

Heights of Characteristic X-Ray Diffraction Peaks of Phases in Pd/K Samples Relative to Height of Peak of Alpha Quartz (d = 3.34 Å)[2]

Sample	Palladium[4] (d = 2.25 Å)	Modified Crystobalite[3] (d = 4.07 Å)	Amorphous Phase (d = 3.2-6.3 Å)
Kieselguhr Lot #202	0	1.4	1.3
51.2 Pd/K	121	2.8	0.9
Fines from 51.2 Pd/K	300	1.3	0.0
51.2 Pd/K - 5 cycles	82	2.0	0.7
73 Pd/K	276	0.0	0.8
10 x Pd/K	6.4	6.0	0.4
2 x Pd/K	0.8	5.9	0.4
48.4 Pd/K - 250 cycles	42	2.9	0.8
55 Pd/KL - 80°C isotherm	84	3.3	0.8
Pd/K - PTDN	27	1.5	0.8

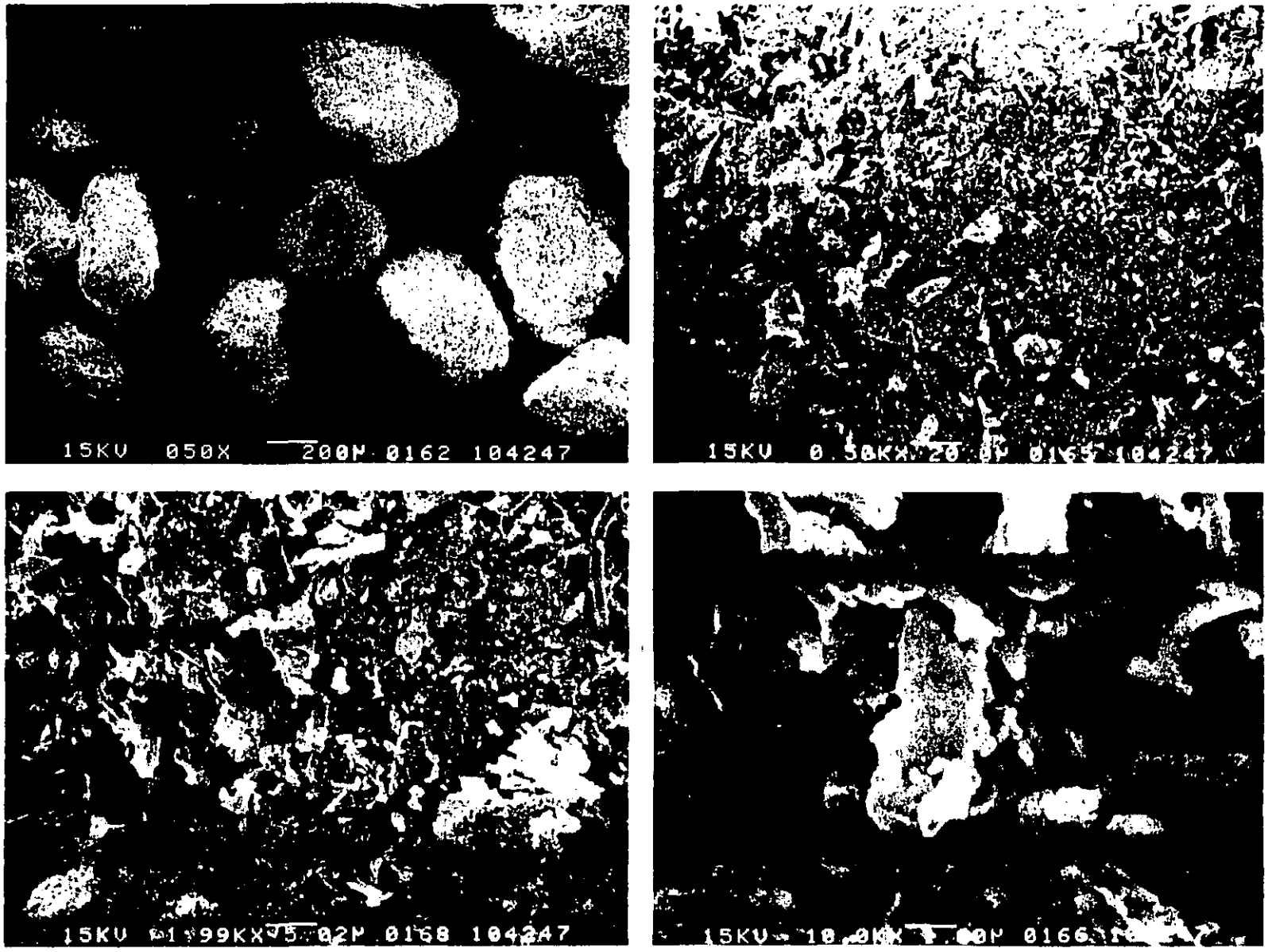


FIGURE 1. Loose Kieselguhr Particles - Lot 202

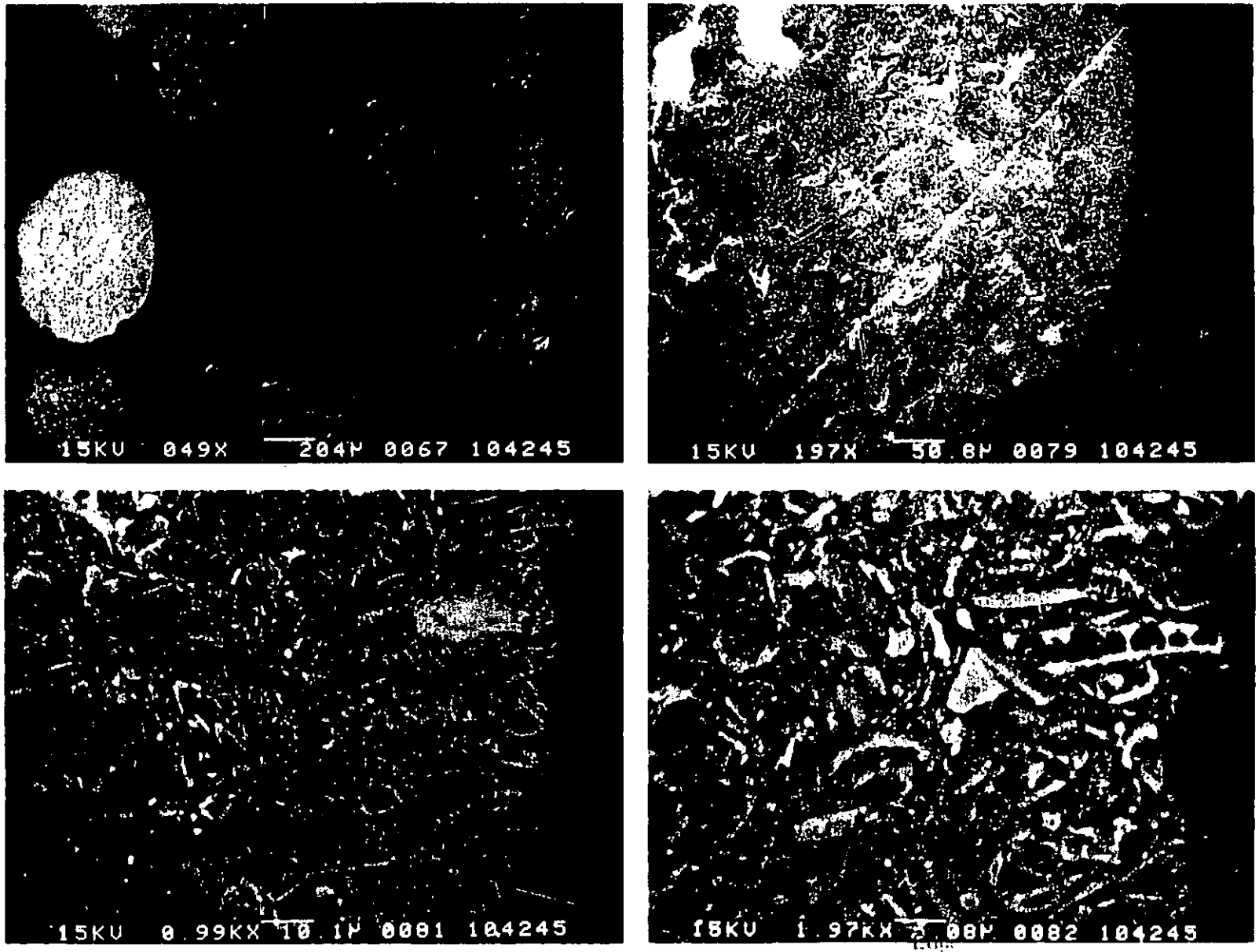
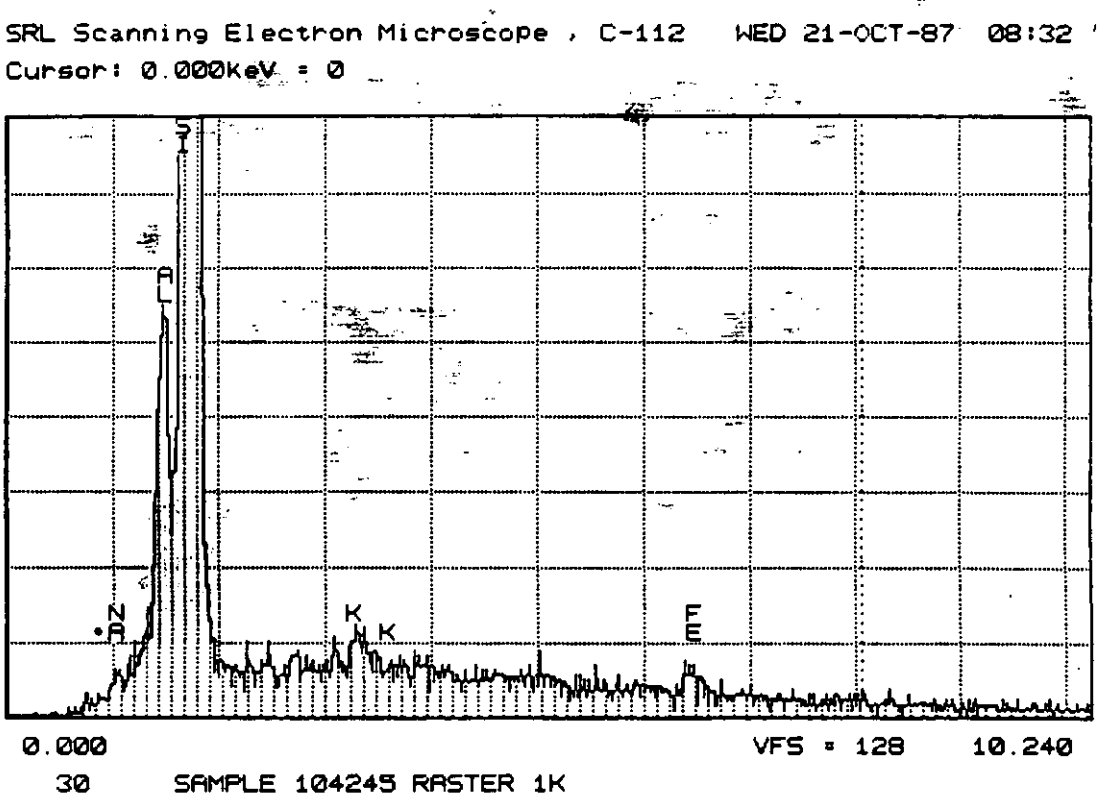


FIGURE 2. Cross Sections of Kieselguhr Particles - Lot 202

a. SEM Inage

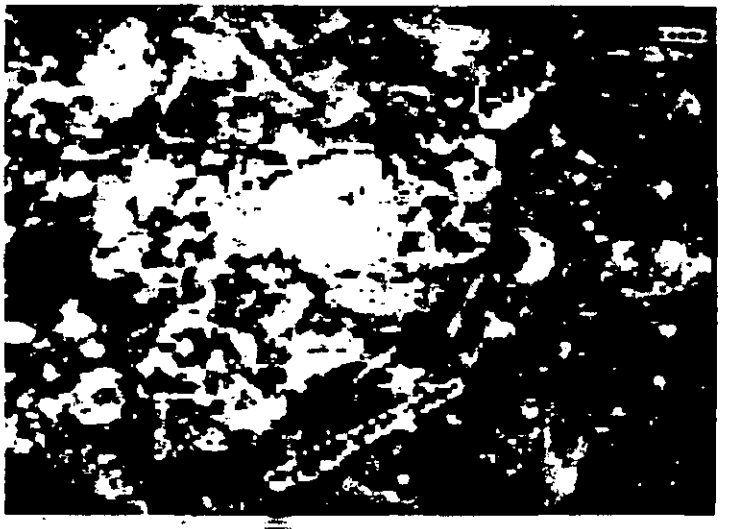


b. Energy Dispersive X-ray Spectrum

FIGURE 3. SEM/EDX Analysis of Kieselguhr - Lot 202

c. Silicon Map

d. Aluminum Map



e. Iron Map

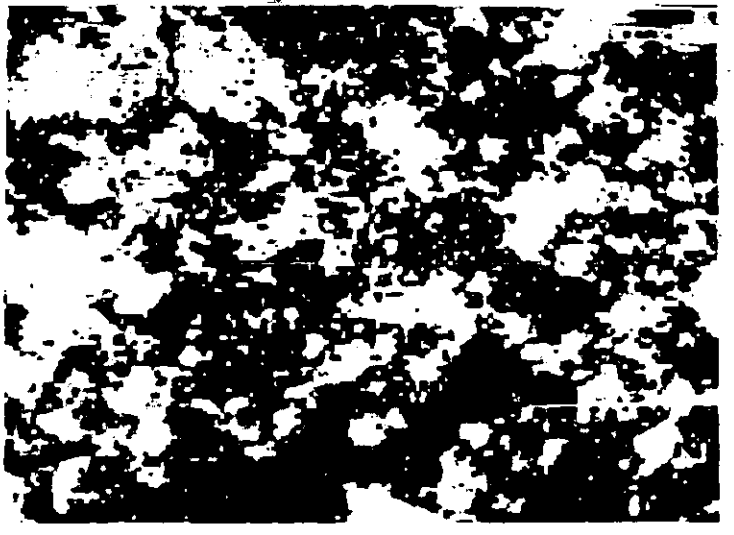
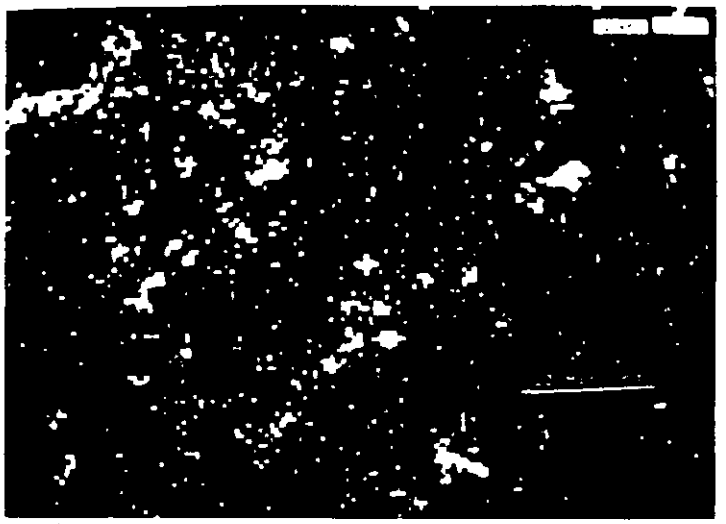


