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**WESTINGHOUSE SAVANNAH RIVER COMPANY  
INTER-OFFICE MEMORANDUM**

January 29, 1991

TO: T. Motyka, 773-A

FROM: W. C. Mosley, 773-A

*WC Mosley* <sup>AL</sup> RECORD COPY**Pd/k FOR RTF AND 232-H TCAP UNITS (U)****INTRODUCTION**

The Thermal Cycling Absorption Process (TCAP) will be used in the Replacement Tritium Facility (RTF) and 232-H Tritium Facility for separation of hydrogen isotopes. These TCAP units will be filled with palladium deposited on kieselguhr (Pd/k) that has been heat treated to reduce particle breakdown and sieved to remove particles smaller than 50 mesh (300 $\mu$ m). This memorandum describes experiences with Pd/k in SRL TCAP units, studies of effects of heat treatment on Pd/k, heat treatment Pd/k for RTF and 232-H TCAP units, and future Pd/k support.

**SUMMARY**

Pd/k ordered for several applications in the RTF, including TCAP, was received at SRL in April 1989. Shortly thereafter, flow restriction caused by breakdown of the Pd/k particles was detected during operation of a TCAP unit in the Advanced Hydride Laboratory (AHL). Subsequent research at SRL showed that heating Pd/k at 1100°C in air for 2 hours greatly reduces mechanical breakdown. Based on these favorable results, sufficient Pd/k was heat treated to fill RTF and Building 232-H TCAP units.

Reserve Pd/k is being procured for the RTF. This Pd/k can be heat treated if needed for TCAP. Processes have been developed for making more breakdown resistant Pd/k and alternatives if problems with heat treated Pd/k are identified in operations of AHL, RTF or 232-H TCAP units.

*T. Motyka* 3/1/91  
Derivative Classifier

## DISCUSSION

### Pd/K for SRL

During 1983-1984, SRL worked with Ionex Research Corporation to develop a process for producing Pd/K. Kieselguhr was in the form of Chromosorb P (AW), an acid-washed calcined diatomite purchased from Manville Sales Corporation. An ammoniacal palladium chloride solution was deposited onto the kieselguhr particles and reduced to palladium metal by heating in hydrogen.[1] Table 1 lists the orders placed for Pd/K used in SRL research and development of several applications including TCAP. Early orders of SRL Pd/K were made using 30-60 mesh (250-600  $\mu\text{m}$ ) Chromosorb P which is the standard particle size range sold by Manville. Attempts to use this Pd/K in an SRL TCAP unit were unsuccessful because of flow restriction caused by the presence of a large percentage of small particles.

### Breakdown of SRL Pd/K

The Advanced Hydride Laboratory (AHL) was built in 1986-1987 to demonstrate RTF metal hydride technology by integration of various unit operations into an overall process. The Pd/K used in AHL TCAP units was made with specially ordered 30-40 mesh (425-600 $\mu\text{m}$ ) Chromosorb P (AW) to avoid the flow restriction problem (Figure 1). However, testing of a stainless steel TCAP unit in the AHL had to be interrupted because of flow restriction. Sieve analysis of the Pd/K removed from this TCAP unit is compared with results for the "as-received" AHL Pd/K in Figure 2. The severe breakdown of the Pd/K particles is evident from these results. Scanning electron microscopy (SEM) of cross-sectioned particles from the AHL TCAP test (Figure 3) showed that breakdown was caused by separation of the outer palladium-rich layer from the inner core with little palladium. The AHL TCAP Pd/K was sieved to remove particles smaller than 50 mesh ( $< 300\mu\text{m}$ ) and the fraction larger than 50 mesh ( $> 300\mu\text{m}$ ) was returned to the AHL TCAP unit for further testing. This fraction contained only 40% palladium (by weight) compared to 51.2% for the "as-received" AHL Pd/K. This measurement confirmed that the particles smaller than 50 mesh produced by breakdown were from the outer palladium-rich layer.

Because of the adverse effects of Pd/K breakdown on TCAP operation, several investigations were made of the mechanical integrity of Pd/K particles under various conditions that occur during TCAP. A study of the stability of AHL Pd/K during 9,000 cycles of absorption and desorption of hydrogen revealed breakdown (Figure 2) similar to that observed for the AHL TCAP Pd/K.[2] SEM revealed that the outer palladium-rich layer was missing on most of the Pd/K particles (Figure 4). Some of this breakdown is attributed to cracking at the interface between the outer palladium-rich layer and the core caused by stresses introduced by expansion and contraction of the palladium during absorption and desorption of hydrogen. A second type of breakdown is attrition caused by impacts between moving Pd/K particles during transfer of hydrogen isotopes on and off of a TCAP column. Attrition causes a wearing or chipping away of the outer palladium-rich layer on the Pd/K particles. A drop test was developed to simulate this type of breakdown.[3] Sieve analysis of as-received AHL Pd/K subjected to the drop test also revealed severe particle breakdown as shown in Figure 2. The attrition rate is expected to decrease at the interface since the degrading effects of the palladium chloride deposition process cause the strength of the outer palladium-rich layer to be lower than that of the kieselguhr core.

#### Heat Treatment of AHL Pd/K

Small batches of AHL Pd/K were heat-treated at 800°C for 1 hour or 1100°C for 1/2 hour and subjected to drop testing.[3] Particle size distributions of samples from these tests are shown in Figure 2. Heating for 1 hour at 800°C in air reduced breakdown moderately during drop tests. Breakdown was almost totally eliminated by heat treatment at 1100°C for 0.5 hour in air.

A breakdown factor (BDF) was defined to quantify the breakdown of Pd/K during testing:  $BDF = 1 - (T/N)$  where T is the weight percentage of particles larger than 50 mesh (300  $\mu\text{m}$ ) for tested Pd/K and N is the corresponding value for untested Pd/K. The 50 mesh dividing point was chosen since acceptance specifications for RTF Pd/K required that at least 80% be larger than 50 mesh. Table 2 lists the breakdown factors for as-received and heat-treated AHL Pd/K subjected to drop testing and cycling in hydrogen determined from results reported in reference 3. Cycling tests caused very little breakdown of both the as-received

(BDF=0.01) and heat-treated AHL Pd/K (BDF=0.00-0.04). The drop test BDF of 0.28 for as-received AHL Pd/K was reduced to 0.16 by heat treatment at 800°C for 1 hour in air. Breakdown of AHL Pd/K during drop testing was essentially eliminated by heat treatment at 1100°C for 0.5 hour in air (BDF=0.00).

#### Pd/K for the RTF

Pd/K for the RTF was made by Ionex Research Corporation on Purchase Order AX840942 using 30-40 mesh Chromosorb P (AW) and the same palladium chloride deposition process that was used for making the AHL Pd/K. The RTF Pd/K was specified to have at least 55.0% palladium compared to 51.2% on AHL Pd/K. Characterization of RTF Pd/K has been described previously.[4]

The RTF Pd/K was received at SRL prior to the detection of flow restriction in the AHL stainless steel TCAP unit. Because of the success of heat treatment at 1100°C in eliminating breakdown of AHL Pd/K during drop testing and cycling in hydrogen, a parametric study of effects of heat treatment on breakdown during drop testing was performed with small samples of RTF Pd/K in preparation for heat treating large batches for use in RTF TCAP units. The initial goal of this study was to determine the lowest temperature and minimum heating time that would reduce the breakdown of the RTF Pd/K to that of the 30-40 mesh Chromosorb P (AW) with a BDF = 0.18 while minimizing the growth of the palladium particles. It was thought that large palladium particles could (1) slow the kinetics for absorption and desorption of hydrogen and (2) retain internal helium-3 from radioactive decay of tritium causing a time dependent change in the pressure-composition-temperature behavior of the palladium which would adversely affect the TCAP.

#### Heat Treatment of Small Batches of RTF Pd/K

Heat treatments were performed on small samples from all three lots of RTF Pd/K. Heat treatments in air were performed by heating 25-30 gram samples of Pd/K contained in alumina crucibles in a small laboratory muffle furnace. Samples were heated to the desired temperatures in about an hour. After heating, the samples were left in the furnace to cool. The furnace temperature dropped to below 200°C after about four hours.

Heat treatment in the muffle furnace caused the loose RTF Pd/K powder to sinter into a cake leaving a small gap between the cake and the crucible wall. The cake was easily pulverized by lightly brushing it on a 25 mesh (710 $\mu$ m) sieve.