FIGURE 3. (Contd) SEM/EDX Analysis of Kieselguhr - Lot 202

f. Potassium Map



g. Sodium Map

FIGURE 3. (Contd) SEM/EDX Analysis of Kieselguhr - Lot 202

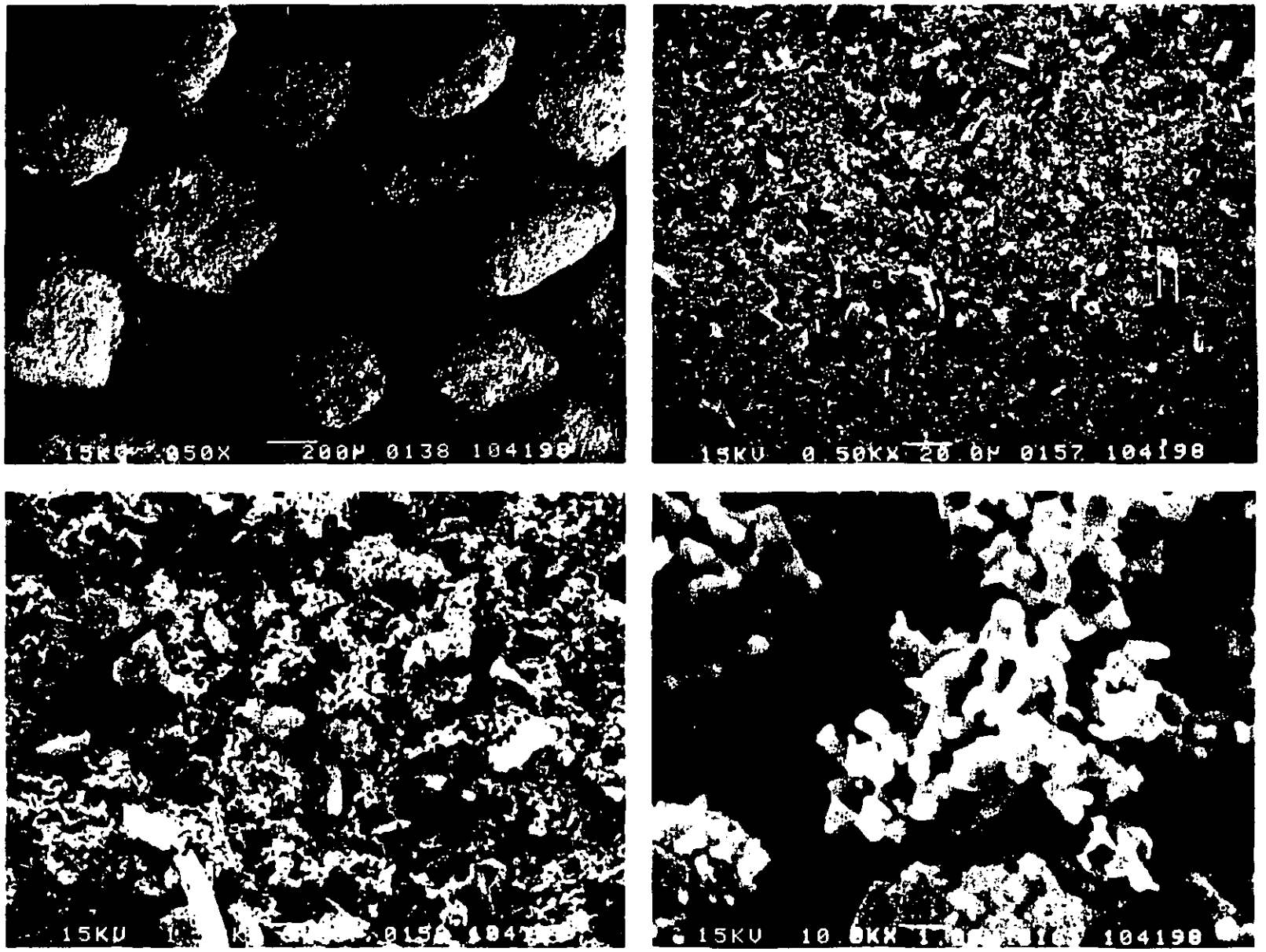
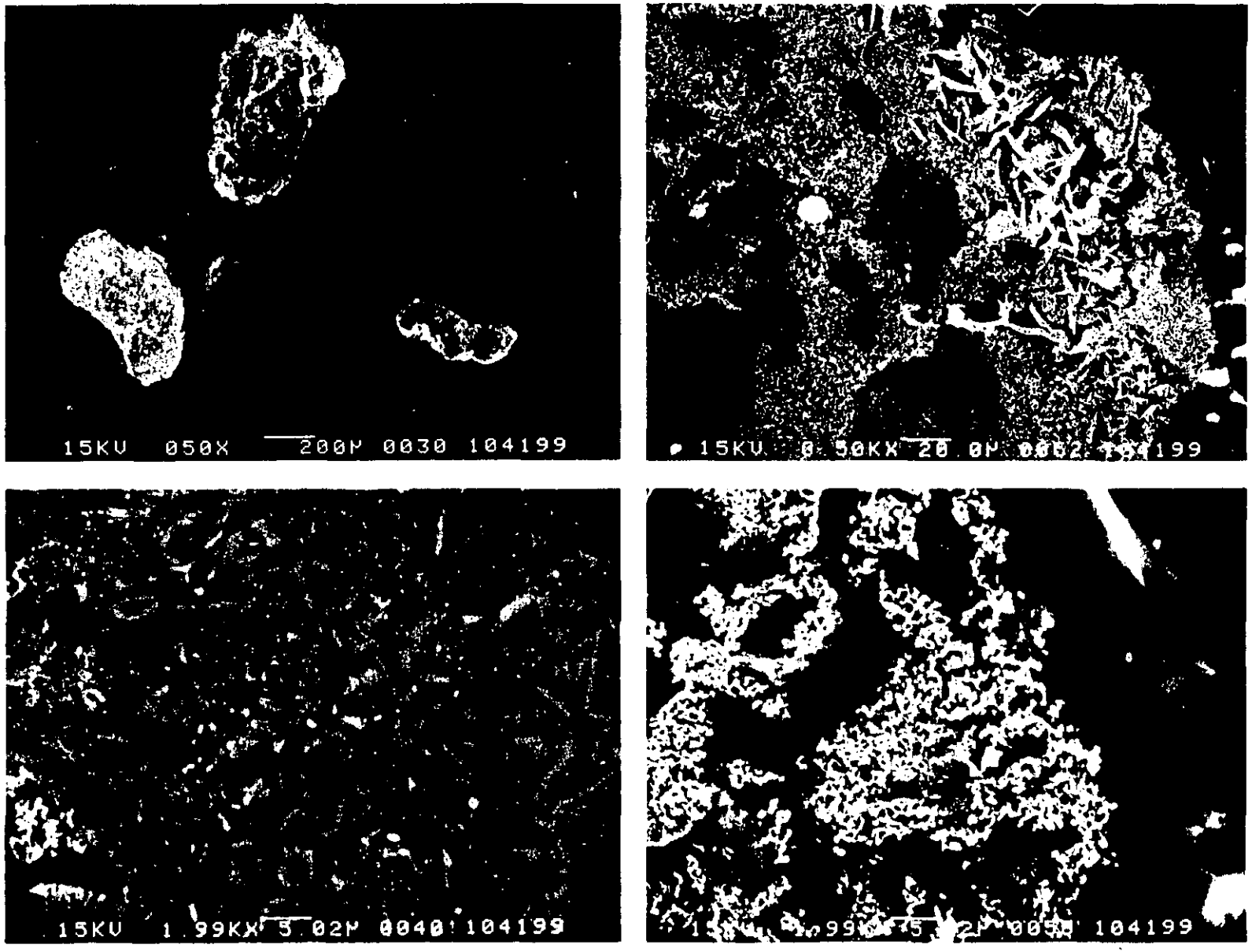