Heat treatments in argon were performed with samples of about 70 grams of Pd/K contained in a 30mm-diameter fritted quartz tube that was heated in a vertical tube furnace. Argon at 0.4-1.2 cc/minute flowed upward through the bed of Pd/K. Again, the Pd/K was heated to the desired temperature in about an hour and remained in the furnace to cool after heating. The cooling rate was about the same as for the muffle furnace. After heating in argon, the Pd/K in the bottom of the tube had the gray color normally expected for Pd/K. Pd/K in the top of the tube was black. A thin layer of purple Pd/K separated the black Pd/K from the gray Pd/K. This gradation in coloration is believed to have been caused by transport of impurities by the flowing argon or different degrees of oxidation caused by back flow of air into the tube. NOTE: Heat treating of Pd/K in argon for use in TCAP was rejected because equipment for heating large batches was not available.

#### Drop Testing of Heat Treated RTF Pd/K

The drop test used to evaluate breakdown of the heat treated RTF Pd/K was a slight modification of the drop test used on the AHL Pd/K. Therefore, several samples of AHL Pd/K were tested with the modified test for comparison with results of the original drop test. Results are given in Table 3. The results for the AHL Pd/K show that the modified drop test (BDF = 0.44) is more severe than the original test (BDF = 0.28). All three lots of as-received RTF Pd/K (BDF=0.43-0.46) had the same susceptibility for breakdown as the as-received AHL Pd/K. Pd/K that was removed from the AHL TCAP and sieved to removed particles smaller than 50 mesh produced by TCAP operation were also subjected to the modified drop test. A BDF = 0.31 indicates that the susceptibility for breakdown of AHL Pd/K decreases as small particles are produced by TCAP operation. It is thought that the breakdown of Pd/K should eventually approach that of Chromosorb P (AW) with BDF = 0.18.

The modified drop testing results showed that heat treatments at 800°C in air and argon (BDF=0.37-0.41) and at 950°C in air (BDF=0.40) produced essentially no reductions in RTF Pd/K breakdown. The failures of these

heat treatments to cause significant reductions in breakdown may be related to the greater severity of the modified drop test. Moderate reduction in breakdown was produced by heating at 950°C for two hours in argon (BDF=0.29). Heating in argon rather than air prevents oxidation and promotes the sintering and growth of palladium particles needed for strengthening Pd/K particles.

Heat treatment of RTF Pd/K at 1100°C in air significantly reduced but did not eliminate breakdown (BDF= 0.08-0.23). Results for Lot 890113A1 indicate that heat treatment for 2 hours (BDF=0.17) is slightly more effective than 1/2 hour heat treatment (BDF=0.23). Also, an argon atmosphere during heat treatment for 2 hours (BDF=0.08) was more effective than air (BDF=0.17) for the reason given above. Heat treatment at 1100°C in air for 2 hours reduced the breakdown of Lots 890116A1 (BDF=0.08) and 890118A1 (BDF=0.08) more than that of lot 890113A1 (BDF=0.17). This effect may be related to more extensive structural degradation of Lot 890113A1 caused by the extended heating performed by Ionex Research Corporation to decrease the chlorine content.[4] Results for Lot 890116A1 indicate that heating at 1100°C in air for 6 hours (BDF=0.10) did not reduce breakdown beyond that achieved by heating for 2 hours.

#### Scanning Electron Microscopy of Heat Treated and Drop Tested RTF Pd/K

Scanning electron microscopy (SEM) was used to determine the effects of heat treatment and drop testing on RTF Pd/K. Loose particles of as-received Lot 890116A1 RTF Pd/K are shown in Figure 5. The outer palladium-rich layer is not continuous. Areas without this palladium-rich layer are thought to be caused by breakdown during processing or handling. The palladium distribution within the palladium-rich layer consists of closely spaced or interconnected submicrometer palladium particles supported on the porous silica of the kieselguhr. In other regions of the Pd/K the submicrometer palladium particles are distributed sparsely on the kieselguhr. This morphology is typical of as-received material from all three lots of the RTF Pd/K.

Figure 6 shows loose particles of Lot 890116A1 RTF Pd/K after heat treatment at 1100°C in air for 2 hours. At low magnifications the particles look similar to those of as-received RTF Pd/K with areas devoid of the palladium-rich layer. However, high magnification examinations show that heat treatment at 1100°C has changed the structure of the

palladium-rich layer. The closely spaced submicrometer palladium particles have sintered together and grown to form a network interlaced with the porous silica of the kieselguhr. Some of the palladium features within this network are 10-20  $\mu\text{m}$  in size. Figure 7 shows cross sections through as-received and heat treated particles of Lot 890113A1 RTF Pd/K that reveal how the submicrometer palladium particles in the palladium-rich outer layer become a network of micrometer size particles.

Apparently, it is the formation of this network that strengthens the Pd/K particles and reduces breakdown. Palladium particles show little or no growth in regions where the palladium is sparsely distributed. Again, this morphology is typical of heat treated material from all three lots of the RTF Pd/K.

Loose particles of as-received RTF Pd/K that were subjected to the modified drop test are shown in Figure 8. Particles smaller than 50 mesh (49.5%) were removed by sieving before this SEM examination. Results show the palladium-rich outer layer had been removed from most of these Pd/K particles by the drop test. Thus, breakdown causes the palladium content of large particles ( $> 50$  mesh) to decrease and that of small particles ( $< 50$  mesh) to increase. Figure 9 shows loose particles of RTF Pd/K that was heat treated at  $1100^{\circ}\text{C}$  in air for 2 hours and subjected to the modified drop test. Most of these particles retained some of the palladium-rich outer layer. This SEM examination confirms the drop test results that heat treatment at  $1100^{\circ}\text{C}$  strengthens Pd/K against mechanical breakdown.

#### Other Effects of Heat Treatment of Small Batches of RTF Pd/K

Samples of RTF Pd/K from some of the small batch heat treatments were submitted for chlorine analyses by neutron activation analysis. Results are given in Table 4 and show that heat treatment at  $1100^{\circ}\text{C}$  greatly reduces the chlorine content of Pd/K.

Weight changes occurred during heat treatments of small batches of RTF Pd/K as indicated in Table 5. Heating in air at  $800^{\circ}\text{C}$  caused weight gains of up to 1.5% because of oxidation of some of the palladium. Palladium oxide (PdO) was detected in these samples by x-ray diffractometry. Only a slight weight gain of 0.1% occurred during heating in air at  $950^{\circ}\text{C}$ . Heating at  $1100^{\circ}\text{C}$  caused small weight changes (both gains and losses) from -0.13% to +0.10%. Heating in argon at 800, 950 and  $1100^{\circ}\text{C}$  caused weight losses up to 0.71%. Apparently, heat treatment causes both weight

gains from oxidation of palladium and weight losses from volatilization of some impurity, possibly a chloride.

As shown in Table 5, heat treatment increased the Pd/K tap density. The increase from heating at 800 and 950°C was only slight, from 0.75 to 0.82-0.91 g/cc. However, heating at 1100°C caused a significant increase to 0.92-1.04 g/cc. This increase in tap density is attributed to shrinkage of the Pd/K particles which is thought to be caused mainly by densification of the outer palladium-rich layer on each particle. The 33% increase in Pd/K tap density caused by 1100°C heat treatment must be considered when filling TCAP vessels.

Tests were performed with both as-received RTF Pd/K and RTF Pd/K that was heat treated at 1100°C in air to compare the kinetics for protium displacement of absorbed deuterium and deuterium displacement of absorbed protium.[5] No significant differences were detected. These results show that the increase in the size of some of the palladium particles caused by heat treatment at 1100°C does not affect hydrogen isotope exchange kinetics. Also, no palladium oxide (PdO) was detected by XRD in samples of the heat treated Pd/K that were used in the hydrogen isotope exchange tests. The several cycles of hydrogen absorption-desorption between room temperature and 120°C given to the heat treated Pd/K prior to isotope exchange testing apparently reduced the oxide. This results indicates that palladium oxide can be removed from heat treated Pd/K during activation of TCAP units.

#### Pd/K for RTF and 232-H TCAP Units

Although an excess of Pd/K was procured for the RTF, there was an insufficient quantity to meet all the RTF needs and have enough remaining to fill the TCAP vessel for Building 232-H. Therefore, some SRL Pd/K which had not been used in ways that would cause contamination or significant particle breakdown was heat treated along with the RTF Pd/K to produce a single large batch of Pd/K so that material with the same characteristics could be used in TCAP units in both the RTF and Building 232-H. This would allow operation of the 232H TCAP unit to be representative of operations of RTF TCAP units. Since the 232-H TCAP unit should be in operation with tritium before the RTF units, any problems that might arise with use of this Pd/K could be identified in time to correct them before they occur in the RTF.