FIGURE 4. Loose Particles of 51.2 Pd/K



Interior

Edge

FIGURE 5. Cross Sections of 51.2 Pd/K

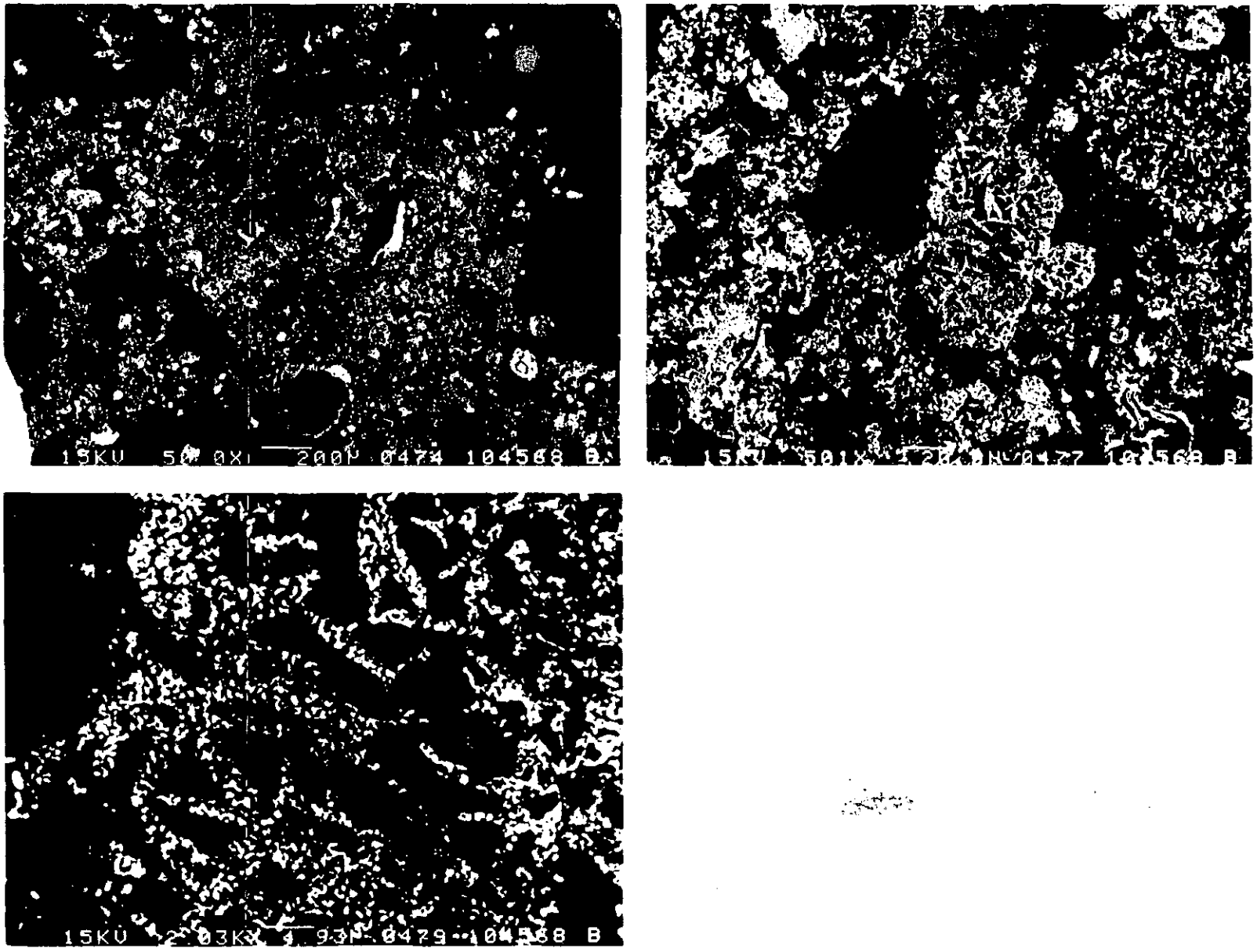


FIGURE 6. Fine Particles (<300 µm) from 51.2 Pd/K

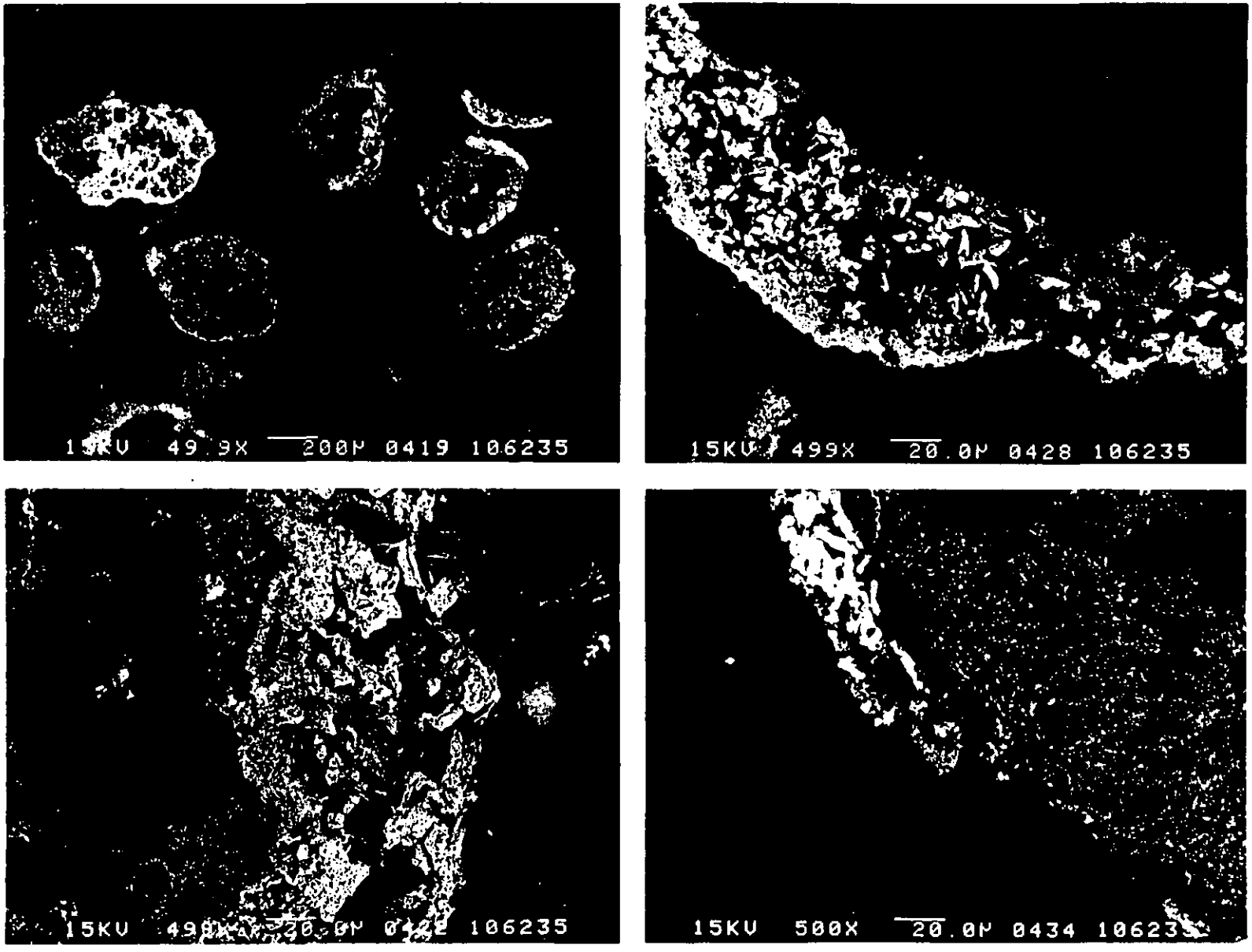


FIGURE 7. 51.2 Pd/K Cycled 5 Times

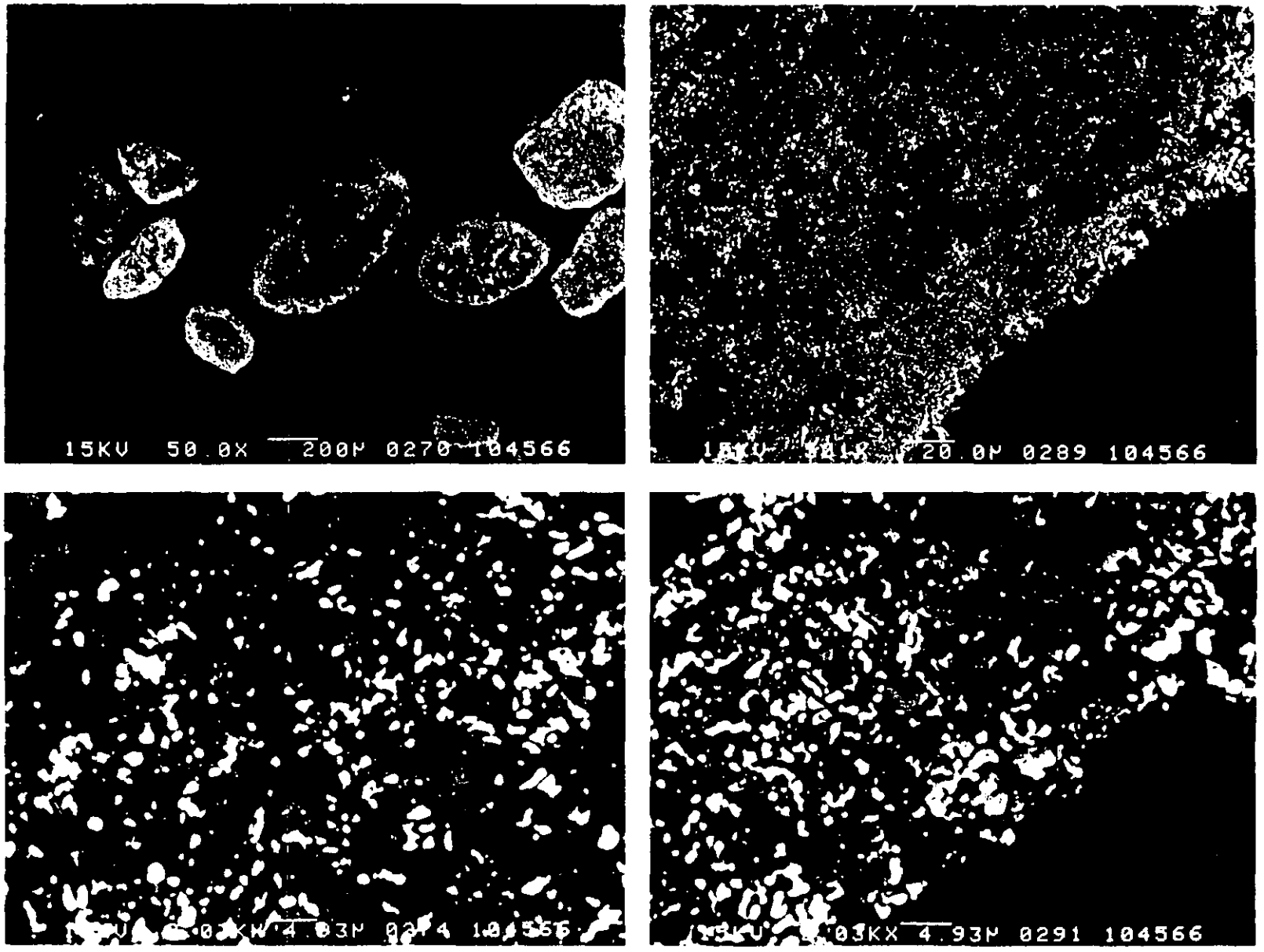
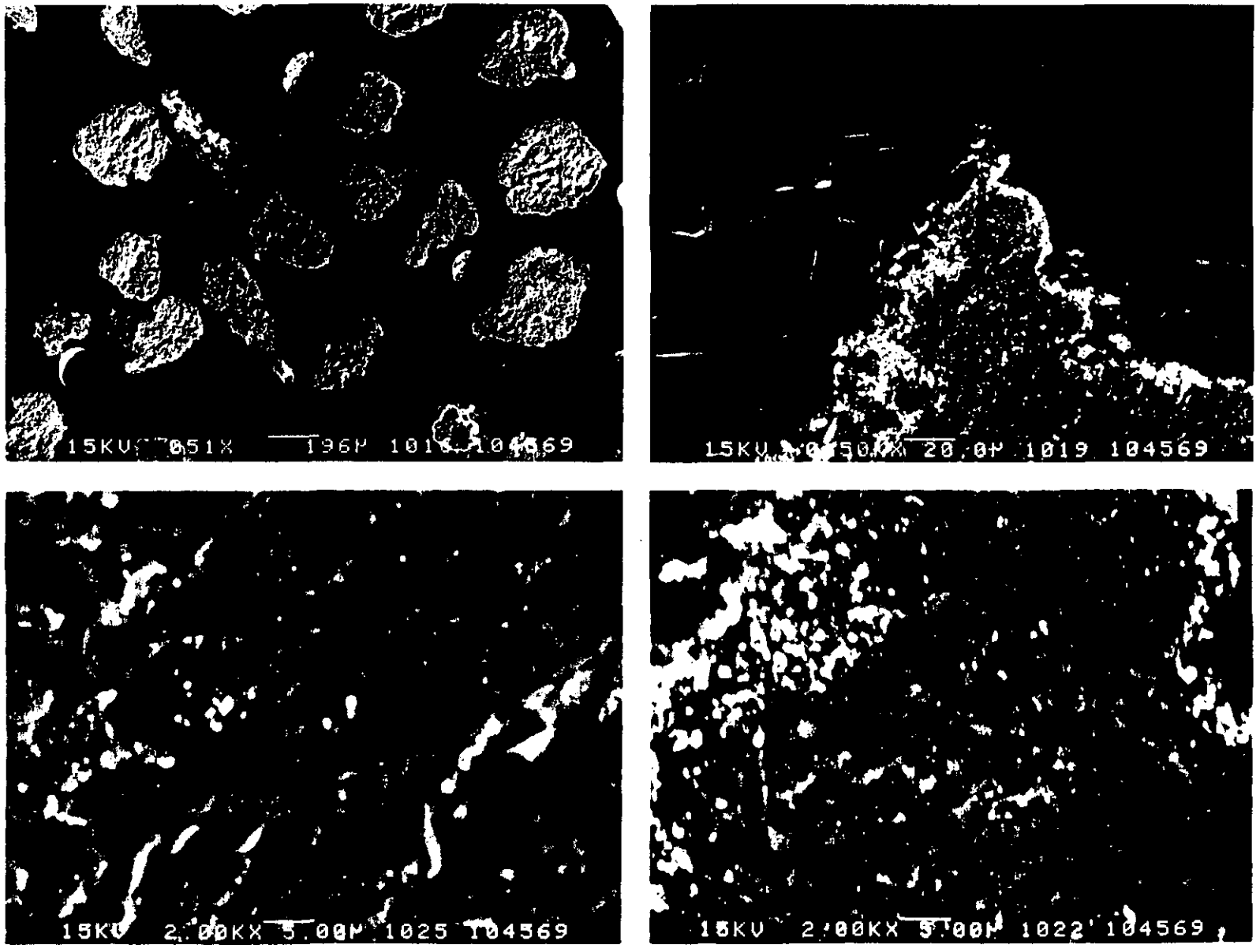


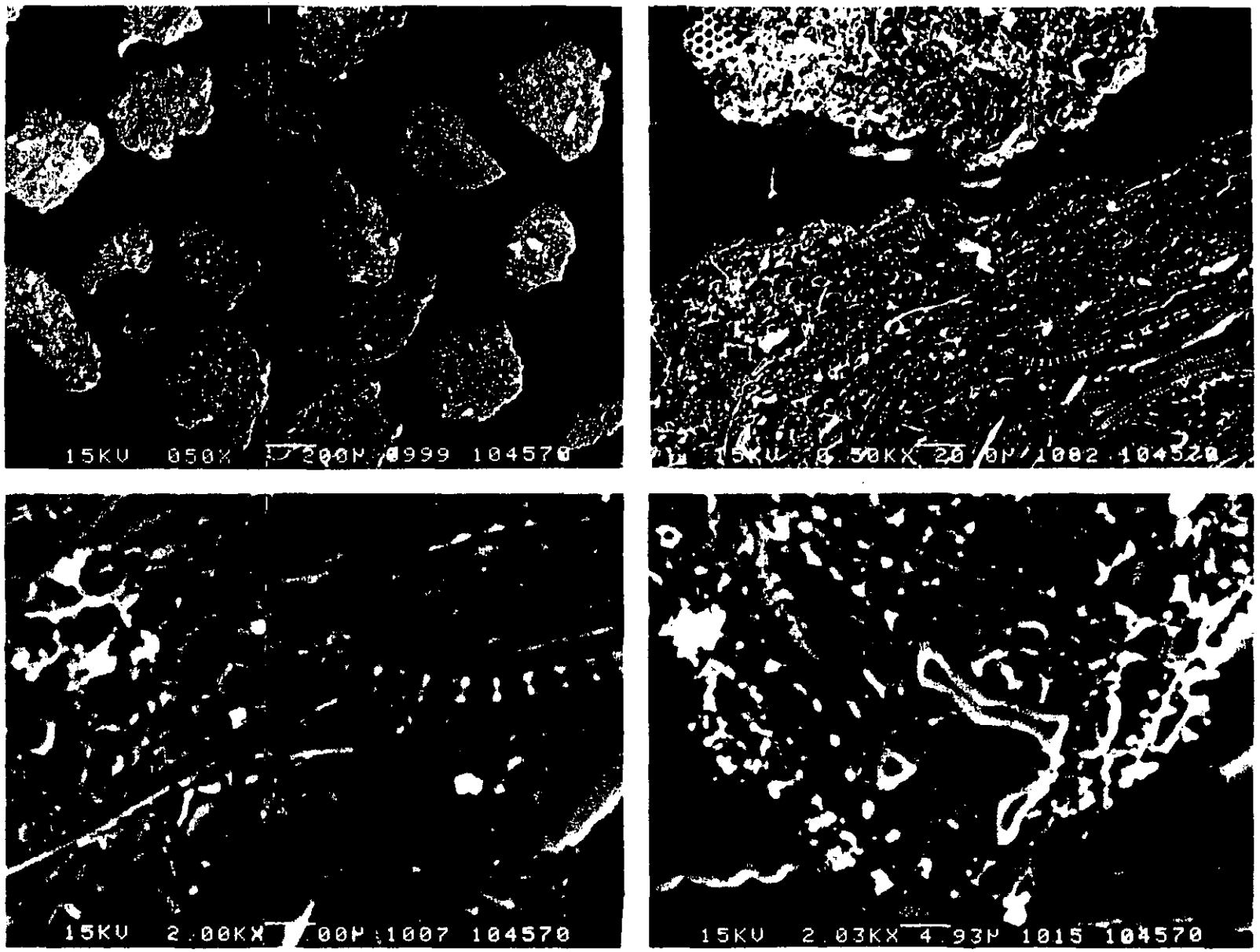
FIGURE 8. 73 Pd/K



Interior

Edge

FIGURE 9. 10X Pd/K (Approx 4 Weight Percent Palladium)



Interior

Edge

FIGURE 10. 2A [illegible] (Approx 0.5 Weight Percent Palladium)