## Heat Treatment of Pd/K for RTF and 232-H TCAP Units

Pd/K for use in RTF and 232-H TCAP units was heat treated in one kilogram batches at 1100°C in air for 2 hours. The Pd/K was contained in alumina crucibles with capacities of 1.76 liters each (Alfa Ceramics, catalog number 201-22145-1600). Each crucible was covered with an alumina disc lid to prevent contamination of the Pd/K by material from the furnace lining that might become detached during heating. The heating was performed by the Materials Technology Section using a large muffle furnace in Lab C-118 of Building 773-A. Table 6 gives a summary of these heat treatments. After an initial trial with a single batch, two batches were heated at a time with one crucible in the front of the furnace near the door and another in the back. Batches of heat treated Pd/K are identified by a six digit number YYMMDD indicating the year (YY =90), month (MM) and day (DD) of the heat treatment followed by an F for "front" or a B for "back".

The heating cycle consisted of heat up at about 200°C per hour to avoid thermal shock that would crack the large alumina crucibles, a 3 hour hold with the furnace temperature at 1140°C, and a slow cool down. Figure 10 shows a typical temperature-time profile for heating batch 900619. The furnace controller was adjusted manually and the set point temperature was increased 35°C every 10 minutes up to 1140°C. To ensure that the entire large batch of Pd/K was heat treated at or above 1100°C, a final set point of 1140°C was used since the temperature in the center of the batch of Pd/K was about 30°C lower than the furnace temperature. During heat up, the furnace temperature lagged the set point temperature by about 5 minutes. Also, the temperature at the center of the Pd/K lagged the furnace temperature by 30-60 minutes. The longest lag of about 60 minutes followed a thermal arrest near 850°C which is attributed to oxidation of part of the palladium. Based on the small weight gains measured for 1100°C heat treatments of small batches of Pd/K, palladium oxide appears to be thermally decomposed on subsequent heat up from 850°C to 1100°C. Because of the 60 minute lag, the Pd/K was heated for 3 hours after the furnace temperature reached 1140°C to ensure a heat treatment time of 2 hours. The initial trial showed that the natural cool down rate of the furnace did not exceed the maximum 200°C per hour that would crack the crucibles from thermal shock. Therefore, after the 3 hour heat treatment, the furnace temperature set point was adjusted to 25°C and the furnace allowed to cool naturally. A cool down period of at least 20 hours was required to reach a temperature below 70°C when the crucibles could be unloaded from the furnace.

### Characteristics of Large Batches of Heat Treated Pd/K

Heat treatment of the large batches of Pd/K caused weight gains up to 1.55% as shown in Table 6. These weight gains are attributed to oxidation of part of the palladium during the slow cool down (PdO was detected by x-ray diffractometry). Pd/K batches from the crucibles in the front of the furnace near the door where exposure to in-leakage of air would be highest showed the largest weight gains.

Heat treatment of the large batches of Pd/K caused the formation of loosely sintered cakes of Pd/K which were easily pulverized by lightly brushing on a 750  $\mu\text{m}$  sieve. Tap density, percentage of particles larger than 50 mesh, and chlorine content were determined for each batch (Table 6). The heat treatment increased the Pd/K tap densities from 0.75-0.86 to 0.94-1.05 grams per cubic centimeter. Percentages of particles larger than 50 mesh ranged from 83.7% to 97.5%. Chlorine contents in all the large batches of heat treated Pd/K were less than the 250 ppm maximum as required by Site Specification 5992.[6] (NOTE: Retesting of several heat treated Pd/K batches revealed that some early analyses may have given erroneously high chlorine contents because of chlorine contamination in some of the capsules used to contain the samples for neutron activation analysis. Later analyses generally detected no chlorine.)

### Sieving and Blending of Heat Treated Pd/K for TCAP Units

Small particles produced during preparation, handling and Pd/K are known to segregate from the larger particles and agglomerate to restrict gas flow through the Pd/K and plug filters in TCAP vessels. Therefore, the heat treated Pd/K to be used in the RTF and 232-H TCAP units was sieved to remove particles smaller than 50 mesh. It is anticipated that use of heat treated and sieved Pd/K will prevent or significantly delay the onset of flow restriction or plugging in RTF and 232-H TCAP units. After sieving, the large batches of heat treated Pd/K were blended together to produce a composite mixture of sufficient quantity to fill both the RTF and 232-H TCAP units.

### Characteristics of Pd/K for RTF and 232-H TCAP Units

SEM images of particles of the heat treated, sieved and blended Pd/K for the RTF and 232-H TCAP units are shown in Figure 11. As expected, they look the same as those from similar heat treatment of small batches shown in Figure 6. Heating at 1100°C caused the submicrometer palladium particles in the palladium-rich outer layer to sinter together and grow forming a network that strengthens the particles against breakdown.

Samples of the Pd/K for the RTF and 232-H TCAP units were analyzed for palladium content, chlorine content, particle size distribution, and powder density. Results are given in Table 7 along with the specifications for the RTF Pd/K.[7]

The palladium content was determined by HTS using hydrogen absorption to be  $51.3 \pm 0.2\%$ . [8] During this determination, the first cycle of hydrogen absorption and desorption indicated that this Pd/K contained about 1% oxygen as palladium oxide. The palladium oxide was reduced and the oxygen removed as H<sub>2</sub>O by this first cycle of hydrogen absorption and desorption. This result shows that the palladium oxide on the Pd/K can be removed during activation of the RTF and 232-H TCAP units by a single cycle of absorption and desorption of deuterium. The palladium content of 51.3% is slightly less than the specified 55.0% minimum for RTF Pd/K.[7] There is no specification on oxide content.

No chlorine was detected in the heat treated, sieved and blended Pd/K by the SRL Analytical Development Section (ADS) using californium neutron activation analysis with a chlorine detection limit of about 50 ppm. Therefore, this Pd/K meets the specified 250 ppm maximum required by Site Specification No. 5992 and the RTF Pd/K procurement specification. [6,7]

The particle size distribution of the heat treated, sieved and blended Pd/K was determined by ADS using sonic sieve analysis. 98.9% of the particles were within the 30-50 mesh (300-600µm) range. Thus, this Pd/K meets the technical requirement of the RTF Pd/K procurement specification that at least 80% of the product shall be between 30 and 50 mesh.[7]

HTS determined the pour density to be 0.84 g/cc and the tap density to be 0.94 g/cc. This tap density value is less than the average tap density of  $1.01 \pm 0.03$  g/cc of the individual large batches of 1100°C heat treated Pd/K because of the removal of particles smaller than 50 mesh by sieving. There are no specifications on Pd/K powder densities. The TCAP units were designed to use Pd/K with a tap density of 0.80 g/cc and containing 50% palladium which corresponds to a palladium density of 0.40 g/cc. The heat treated, sieved and blended Pd/K with a tap density of 0.94 g/cc and a palladium content of 51.3% has a palladium density of 0.48 g/cc. Thus, a smaller volume of the heat treated, sieved and blended Pd/K will be needed to achieve the design capacity of the RTF and 232-H TCAP units.

#### Filling of the 232-H TCAP Unit

One-third of the heat treated, sieved and blended Pd/K was used to fill the TCAP unit for Building 232-H on September 13, 1990, according to procedure PX-09-10-90.

#### Filling of the RTF TCAP Units

The remaining two-thirds of the heat treated, sieved and blended Pd/K was used to fill two RTF TCAP units on January 15, 1991, according to procedure WSRC-03-RTF-H-50004.

#### Additional Testing of Heat Treated Pd/K

Small scale tests are being performed to determine the breakdown of 1100°C heat treated Pd/K in reversing gas flow streams, during fluidization and during cyclic absorption/desorption of protium. These tests will simulate the conditions occurring during TCAP operation better than drop testing. Also, an order has been submitted to procure additional Pd/K from Ionex Research Corporation for use in full scale tests in a TCAP unit in the AHL. The Pd/K for these full scale tests will be heat treated and sieved to produce material like that prepared for the RTF and 232-H TCAP units.

Accurate isotherm measurements (pressure-composition-temperature) are being made for the absorption and desorption of protium on 1100°C

heat treated Pd/K and as-received RTF Pd/K for comparison with results with a reference palladium powder. These test should reveal the effects of heat treatment on the thermodynamics of absorption and desorption of protium.