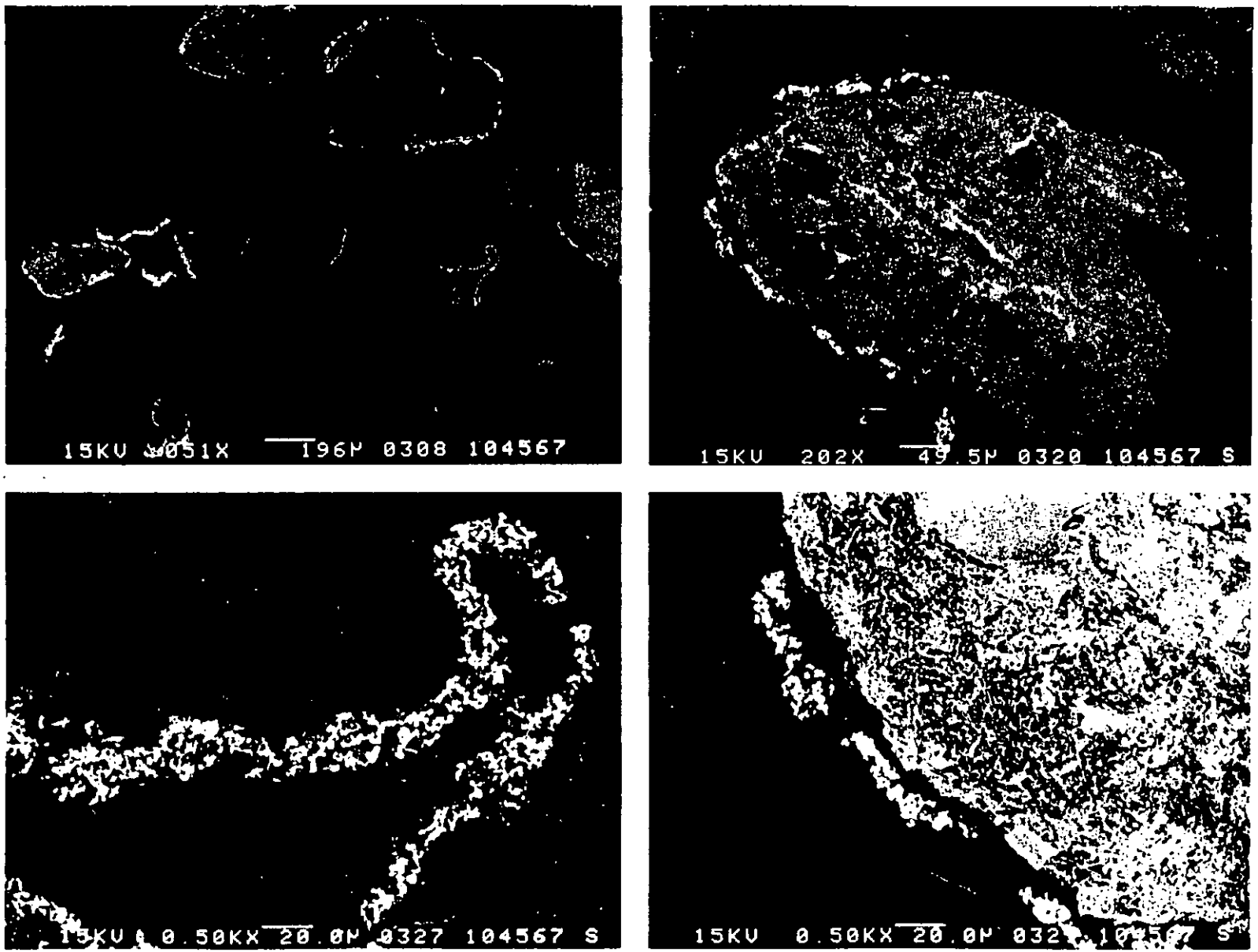


FIGURE 11. 48.4 Pd/K Cycled 250 Times

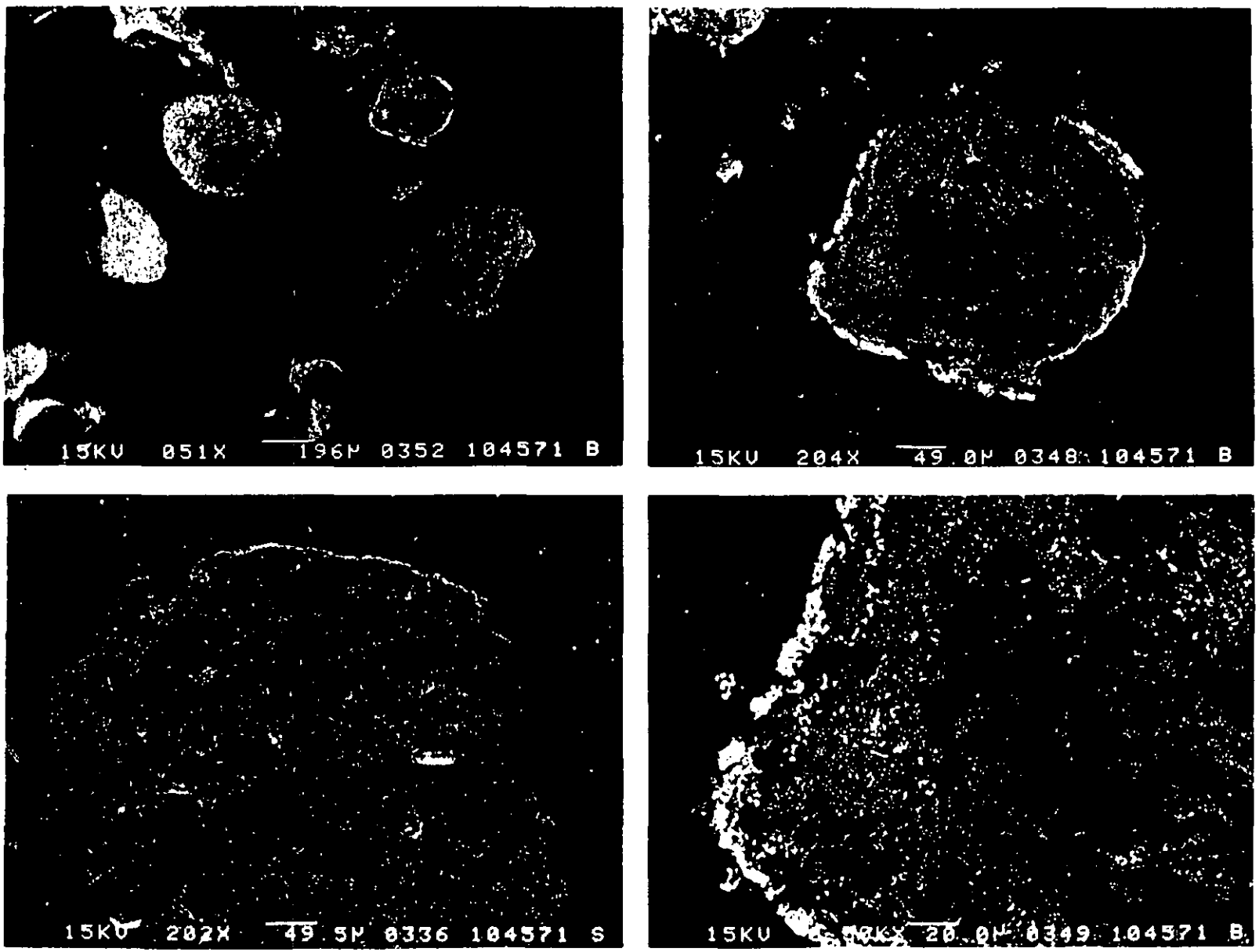
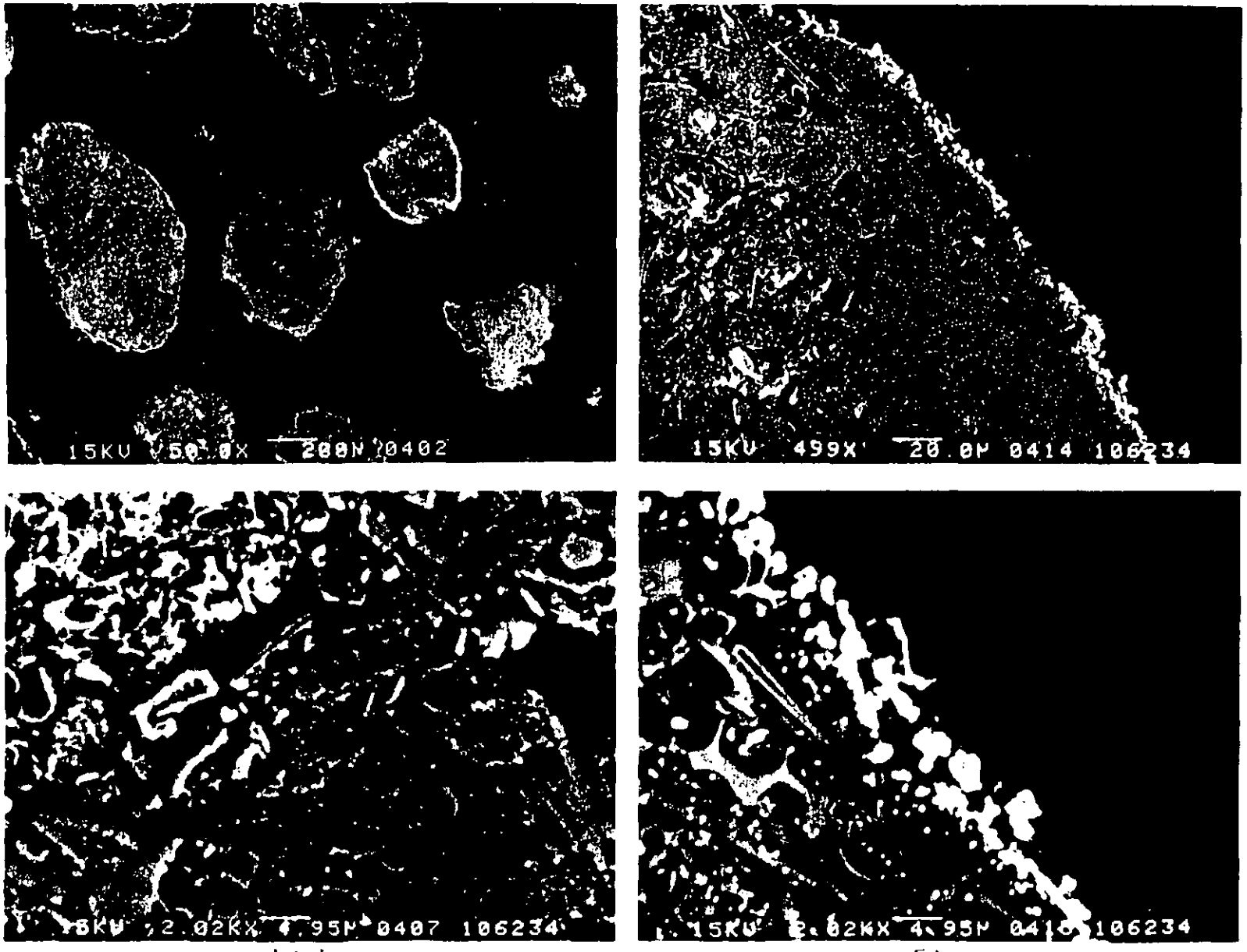


FIGURE 12. 55 Pd/K from 80°C Isotherm Test



Interior

Edge

FIGURE 13. Pd/K-PTDN (25-30 Weight Percent Palladium)

242528

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Key Words: Palladium
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Replacement Tritium Facility (RTF)
Chlorine

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TO: T. L. CAPELETTI, 773-A

FROM: W. C. MOSLEY, 773-A W C Mosley

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Recommendations for improving the Pd/K product are presented.

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Kieselguhr used in development of the palladium deposition process was purchased from Johns-Manville as Chromosorb P (AW). This material had been washed with hydrochloric acid to remove soluble iron. Figure 1 shows SEM photos of material from Lot #202, which consisted of rounded particles. The particle size range of Lot #202 was nominally 30-40 mesh but sieve analysis yielded 70.4 weight percent (w/o) 30-40 mesh (425-600 μm), 28.0 w/o 40-50 mesh (300-425 μm), and 1.6 w/o smaller than 50 mesh. High magnification SEM examination of particle surfaces revealed skeletal fragments of diatoms and clusters of submicron spheroidized grains.

Cross sections of particles from Lot #202 shown in Figures 2 and 3a reveal dense blocky components along with the porous skeletal fragments. Also, regions between these large features are densely packed with the submicron granular material. Energy dispersive x-ray analysis (Figure 3b) detected silicon, aluminum, potassium, iron, and sodium (in order of decreasing x-ray intensity). Figure 3c-g shows elemental maps for the elements in the region of Figure 3a. Silicon is detected throughout the kieselguhr structure with the dense blocky components containing the highest concentrations. Iron appears to be associated with silicon in these dense components. Aluminum appears to be concentrated in the outer surfaces of the skeletal fragments. Potassium and sodium are concentrated in small features, possibly corresponding to the submicron granular material.

X-ray diffractometry suggests that Lot #202 consists of at least three crystallographically distinct phases. One phase is the alpha quartz form of silicon dioxide[2] with its strongest diffraction peak (hexagonal 101) corresponding to an interplanar spacing (d-value) of 3.34 angstroms (Å). A second phase is crystallographically similar to the alpha crystobalite[3] form of silicon dioxide (tetragonal; a = 4.971 Å and c = 6.918 Å) but with a larger unit cell with a = 4.998 Å and c = 6.985 Å, possibly caused by additional elements in the structure. The strongest diffraction peak from this crystobalite-like phase corresponds to d = 4.07 Å. A very broad diffraction band between d = 6.3 Å and 3.2 Å indicates an amorphous component in the kieselguhr.

Pd/K Made by the $PdCl_2/NH_3$ Process

51.2 Pd/K

Figure 4 shows particles of 51.2 Pd/K (51.2 w/o palladium on kieselguhr) prepared using eight cycles of $PdCl_2/NH_3$ deposition on kieselguhr from Chromosorb P Lot #202.[1] The particles retained their rounded shapes during processing but the surfaces were changed by the palladium deposition. The palladium is present as a lace-like network of interconnected submicron particles rather than as a thin coating layer.

Cross sections of the Pd/K particles (Figure 5) reveal the nonuniform distribution of the palladium (bright phase) throughout the particles. Outer regions of the particles contained high concentrations of palladium to depths up to 100 μm with channels containing moderate concentrations extending into the particle interiors. Except for a few dense spots, the palladium deposits in the kieselguhr are in the form of submicron particles. In regions of high palladium deposition, the kieselguhr structure has been altered by removal of the submicron granular material between the

skeletal fragments. Some granular material remains in the regions with low palladium deposition, but it is not as dense as in the original kieselguhr. The palladium deposition process appears to selectively remove the granular material from the kieselguhr.

X-ray diffractometry of 51.2 Pd/K detected palladium along with the three phases in the kieselguhr.[4] Ratios of characteristic diffraction peak heights of the phases with respect to that of the alpha quartz in the kieselguhr are given in Table 1.

Figure 6 shows an agglomerate of small particles removed from 51.2 Pd/K with a 50 mesh (300 μm) sieve. Comparison with Figure 5 reveals a much higher palladium content on the smaller particles. This fact is confirmed by x-ray diffractometry which yielded a high Pd peak height to alpha-quartz peak height ratio (Table 1). Irregular shaped particles are probably palladium-bearing outer portions of large particles that became detached during deposition or subsequent handling. Rounded particles are probably fines in Lot #202 that were more thoroughly penetrated by palladium during deposition. These indications of higher palladium content on fine particles contrast with results of earlier tests on other Pd/K samples that showed the same percentages of palladium on fines as on material that did not pass through the sieve.[5]

Figure 7 shows cross sections through 51.2 Pd/K particles that have undergone five cycles of hydrogen absorption and desorption. Comparison with Figure 5 suggests that some of the outer regions containing high palladium concentrations have become detached as a result of the cycling in hydrogen. The lower palladium-to-alpha quartz x-ray peak height ratio (Table 1) is caused by broadening of the palladium peak during cycling in hydrogen.

73 Pd/K

Figure 8 shows cross sections of particles of 73 Pd/K prepared by the $PdCl_2/NH_3$ process. Comparison with Figure 5 indicates higher palladium deposition in the interior of the kieselguhr particles for 73 Pd/K than for 51.2 Pd/K. Thus, 73 Pd/K has a more uniform palladium distribution than 51.2 Pd/K. Also, the palladium particles in 73 Pd/K are larger than those in 51.2 Pd/K. These differences are probably related to variations in the $PdCl_2/NH_3$ deposition process.

XRD detected palladium oxide[6] along with palladium, alpha quartz, and the amorphous phase. The detection of PdO suggests that 73 Pd/K may have been heated in impure hydrogen to remove chlorine. Also, the absence of XRD peaks for modified crystobalite suggests that the kieselguhr in 73 Pd/K came from a lot significantly different from Lot #202.

Pd/K Made by the $PdCl_2$ Proces (No NH_3)

10 x Pd/K

Figure 9 shows cross sections of particles from a Pd/K sample prepared with ten deposition-drying cycles using $PdCl_2$ solution followed by heating at 700°C for ten hours in hydrogen to reduce the chloride to metal. The palladium is present as submicron particles mostly concentrated within 5-20 µm of the kieselguhr surface. XRD results (Table 1) suggest that this Pd/K contains ~4 weight percent palladium. Correlation of the high proportion of modified crystobalite detected by XRD (Table 1) with the observance of more skeletal fragments by SEM suggests that the skeletal fragments correspond to the modified crystobalite.