The formation of internal helium-3 in palladium from the radioactive decay of absorbed tritium has been found to change the thermodynamics of absorption/desorption of hydrogen isotopes.[9] These changes will be influenced by the retention of the helium-3 which is a function of the crystallite size of the palladium which, in turn, is affected by heat treatment. Therefore, small samples of 1100°C heat treated Pd/K and as-received RTF Pd/K will be charged with tritium in the Materials Test Facility and cycled periodically to determine how in-growth and retention of helium-3 influence absorption and desorption of tritium.

#### Reserve Pd/K for the RTF

Requisitions have been submitted to procure palladium chloride (B44655) and 30-40 mesh Chromosorb P (AW) (B44654) for use in making additional Pd/K as reserve material for the RTF. This reserve Pd/K will be made by Ionex Research Corporation (B44653) using the same process as used previously for making Pd/K for SRL and the RTF. The reserve Pd/K will be stored at SRL so it will be readily available if needed in the RTF. It can be heat treated if needed for TCAP.

#### An Improved Form of Pd/K

A chlorine-free process has been developed to produce Pd/K with palladium distributed uniformly throughout the kieselguhr. This improved form of Pd/K shows about the same resistance to breakdown during modified drop testing (BDF = 0.12) as RTF Pd/K heat treated at 1100°C for at least 2 hours (BDF = 0.08 - 0.17). Details of the preparation of the improved form of Pd/K will be the subject of a future report.

#### Alternatives to Pd/K

Palladium deposited on aluminum oxide has been proposed as an alternative to Pd/K. However, palladium deposited on "activated" alumina with a high specific surface area did not function properly in early

hydrogen absorption/desorption tests at SRL. X-ray diffractometry of this "activated" alumina showed it to have the poorly crystallized structure of gamma ( $\gamma$ )- $\text{Al}_2\text{O}_3$  which is a transition alumina containing hydroxyl ions.[10] Therefore, the undesirable behavior observed in the early tests is attributed to the hydroxyl ions interfering with hydrogen absorption and desorption.

Another chlorine-free process similar to the one used to make the improved form of Pd/K has been used to deposit palladium on particles of porous, sintered alumina procured as SA 5421 from the Norton Company. The aluminum oxide form in this sintered alumina is highly crystallized  $\alpha$ - $\text{Al}_2\text{O}_3$ , corundum, that is free of water and hydroxyl ions. Use of this sintered alumina is not expected to interfere with hydrogen absorption and desorption. However, alumina-supported palladium, but not silica-supported palladium, has been found to have different hydrogen absorption kinetics than unsupported palladium at high hydrogen contents.[11]

Palladium has been deposited on other candidate support materials in small scale experiments. Larger quantities of alternatives may be prepared for further evaluation depending on the behavior of heat treated Pd/K in additional testing and during AHL, RTF and 232-H TCAP operations. Details of the deposition of palladium on SA 5421 and other support materials will be the subject of a future report.

## **CONCLUSIONS**

Heat treatment at 1100°C for 2 hours in air was determined to reduce mechanical breakdown of Pd/K so that it could be used in TCAP units. Sufficient Pd/K has been heat treated to fill TCAP units in the RTF and Building 232-H. The heat treated P/K was sieved to remove particles smaller than 50 mesh (300  $\mu\text{m}$ ). This Pd/K meets the technical requirements of the procurement specifications concerning particle size distribution and chlorine content but contains 51.3 % palladium rather than the required minimum of 55.0 %.[7] However, an increase in tap density during heat treatment compensates for the low palladium content so that the TCAP vessels can be filled with the required amount of palladium.

Heat treated Pd/K is undergoing additional testing. Processes for making an improved form of Pd/K and alternatives with palladium deposited other supports have been developed and can be used to produce large quantities of these materials if problems are identified in testing or are experienced with the use of heat treated Pd/K in TCAP units.

### **ACKNOWLEDGEMENTS**

Many people contributed to this study of the effects of heat treatment on Pd/K and the preparation of Pd/K for the RTF and 232-H TCAP units. John Scogin of HTS performed the modified drop testing. Laura Feezel and Joyce Hunter of ADS determined particle size distributions of sonic sieve analysis. Glenda Fulmer determined chlorine contents by californium neutron activation analysis. Art Jurgensen and Roy Howell of ADS analyzed samples by x-ray diffractometry. Tom Walters of HTS determined palladium and oxygen contents using hydrogen absorption. Kit Heung performed the hydrogen isotope exchange kinetics tests. Heat treating of the large batches of Pd/K was performed by Sam Brunson and Tommy Sims.

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4. W. C. Mosley, Palladium Deposited on Kieselguhr (Pd/K) for the Replacement Tritium Facility (RTF) - (U), WSRC-TR-90-24, January 11, 1990
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7. W. C. Mosley, Procurement Specification for Palladium Deposited on Chromosorb P (AW), No. WCM-3, February, 11, 1988, Revision #1, WSRC-TR-90-343, August 2, 1990.
8. R. T. Walters, Determination of Weight Percent Palladium on Palladium/Supports (Pd/S), DPST-88-898, October 17, 1988.
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**TABLE 1****SPECIFICATIONS FOR Pd/K USED IN SRL**

<b><u>ORDER</u></b>	<b><u>DATE</u></b>	<b><u>QUANTITY</u></b>	<b><u>Pd</u></b> %	<b><u>Cl</u></b> ppm	<b><u>PARTICLE SIZE</u></b>
641434	11/15/83	100L	≥51	NS*	≤2w/o smaller than 80 mesh
654558	4/13/84	20L	≥51	<250	≤2w/o smaller than 80 mesh
654559	4/13/84	50L	≥51	<250	≤2w/o smaller than 80 mesh
667693	5/4/84	25L	50	NS*	Made with 30-60 mesh Chromosorb P (AW)
767302 (AHL Pd/K)	9/2/86	50L	51-53	<250	Made with 30-40 mesh Chromosorb P(AW)

\* NS = Not Specified

**TABLE 2****BREAKDOWN OF AHL Pd/K**

<b><u>HEAT TREATMENT</u></b>	<b><u>TEST</u></b>	<b><u>BREAKDOWN FACTOR*</u></b>
None	Drop Test	0.28
	20 Cycles in H <sub>2</sub>	0.01
800°C, 1 Hour	Drop Test	0.16
	20 Cycles in H <sub>2</sub>	0.04
1100°C, 0.5 Hour	Drop Test	0.00
	20 Cycles in H <sub>2</sub>	0.00
	100 Cycles in H <sub>2</sub>	0.01
	1000 Cycles in H <sub>2</sub>	0.00
* BDF = 1 - (T/N)	T = w/o >50 mesh after test N = w/o >50 mesh for no test	

TABLE 3

## AHL AND RTF Pd/K BREAKDOWN DURING MODIFIED DROP TESTING

<u>IDENTIFICATION</u>	<u>HEAT TREATMENT</u>	<u>BREAKDOWN FACTOR</u>
AHL Pd/K	None	0.44
Lots 870224 and 870416	1100°C, 2 hours, air	0.17
Pd/K removed from AHL stainless steel TCAP, sieved +50 mesh	None	0.31
RTF Pd/K	None	0.43
Lot 890113A1	800°C, 1/2 hour, air	0.41
	800°C, 2 hours, air	0.37
	800°C, 2 hours, argon	0.39
	950°C, 1 hour, air	0.40
	950°C, 1 hour, argon	0.29
	1100°C, 1/2 hour, air	0.23
	1100°C, 2 hours, air	0.17
	1100°C, 2 hours, argon	0.08
RTF Pd/K	None	0.44
Lot 890116A1	1100°C, 2 hours, air	0.08
	1100°C, 6 hours, air	0.10
RTF Pd/K	None	0.46
Lot 890118A1	1100°C, 2 hours, air	0.08
Chromosorb P (AW) 30-40 mesh, Lot 202	None	0.18

TABLE 4

**REDUCTION OF CHLORINE IN RTF Pd/K CAUSED BY HEAT  
TREATMENTS OF SMALL BATCHES**

<b><u>IDENTIFICATION</u></b>	<b><u>HEAT TREATMENT</u></b>	<b><u>CHLORINE CONTENT</u></b> ppm
RTF Pd/K Lot 890113A1	None 1100°C, 2 hours, air 1100°C, 2 hours, argon	311 0 3
RTF Pd/K Lot 890116A1	None 1100°C, 2 hours, air	202 7
RTF Pd/K Lot 890118A1	None 1100°C, 2 hours, air	180 0