2 x Pd/K

Cross sections of particles of a sample of Pd/K prepared with two $PdCl_2$ deposition-drying cycles and reduction heating at 350-450°C for two hours are shown in Figure 10. Submicron palladium particles are sparsely distributed near the kieselguhr surface with a few being detected within the kieselguhr. X-ray diffractometry (Table 1) suggests a palladium content of about 0.5 weight percent. SEM photos and x-ray diffractometry suggest that the kieselguhr in this material is the same as in 10 x Pd/K.

48.4 Pd/K

Preparation of this material involved about thirty $PdCl_2$ deposition-drying cycles. Figure 11 shows cross sections of 48.4 Pd/K particles that had been cycled in hydrogen 250 times. Palladium is deposited generally as submicron particles non-uniformly throughout the kieselguhr but the outer 5-20 µm of the kieselguhr surface contains very high concentrations of palladium in the form of interconnected 1-2 µm particles. As Figure 11 shows, this outer portion of the surface tends to become detached, supposedly during cyclic absorption and desorption of hydrogen.

55 Pd/K

Details of the preparation of this material by the $PdCl_2$ process are not available. It had been cycled in hydrogen to collect pressure-composition-temperature (isotherm) data at 80°C. As shown in Figure 12, palladium particles are distributed non-uniformly throughout the kieselguhr. Some kieselguhr particles exhibit high surface concentrations of palladium while others do not. In some particles, this 5-20 µm thick, palladium-bearing

outer layer appears to be in the process of becoming detached. This observation suggests that, in Pd/K prepared by the $PdCl_2$ process, detachment can occur during the first few cycles of absorption and desorption of hydrogen.

Pd/K Made with Palladium Tetraammine Dinitrate

Several attempts were made to prepare Pd/K using a chlorine-free chemical plating process developed at SRL for making palladium-californium oxide cermet.[7] The kieselguhr was suspended in a solution of palladium tetraamine dinitrate (PTDN) and hydrazine hydrate was added to reduce the palladium to metal. Figure 13 shows cross sections of Pd/K made by this process. Since this is a plating process rather than a deposition process, much of the palladium is present as a thin layer of interconnected micron-sized particles on the surface of the kieselguhr. Individual submicron particles of palladium are sparsely distributed near the surface of the kieselguhr and practically none are present near the center. X-ray diffractometry suggests an overall palladium loading of 25-30 weight percent. High magnification photos of Pd/K-PTDN shows the kieselguhr structure to be fairly open because the coating process has removed much of the submicron granular material between the skeletal fragments.

CONCLUSIONS

Conclusions derived from these characterizations of Pd/K samples are as follows:

1. Kieselguhr consists of at least three components: alpha quartz, modified crystobalite, and an amorphous phase. Fragments of silicified diatom skeletons are probably the modified crystobalite. The amorphous phase is probably the submicron granular material between the fragments that is removed by deposition and coating processes. The large blocky features are probably the alpha quartz.

2. The $PdCl_2$ deposition process, with or without ammonia, produces palladium as submicron particles distributed nonuniformly throughout the kieselguhr rather than as a surface layer. The $PdCl_2$ deposition process with ammonia produces deeper penetration of palladium into the kieselguhr than the process without ammonia.

3. Absorption and desorption of hydrogen causes outer portions of the Pd/K particles containing high concentrations of palladium to become detached. Detachment during cycling in hydrogen was extensive in Pd/K prepared by the $PdCl_2$ deposition process without ammonia. Stresses at the interface between the interior and the palladium-bearing outer region during cycling probably cause cracking and detachment.

RECOMMENDATIONS

Although the Pd/K used in pilot-scale hydride apoplications to date has operated satisfactorily, a material in which palladium is distributed more uniformly throughout the support structure would be desirable. Detachment of palladium-rich surface regions might be avoided. Higher palladium loading might be achievable that would reduce the size of process vessels. Deposition of palladium from a chloride-free solution would eliminate the need for lengthy heatings to remove chlorine. These improvements could probably be made with slight changes in the present deposition process.

The following deposition process changes are recommended:

1. Pretreat the kieselguhr to remove the amorphous, submicron granular material and produce a more open structure that allows the palladium solution to penetrate the particles more thoroughly. Testing is needed to determine the correct pretreatment.

2. Use a palladium deposition process like the one developed using $PdCl_2$ except use a palladium salt-like PTDN to eliminate chlorine from the process.

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3. ASTM Powder Diffraction File #11-0695.

4. ASTM Powder Diffraction File #5-0681.

5. M. S. Ortman, Private Communication.

6. ASTM Powder Diffraction File #6-0515.

7. W. S. Mosley, P. K. Smith, and P. E. McBeath. Neutron Sources of Palladium-^{252}Cf Oxide Cermet Wire, DP-MS-72-40.

TABLE 1

Heights of Characteristic X-Ray Diffraction Peaks of Phases in Pd/K Samples Relative to Height of Peak of Alpha Quartz (d = 3.34 Å)[2]

Sample	Palladium[4] (d = 2.25 Å)	Modified Crystobalite[3] (d = 4.07 Å)	Amorphous Phase (d = 3.2-6.3 Å)
Kieselguhr Lot #202	0	1.4	1.3
51.2 Pd/K	121	2.8	0.9
Fines from 51.2 Pd/K	300	1.3	0.0
51.2 Pd/K - 5 cycles	82	2.0	0.7
73 Pd/K	276	0.0	0.8
10 x Pd/K	6.4	6.0	0.4
2 x Pd/K	0.8	5.9	0.4
48.4 Pd/K - 250 cycles	42	2.9	0.8
55 Pd/KL - 80°C isotherm	84	3.3	0.8
Pd/K - PTDN	27	1.5	0.8

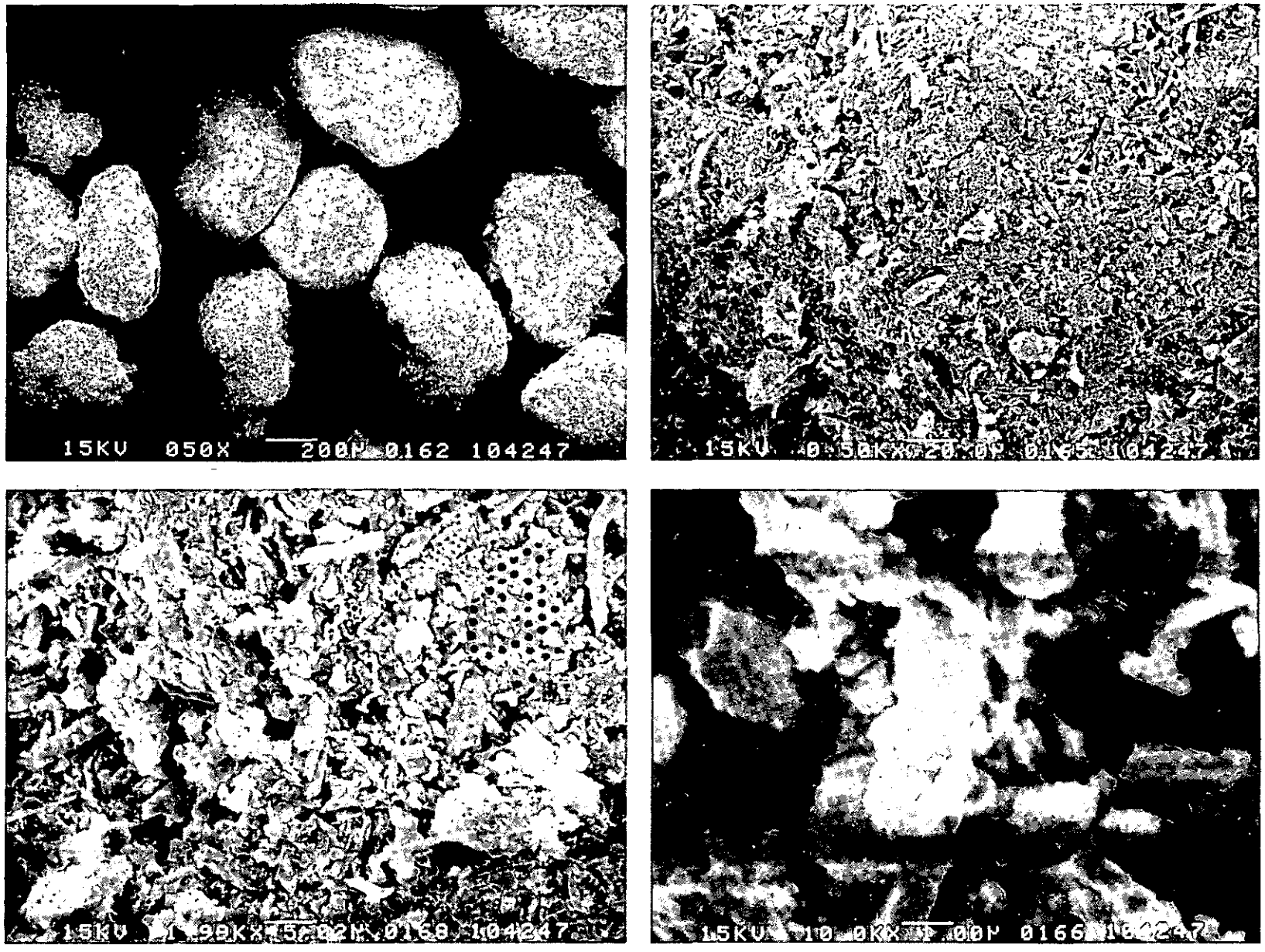

FIGURE 1. Loose Kieselguhr Particles - Lot 202

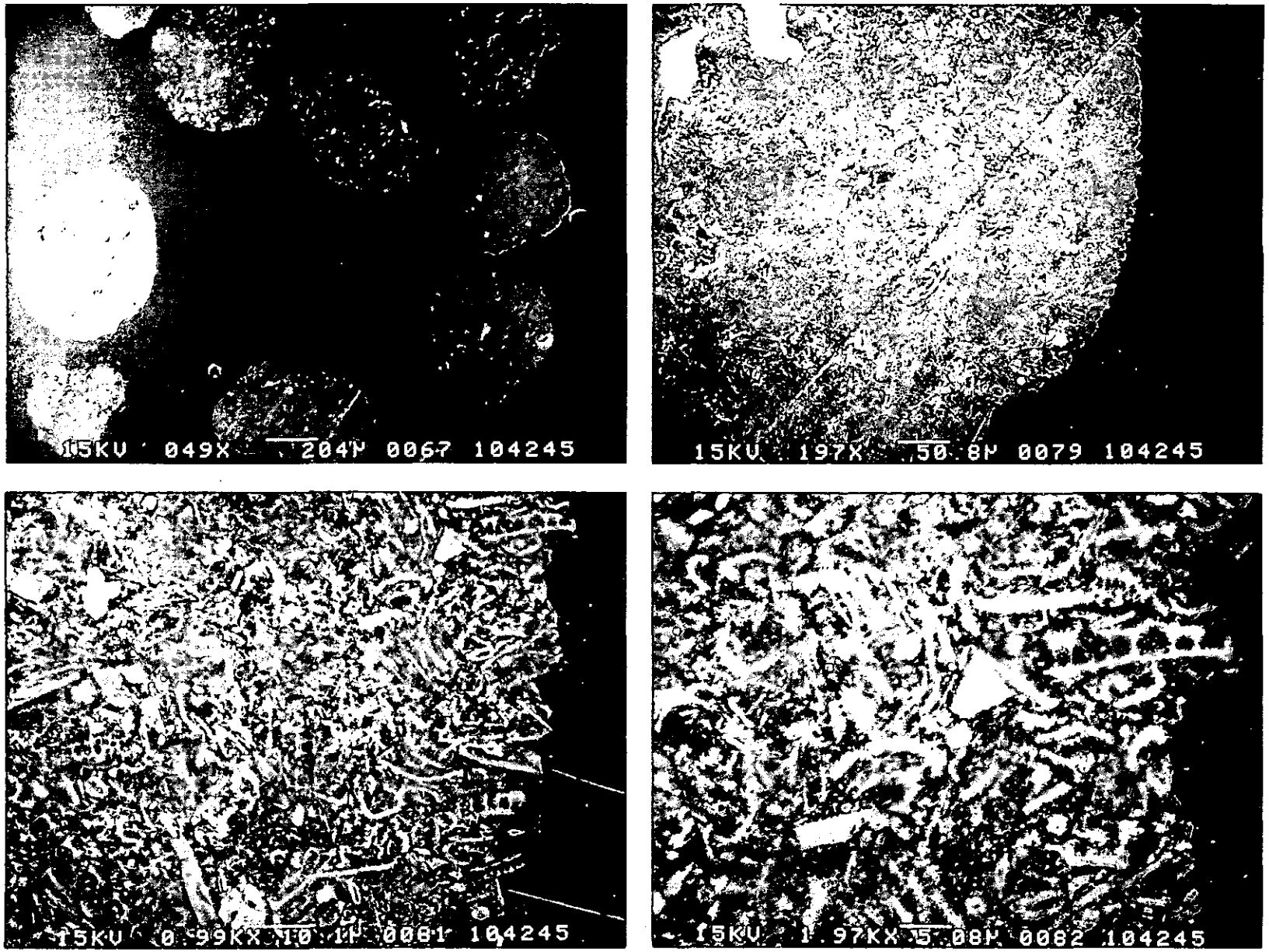

FIGURE 2. Cross Sections of Kieselguhr Particles - Lot 202

a. SEM Inage

SRL Scanning Electron Microscope , C-112 WED 21-OCT-87 08:32
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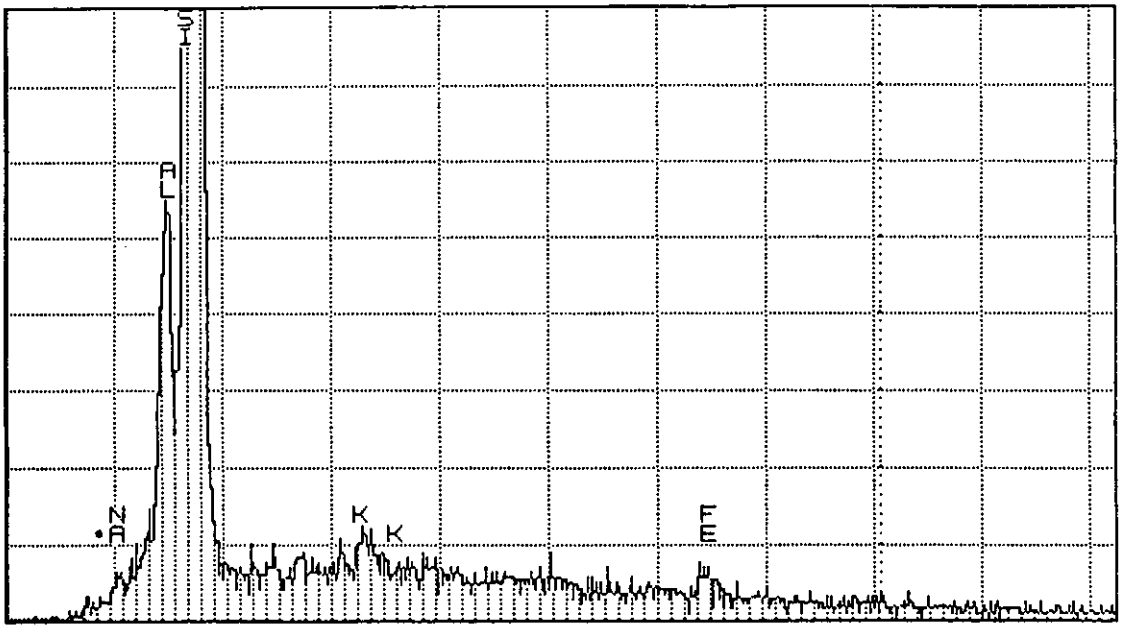
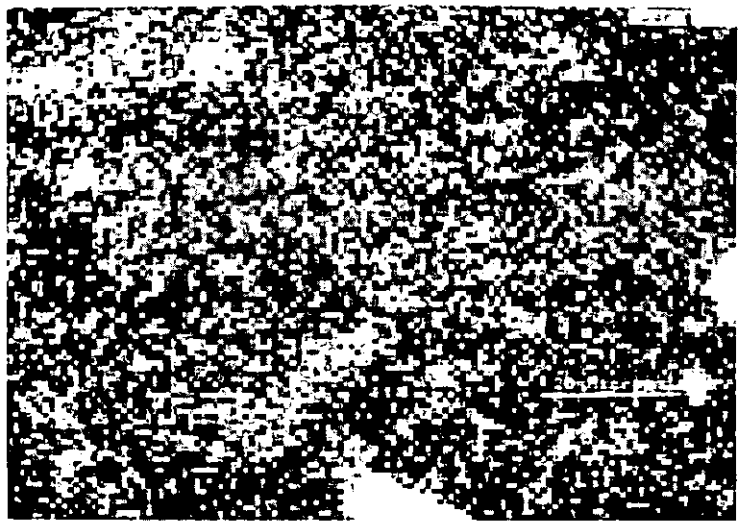