TABLE 5

**CHANGES IN PHYSICAL PROPERTIES OF RTF Pd/K CAUSED BY HEAT TREATMENTS OF SMALL BATCHES**

<u>IDENTIFICATION</u>	<u>HEAT TREATMENT</u>	<u>WEIGHT CHANGE</u> %	<u>TAP DENSITY</u> g/cc	<u>PARTICLES &gt; 50 MESH</u> %
RTF Pd/K	None	-	0.75	83.3
Lot 890113A1	800°C, 1/2 hour, air	+1.29	0.82	82.1
	800°C, 2 hours, air	+1.47	0.82	80.5
	800°C, 2 hours, argon	-0.71	0.84	92.4
	950°C, 1 hour, air	+0.14	0.91	79.2
	950°C, 1 hour, argon	-0.16	0.84	92.4
	1100°C, 1/2 hour, air	+0.16	1.04	90.5
	1100°C, 2 hours, air	-0.01	0.95	88.8
	1100°C, 2 hours, argon	-0.39	0.92	89.0
RTF Pd/K	None	-	0.75	92.8
Lot 890116A1	1100°C, 2 hours, air	-0.06	0.96	90.3
	1100°C, 6 hours, air	-0.13	0.93	94.7
RTF Pd/K	None	-	0.75	93.6
Lot 890118A1	1100°C, 2 hours, air	+0.10	1.01	85.9

TABLE 6

**HEAT TREATMENT OF 1kg BATCHES OF Pd/K  
1100°C FOR 2 HOURS IN AIR**

<u>BATCH</u>	<u>QUANTITY</u> g	<u>TAP DENSITY</u> g/cc	<u>CHLORINE</u> ppm	<u>&gt;50 MESH</u> %	<u>WEIGHT GAIN</u> %
900619	1017.3-b	0.95	178/35	94.7	0.66
900621F	1000.4-a	0.97	155/0	92.1	1.55
900621B	1001.4-b	1.00	196	92.0	0.17
900625F	1017.3-a	1.01	176/164	89.6	1.10
900625B	1038.5-a	0.99	135	92.6	0.80
900627F	1040.5-a	1.00	207/0	92.9	1.10
900627B	961.1-a	1.04	217	87.0	0.96
900629F	985.5-a	1.02	158/148	86.1	1.13
900629B	1015.1-a	0.99	137	86.9	0.87
900702F	1042.8-a	1.05	0/168	87.4	1.05
900702B	999.4-a	1.04	23	91.2	0.77
900709F	997.4-a	1.03	35	86.4	1.35
900709B	1016.5-a	1.02	4	88.8	0.93
900711F	1060.3-a	0.99	151	91.9	0.93
900711B	1025.2-a	1.03	0	90.1	0.86
900713F	1043.9-a	1.00	0/5	92.6	1.02
900713B	984.2-a	1.02	0	90.6	0.90
900716F	1076.4-a	0.99	0	90.5	1.09
900716B	995.5-a	1.01	0	90.4	0.85
900718F	1001.0-a	1.06	0	83.7	1.20
900718B	1095.8-a	1.01	0	85.0	0.90
900720F	1163.0-a&b	1.02	0	91.3	0.24
900720B	1054.7-b&c	0.94	0	97.5	0.03
900723F	1110.6-b,d&e	0.96	0	85.5	0.22

F = Crucible in front of furnace    B = Crucible in back of furnace

Pd/K SOURCES:

a - RTF Pd/K	0.75	202	88.1
b - AHL Pd/K	0.81	392	90.2
c - Used Pd/K from TCAP II	-	-	-
d - Used Pd/K from TCAP III, Column #1	0.86	1481	65.8
e - Used Pd/K from AHL Vacuum Beds	0.77	190	90.9

TABLE 7

**PROPERTIES OF HEAT TREATED, SIEVED AND BLENDED Pd/K  
FOR RTF AND 232-H TCAP UNITS**

<u>PROPERTY</u>	<u>Pd/K</u>	<u>SPECIFICATION WCM-3</u>
Palladium Content	51.3 ± 0.2 %	≥ 55%
Chlorine Content	None Detected*	<250 ppm
Particle Size Distribution 30-50 Mesh (300-600 μm)	98.9 %	> 80 %
Pour Density	0.84 g/cc	NS***
Tap Density	0.94 g/cc	NS***
Oxygen Content	≈ 1 %**	NS***

\* Neutron Activation Analysis Detection Limit for Chlorine ≈ 50 ppm

\*\* Removed by absorption and desorption of hydrogen

\*\*\* NS = Not Specified

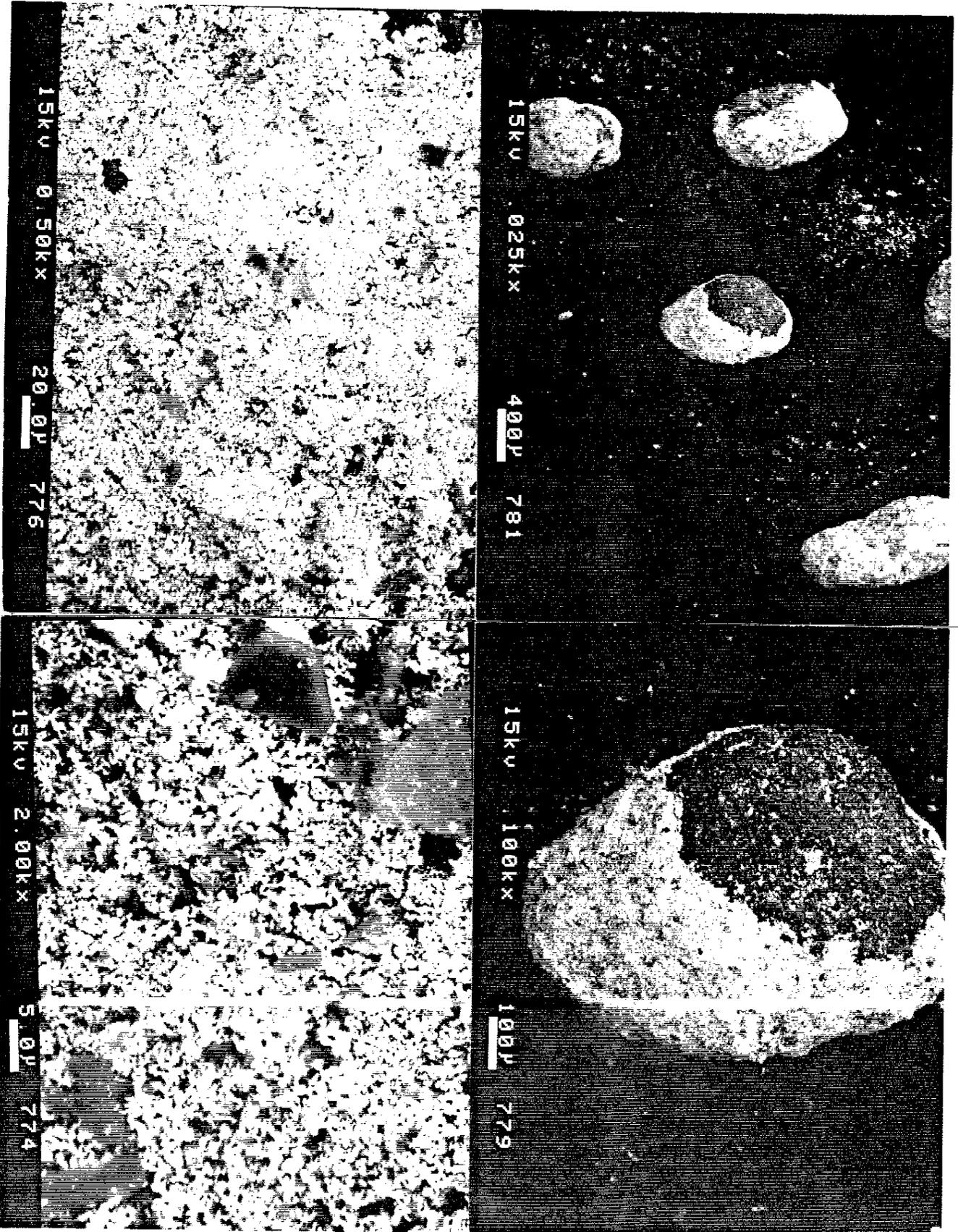


Figure 1 SEM of particles of Pd/k procured for the AHL

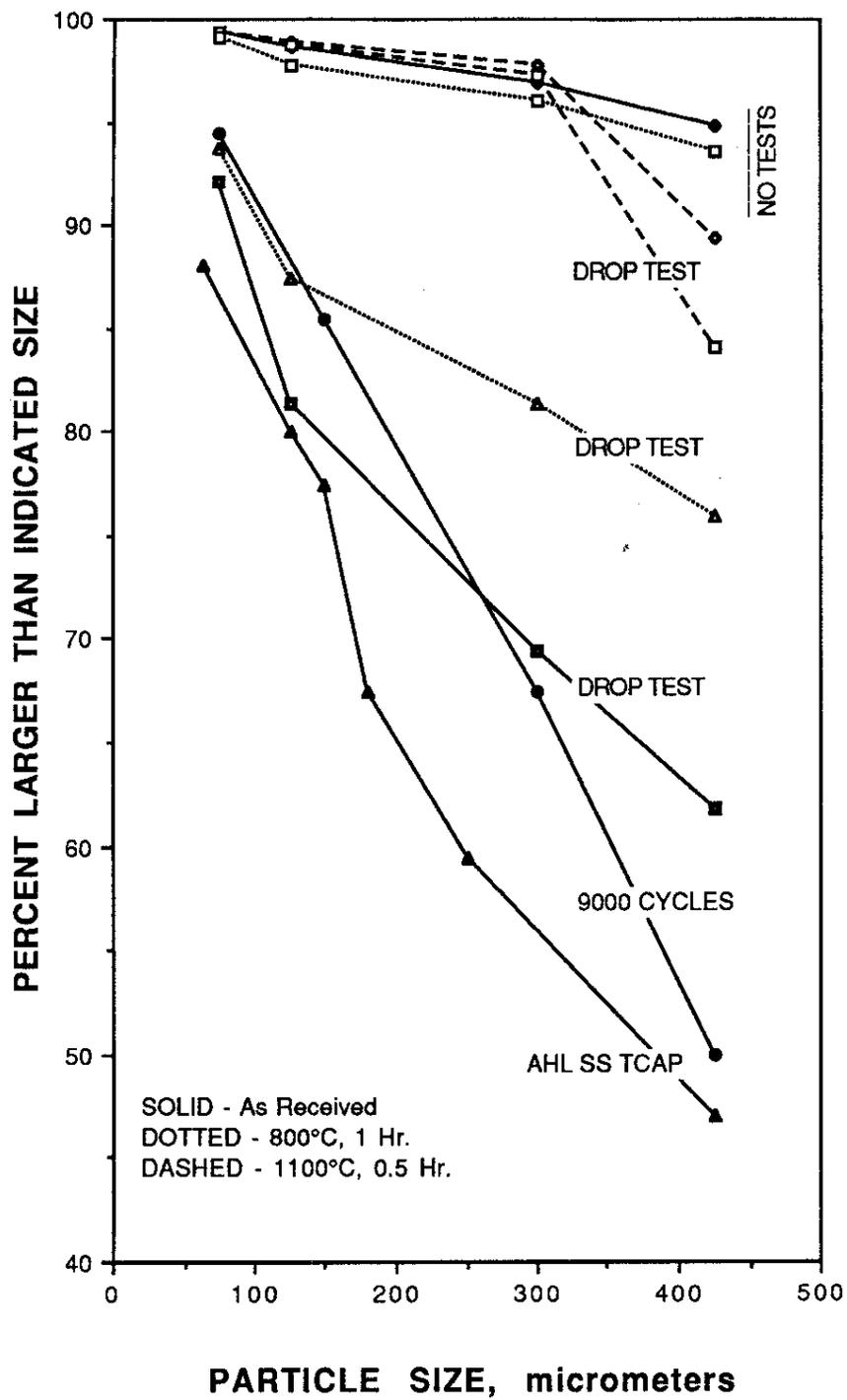


Figure 2

Particle size distributions of as-received and heat-treated AHL Pd/k from drop tests, cycling tests and AHL stainless steel TCAP

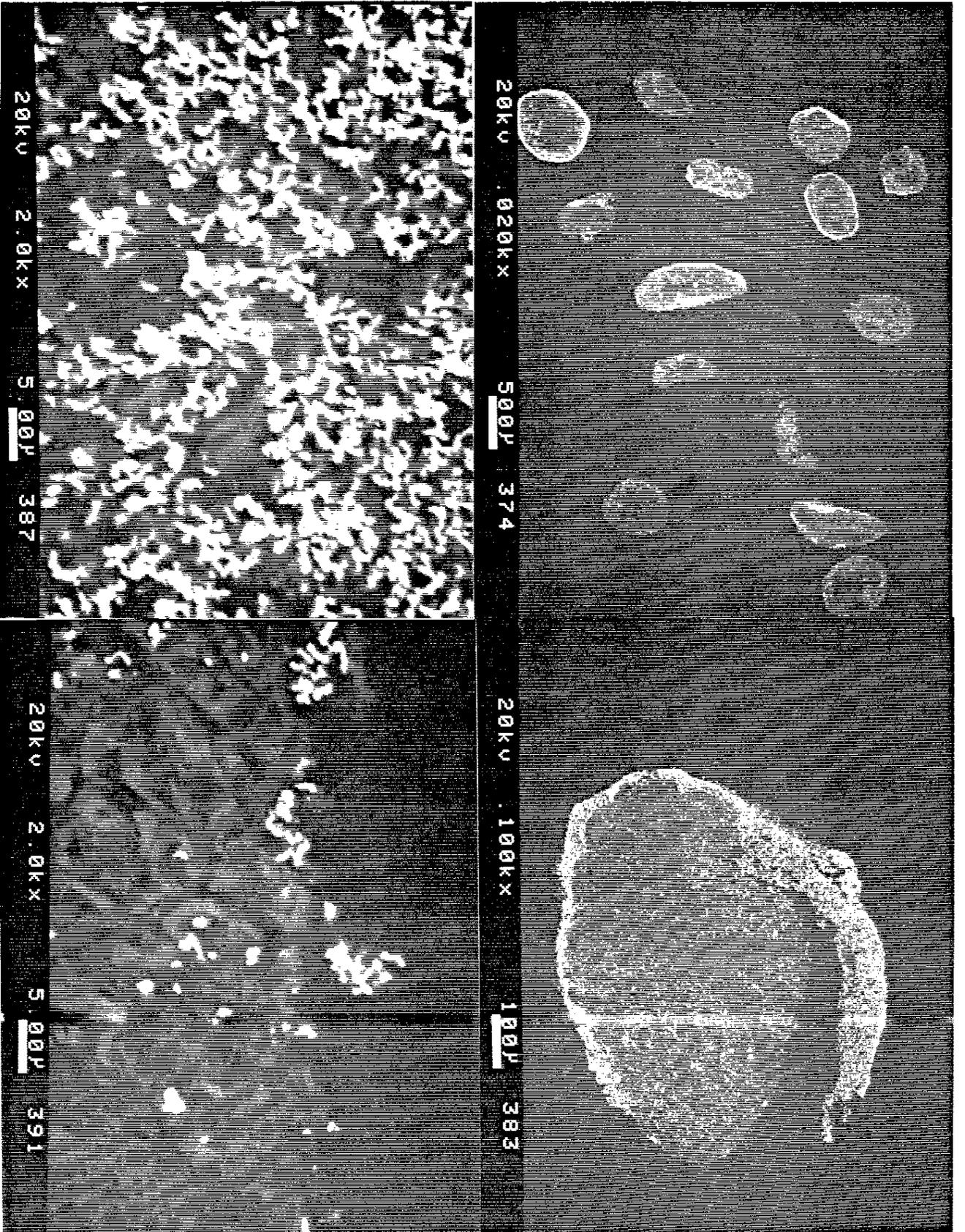
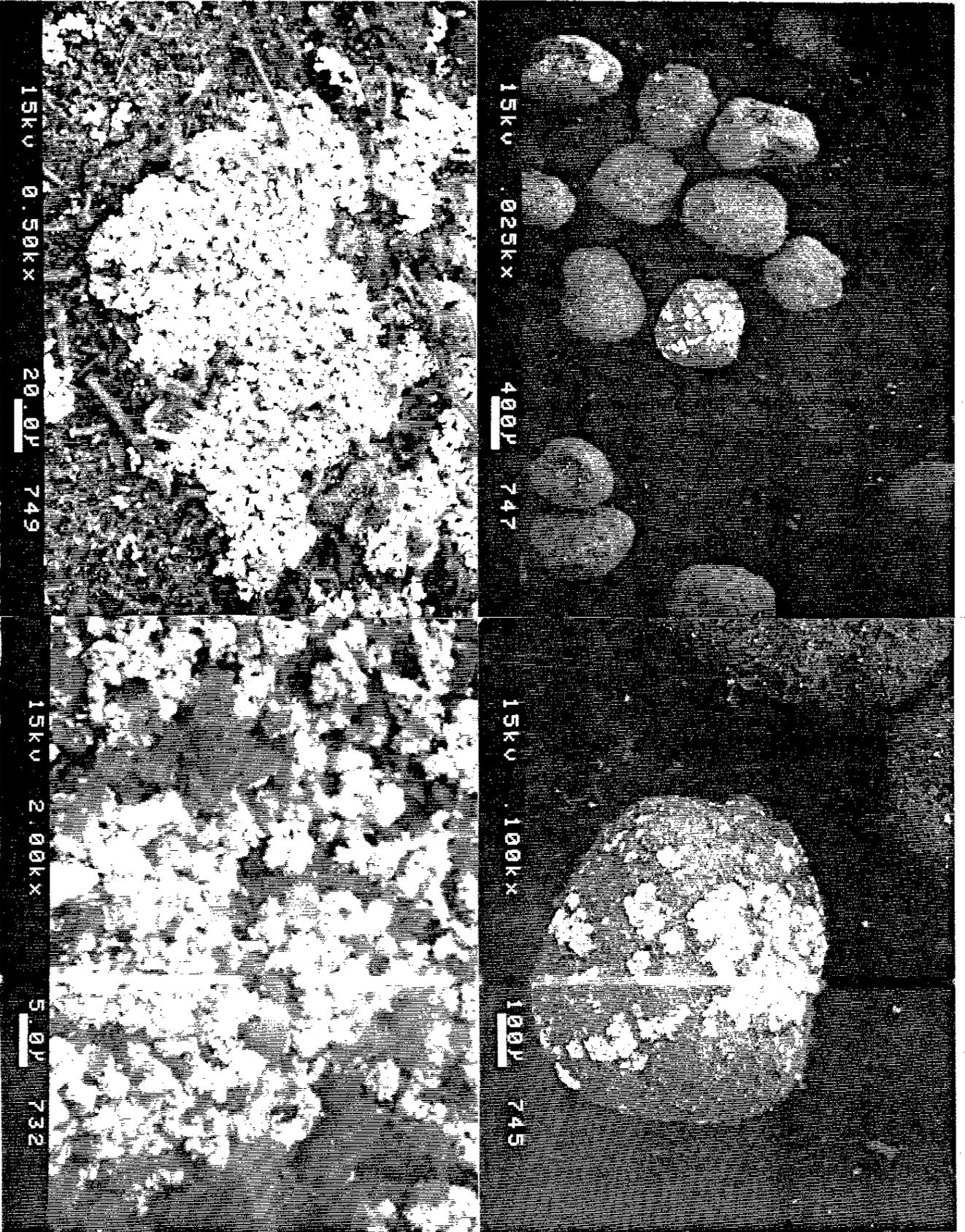