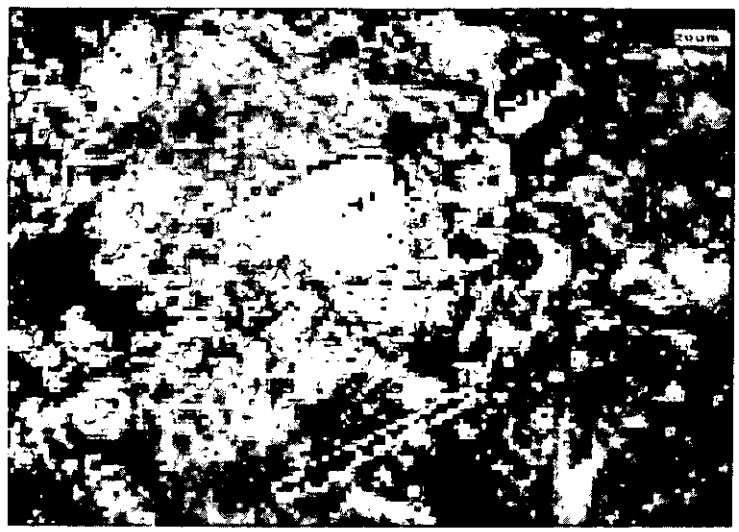
b. Energy Dispersive X-ray Spectrum

FIGURE 3. SEM/EDX Analysis of Kieselguhr - Lot 202

c. Silicon Map



d. Aluminum Map



e. Iron Map

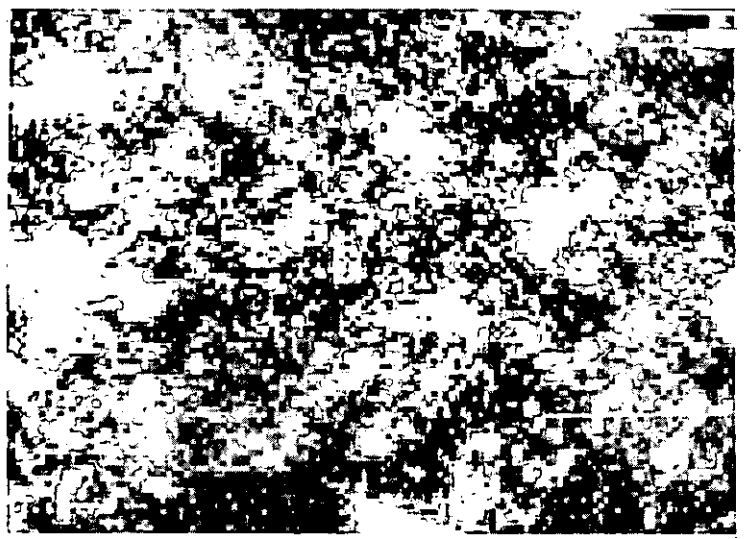
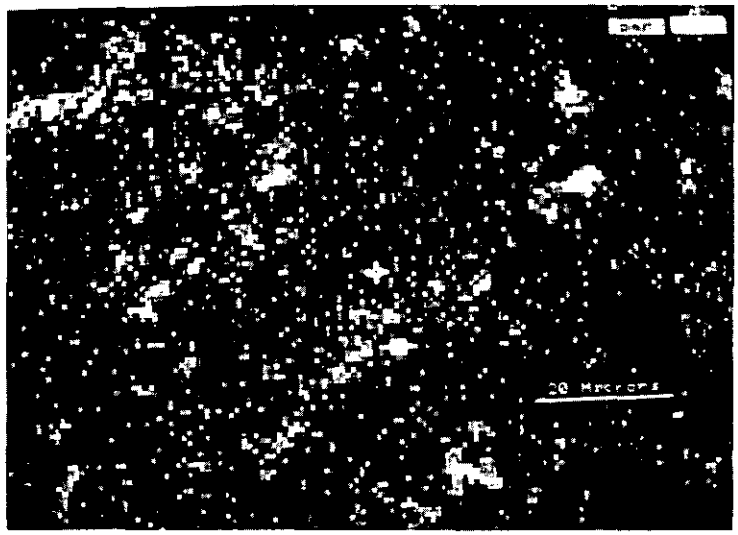


FIGURE 3. (Contd) SEM/EDX Analysis of Kieselguhr - Lot 202

f. Potassium Map



g. Sodium Map

FIGURE 3. (Contd) SEM/EDX Analysis of Kieselguhr - Lot 202

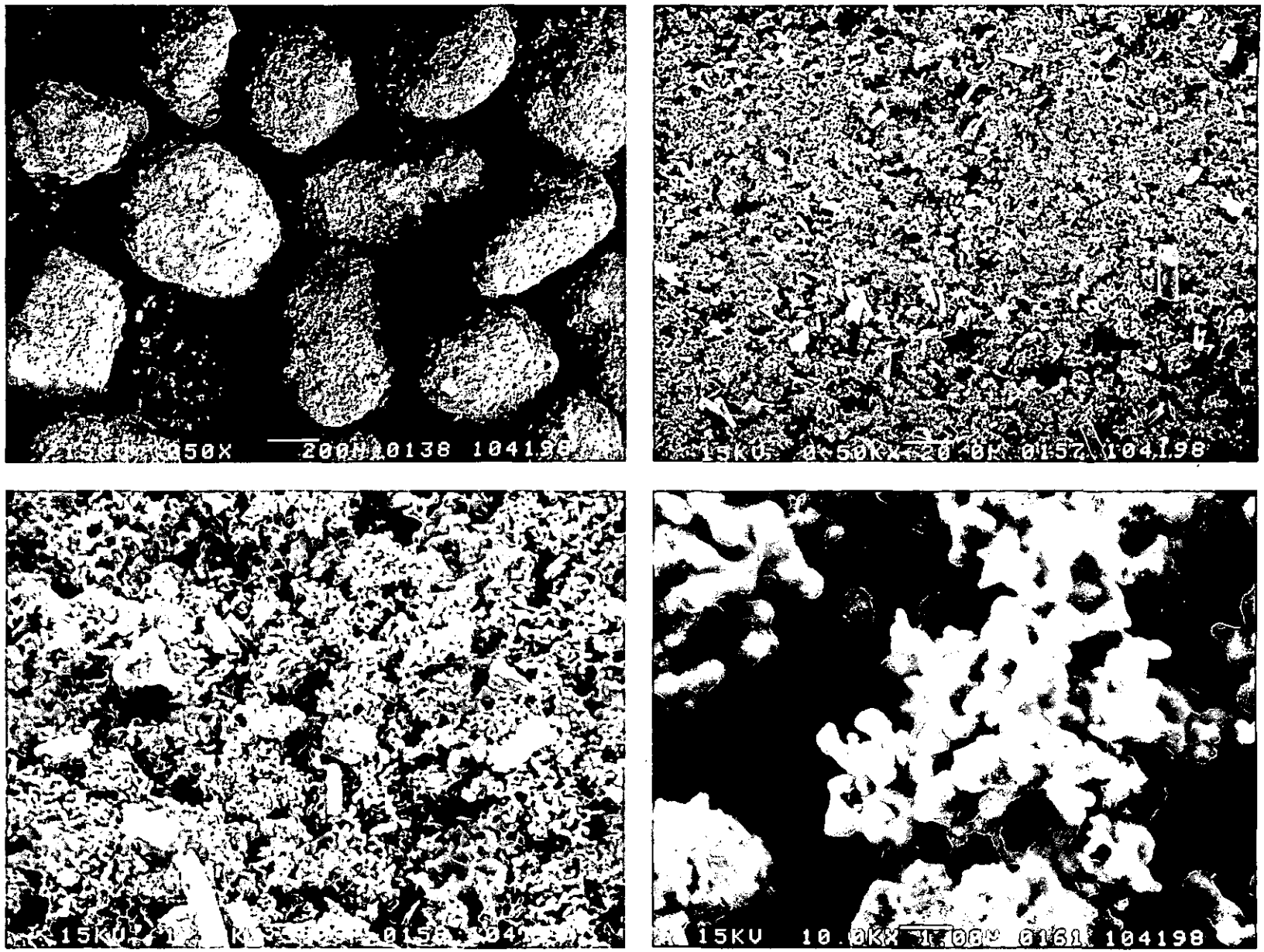
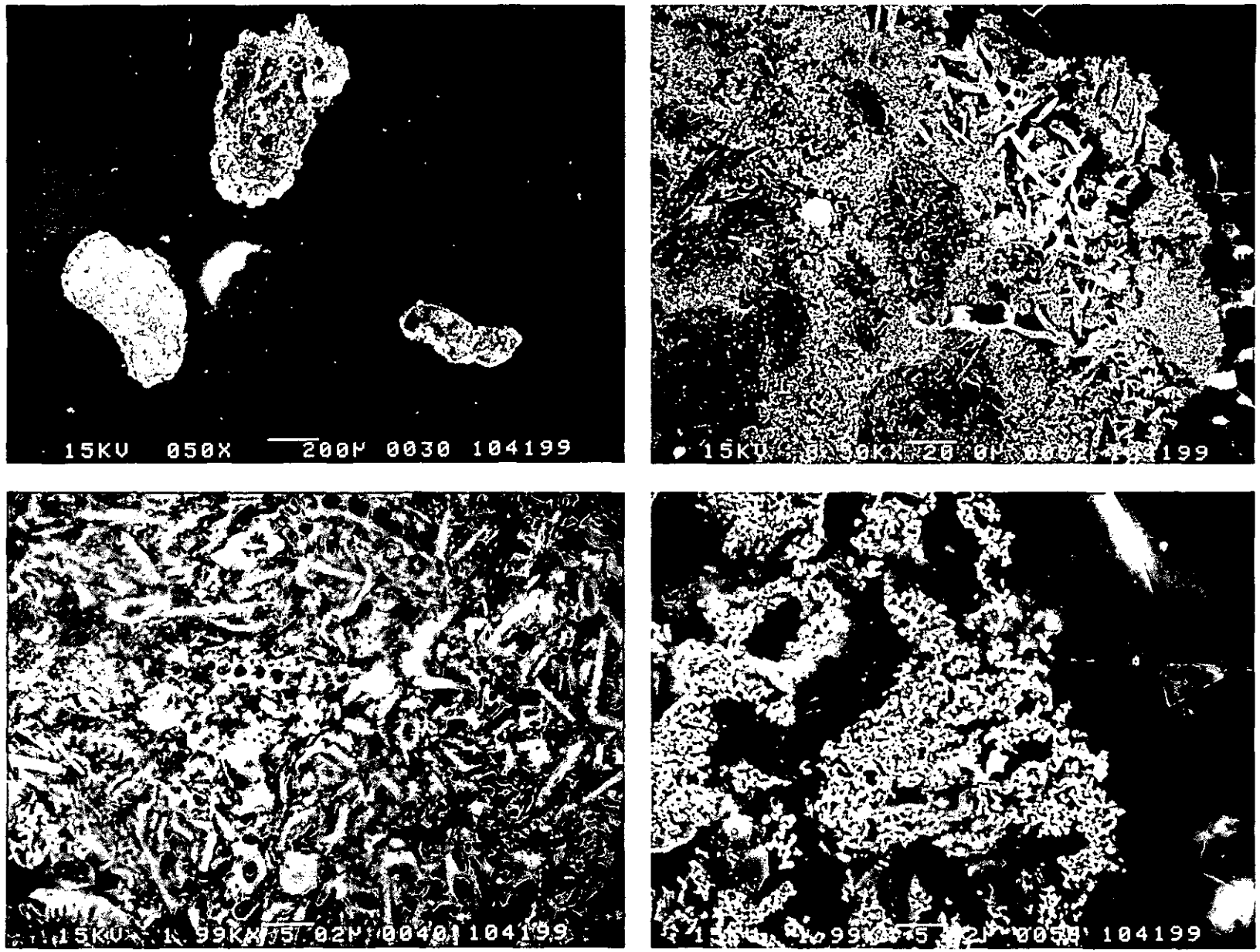


FIGURE 4. Loose Particles of 51.2 Pd/K



Interior

Edge

FIGURE 5. Cross Sections of 51.2 Pd/K

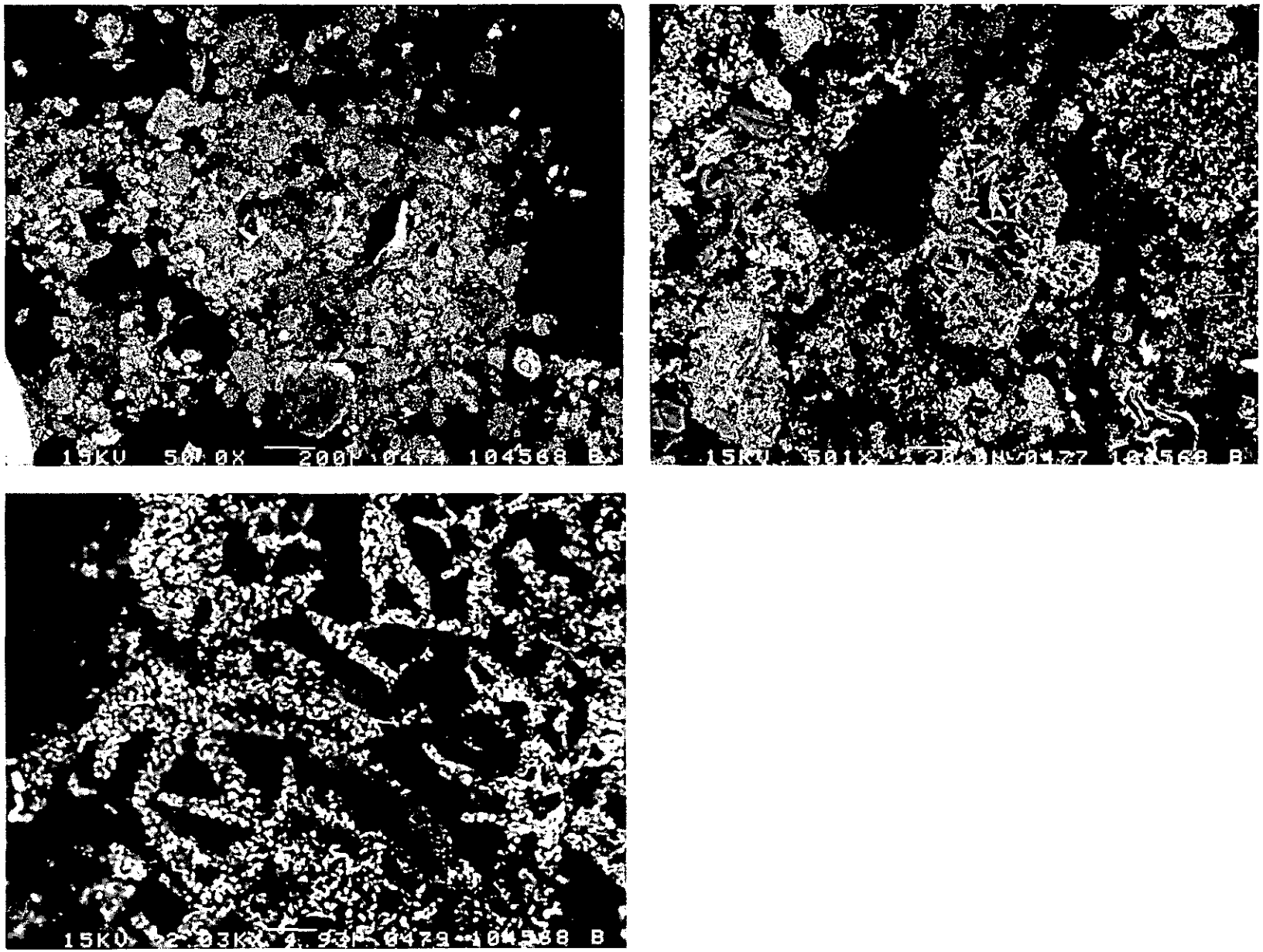


FIGURE 6. Fine Particles (<300 µm) from 51.2 Pd/K

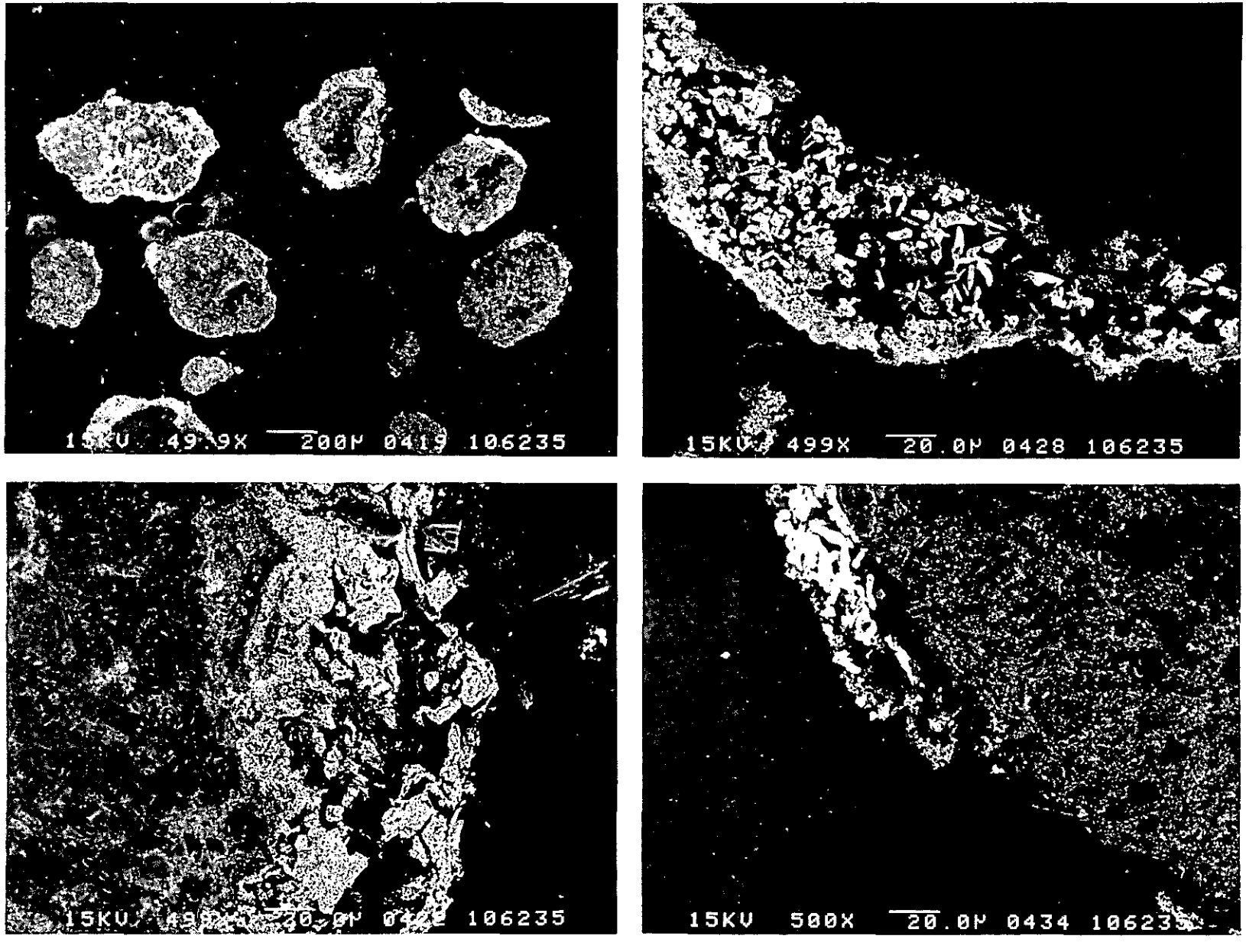


FIGURE 7. 51.2 Pd/K Cycled 5 Times

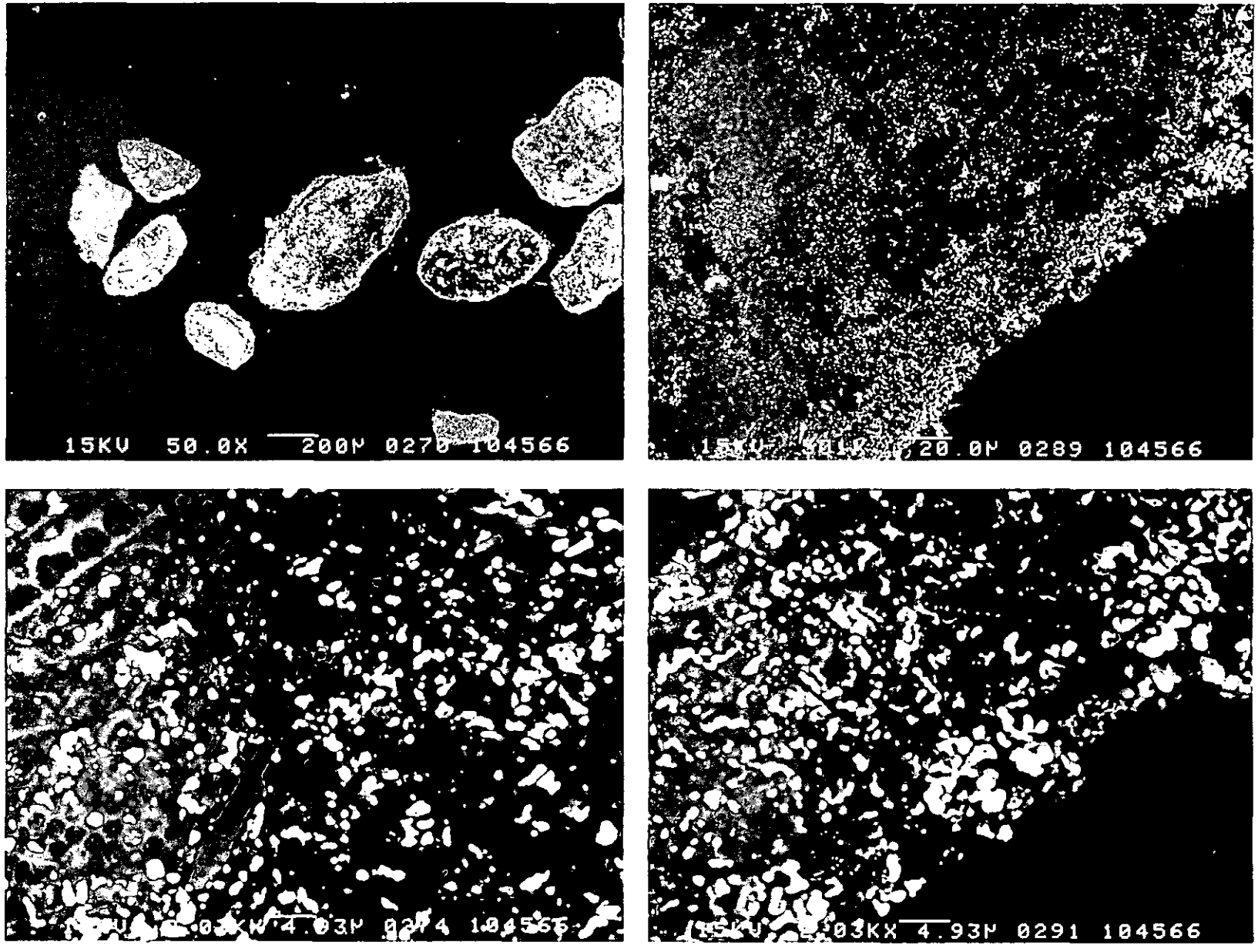
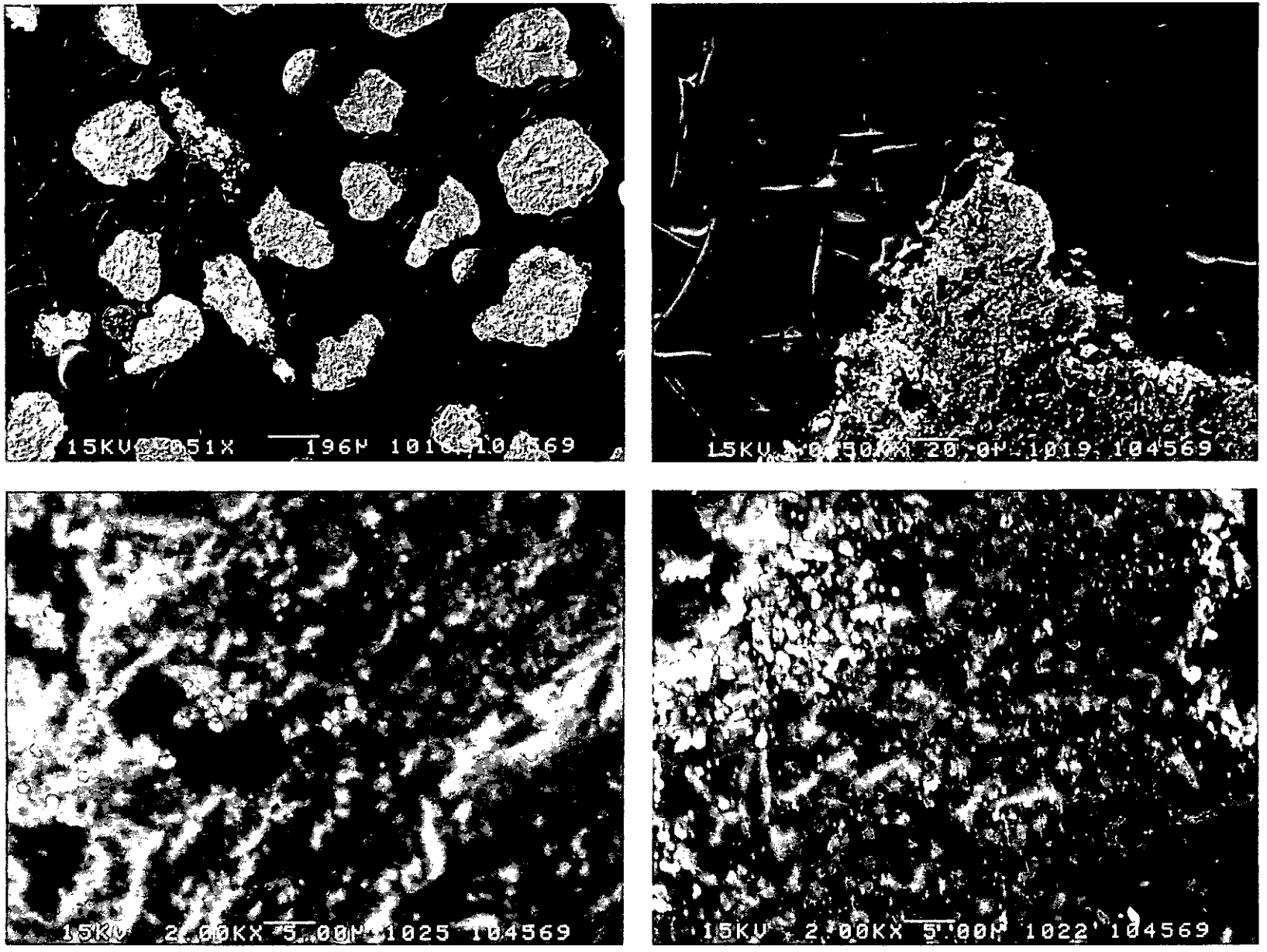