Figure 3 SEM of cross-sectioned AHL Pd/k particles from the AHL stainless steel TCAP



**Figure 4 SEM of AHL Pd/k cycled 9000 times in hydrogen**

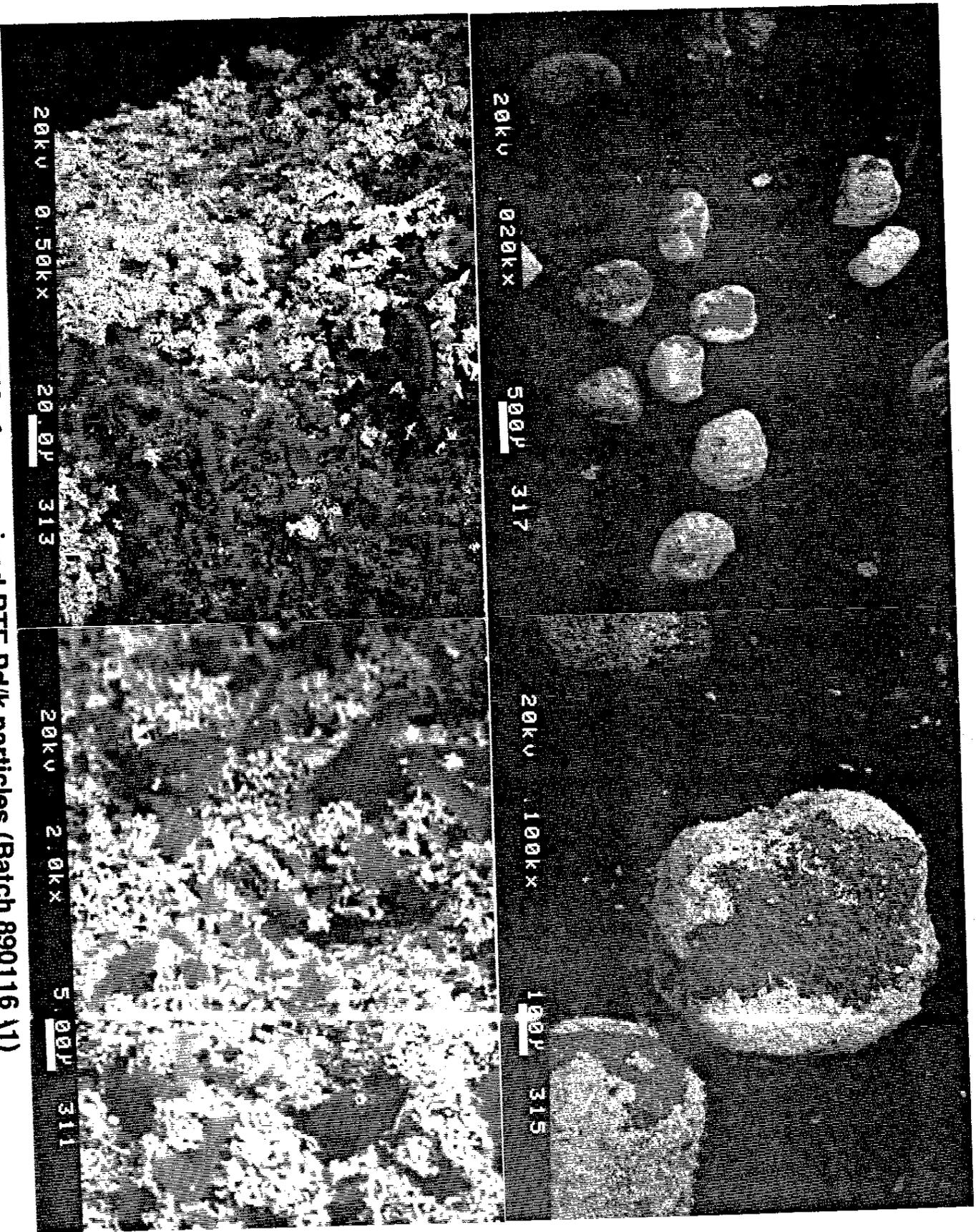


Figure 5 SEM of as-received RTF Pd/k particles (Batch 890116 A1)