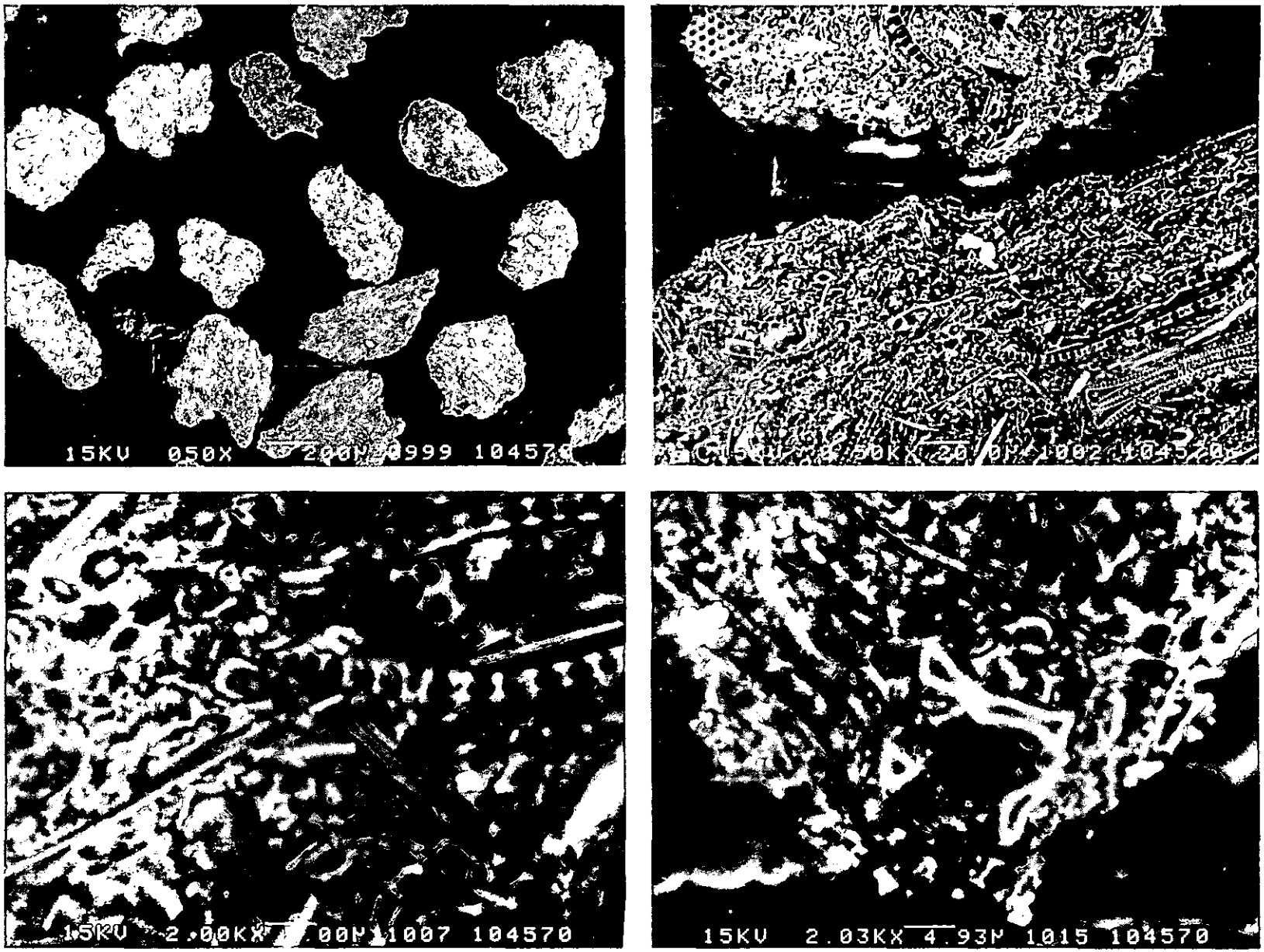
FIGURE 8. 73 Pd/K



Interior

Edge

FIGURE 9. 10X Pd/K (Approx 4 Weight Percent Palladium)



Interior

Edge

FIGURE 10. 2X Pd/K (Approx 0.5 Weight Percent Palladium)

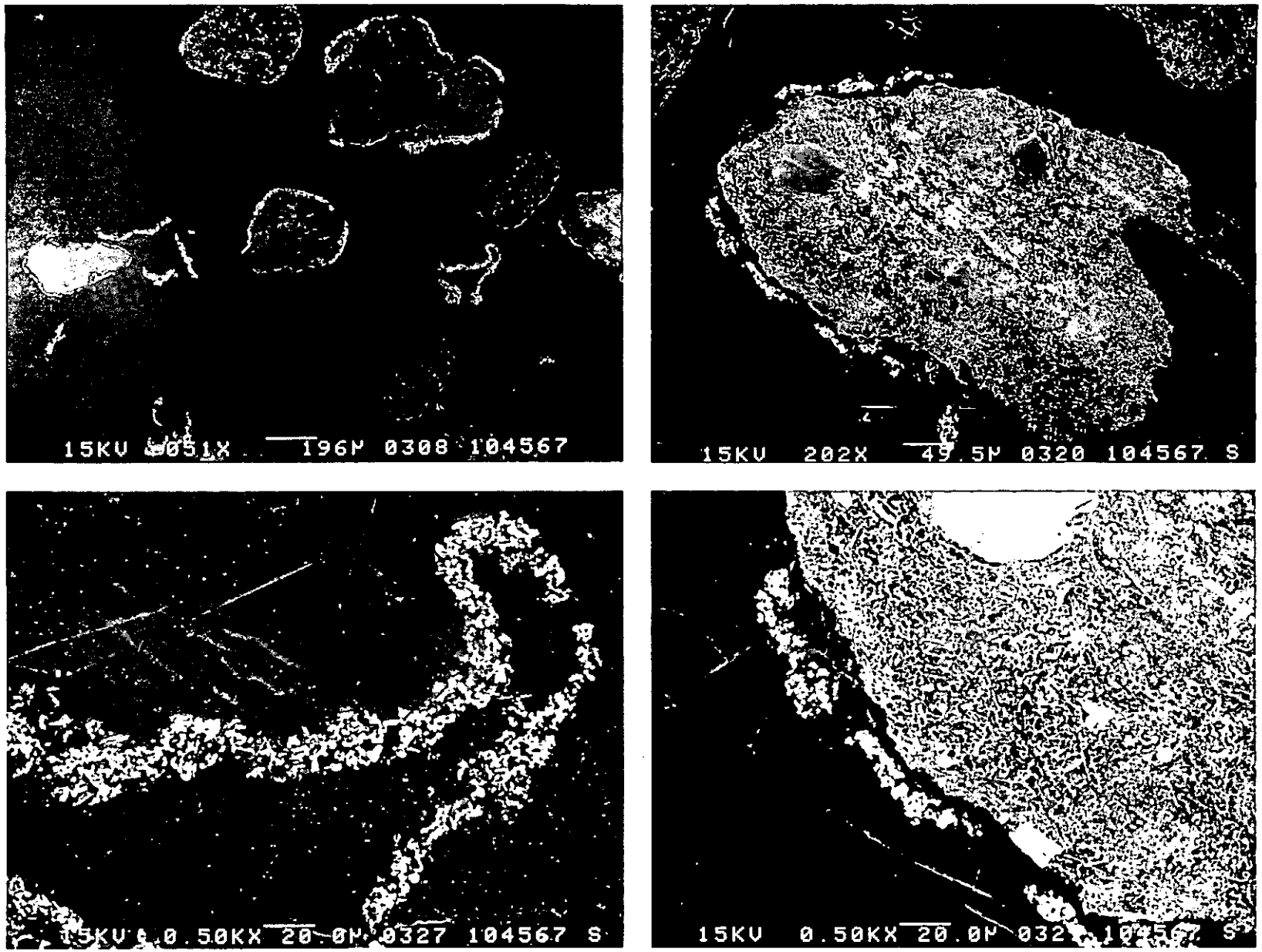


FIGURE 11. 48.4 Pd/K Cycled 250 Times

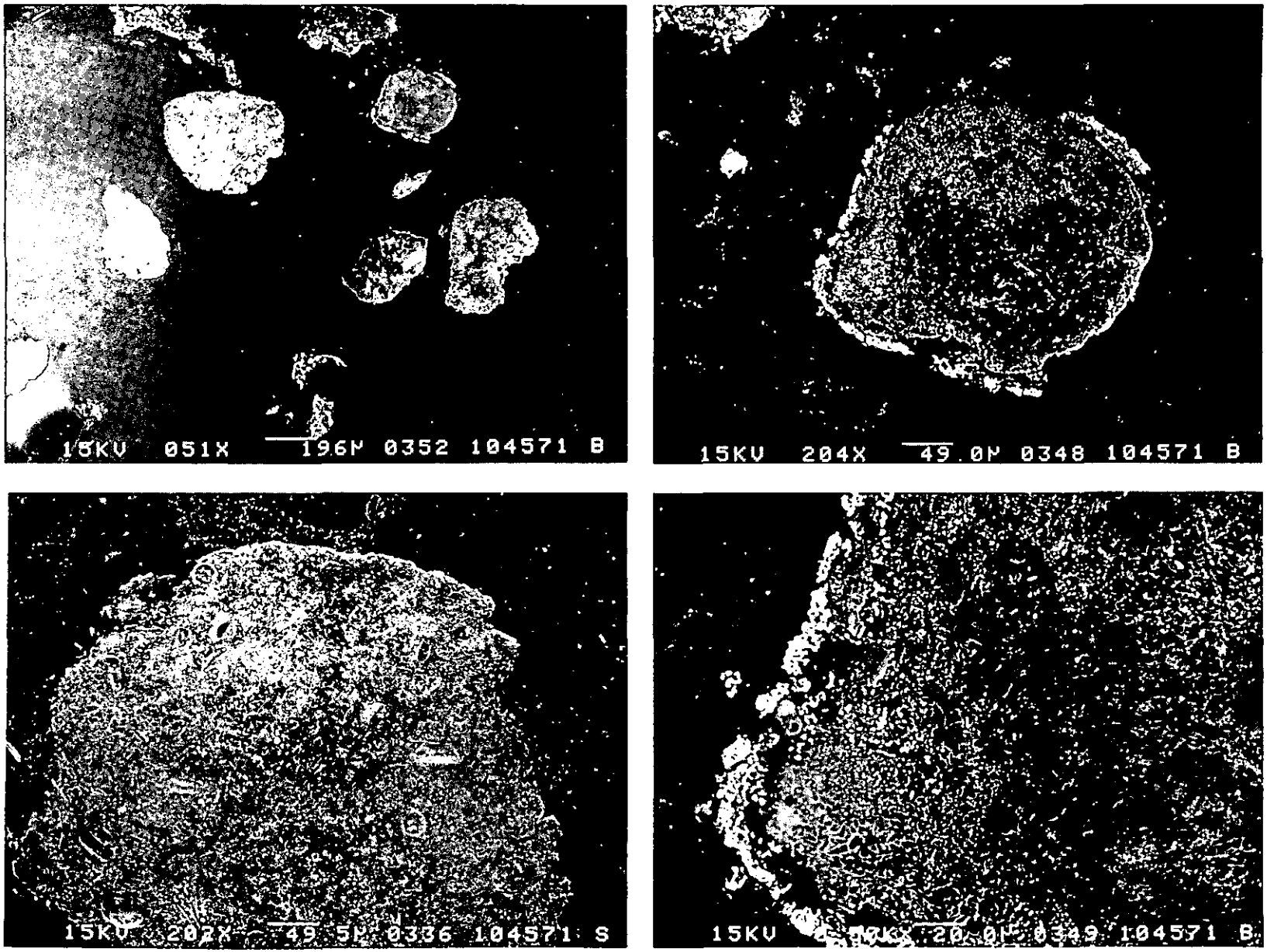
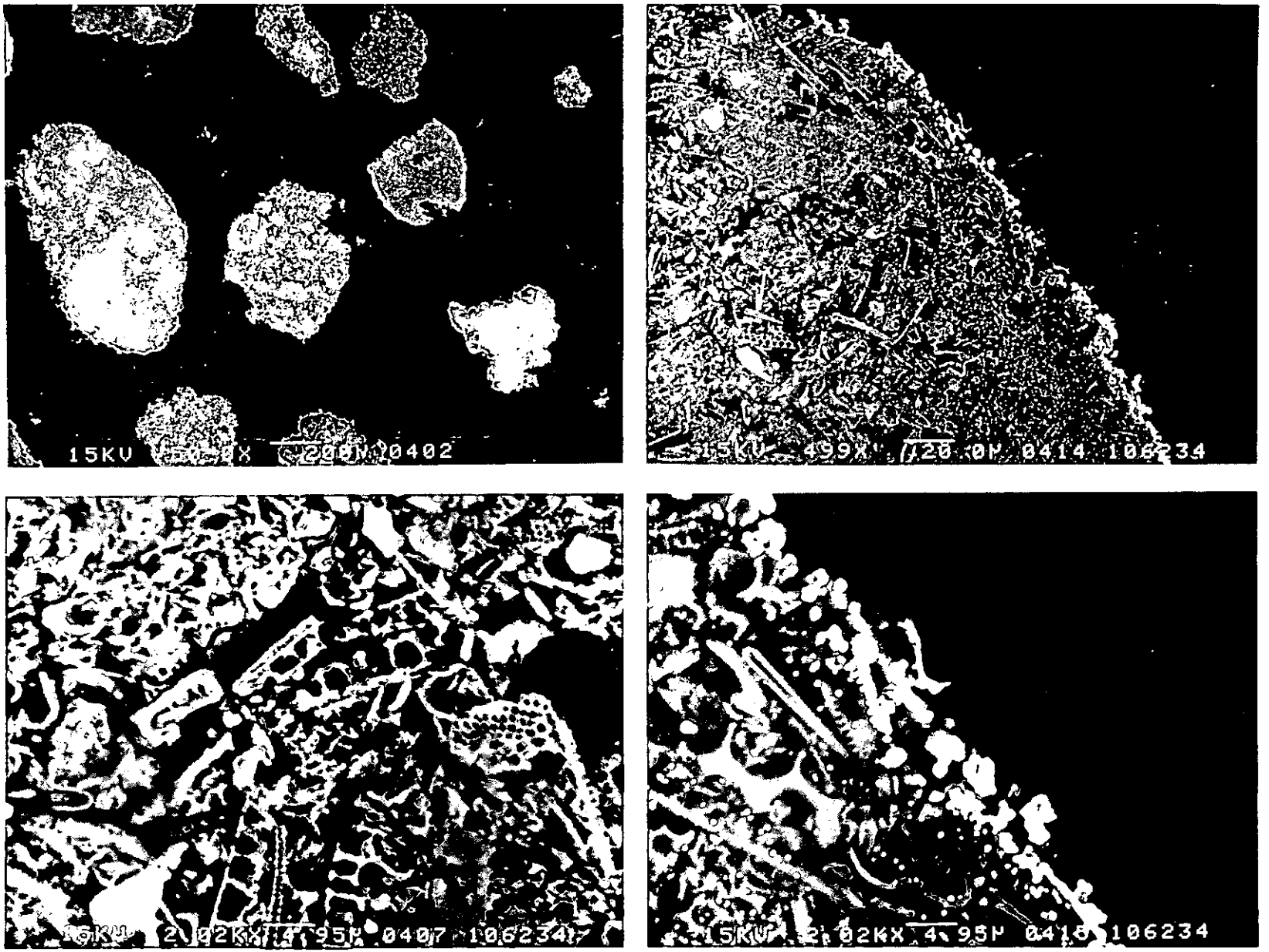


FIGURE 12. 55 Pd/K from 80°C Isotherm Test



Interior

Edge

FIGURE 13. Pd/K-PTDN (25-30 Weight Percent Palladium)