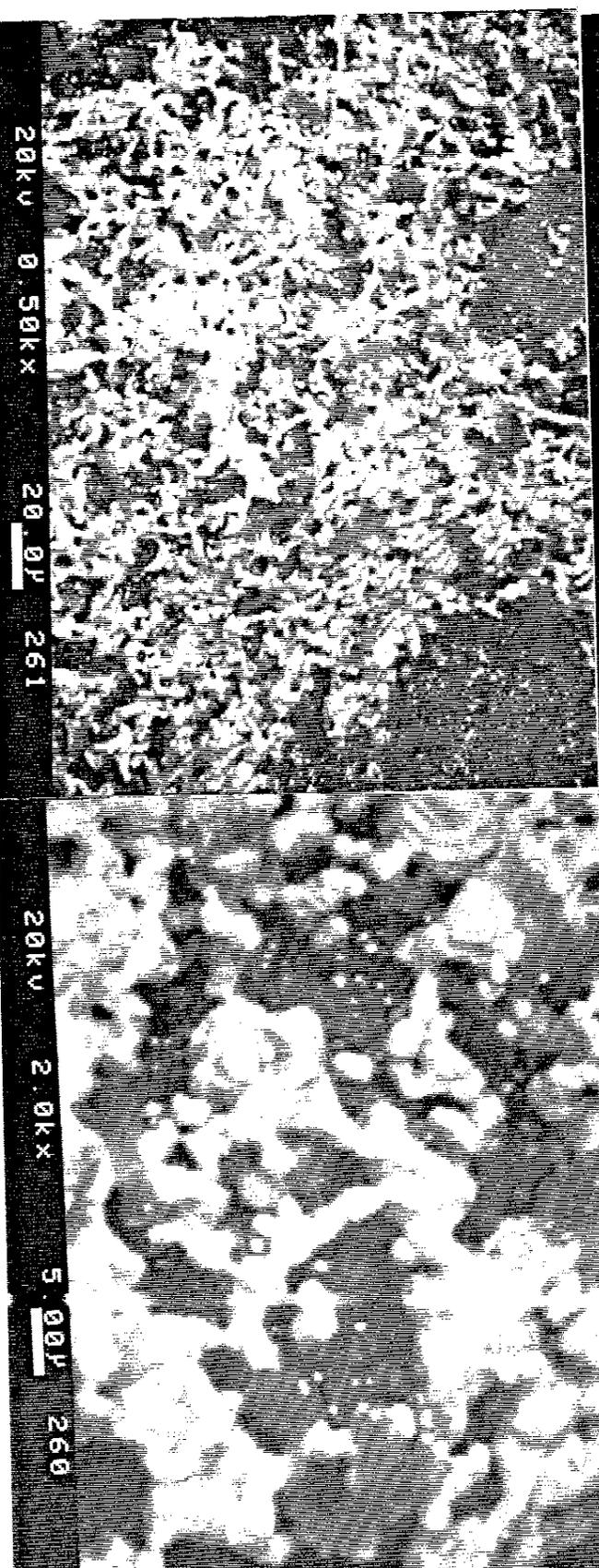
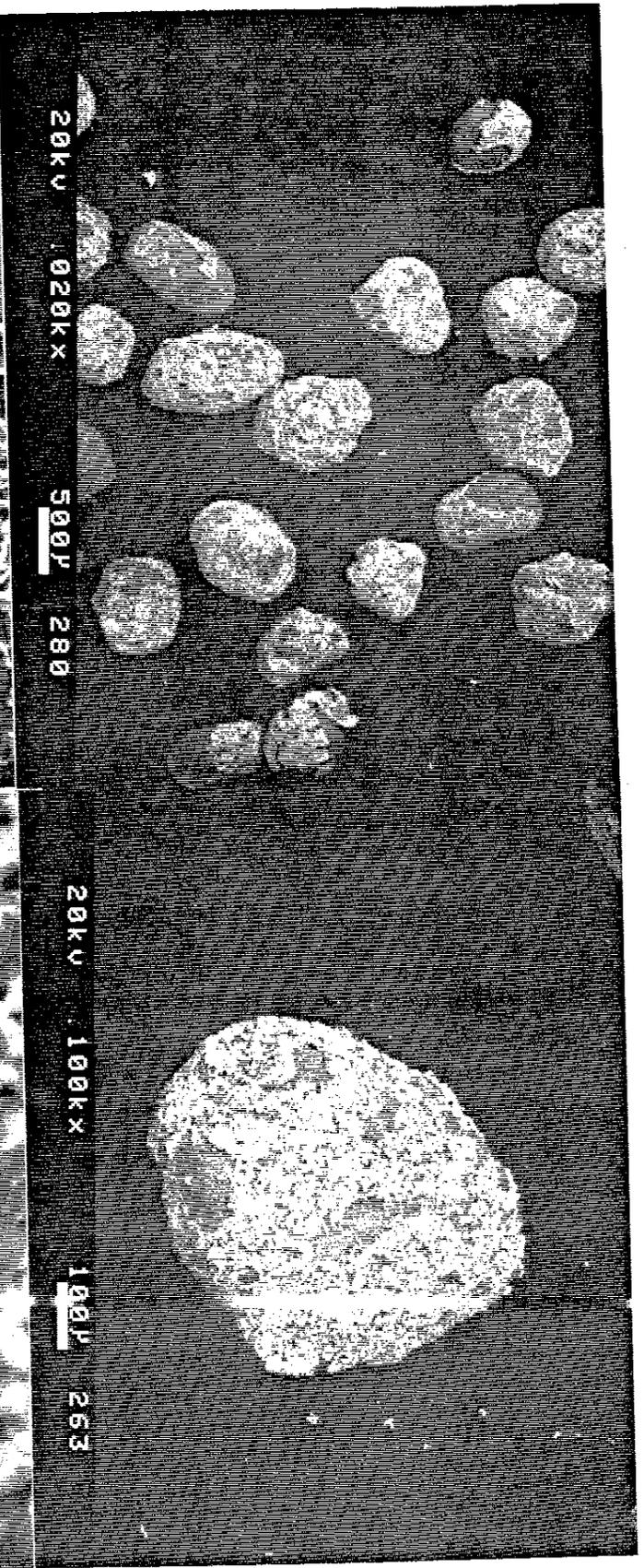


Figure 6 SEM of RTF Pd/k particles (Batch 890116A1) heated at 1100°C for 2 hours in air

As Received

1100°C, 2 Hours, Air

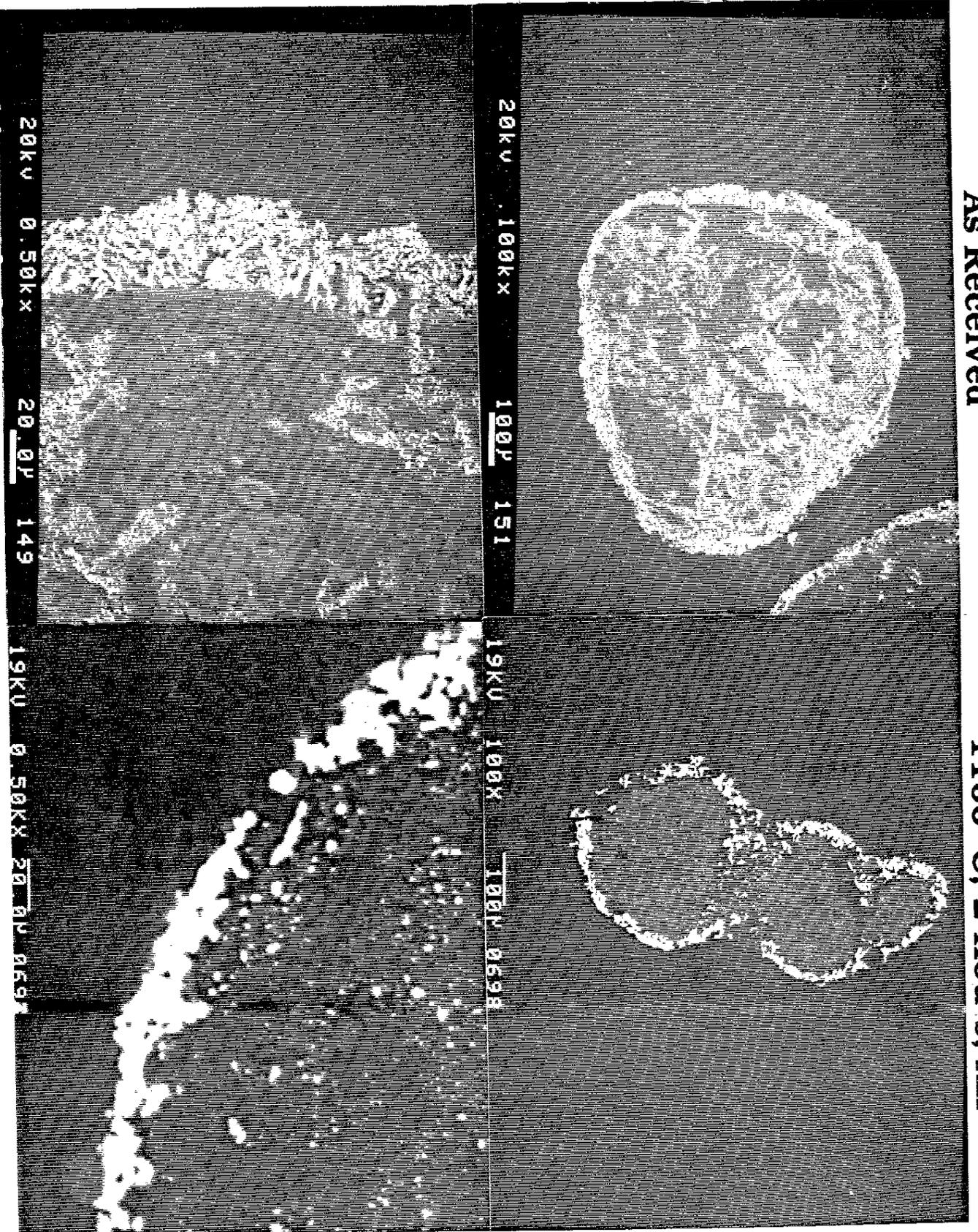
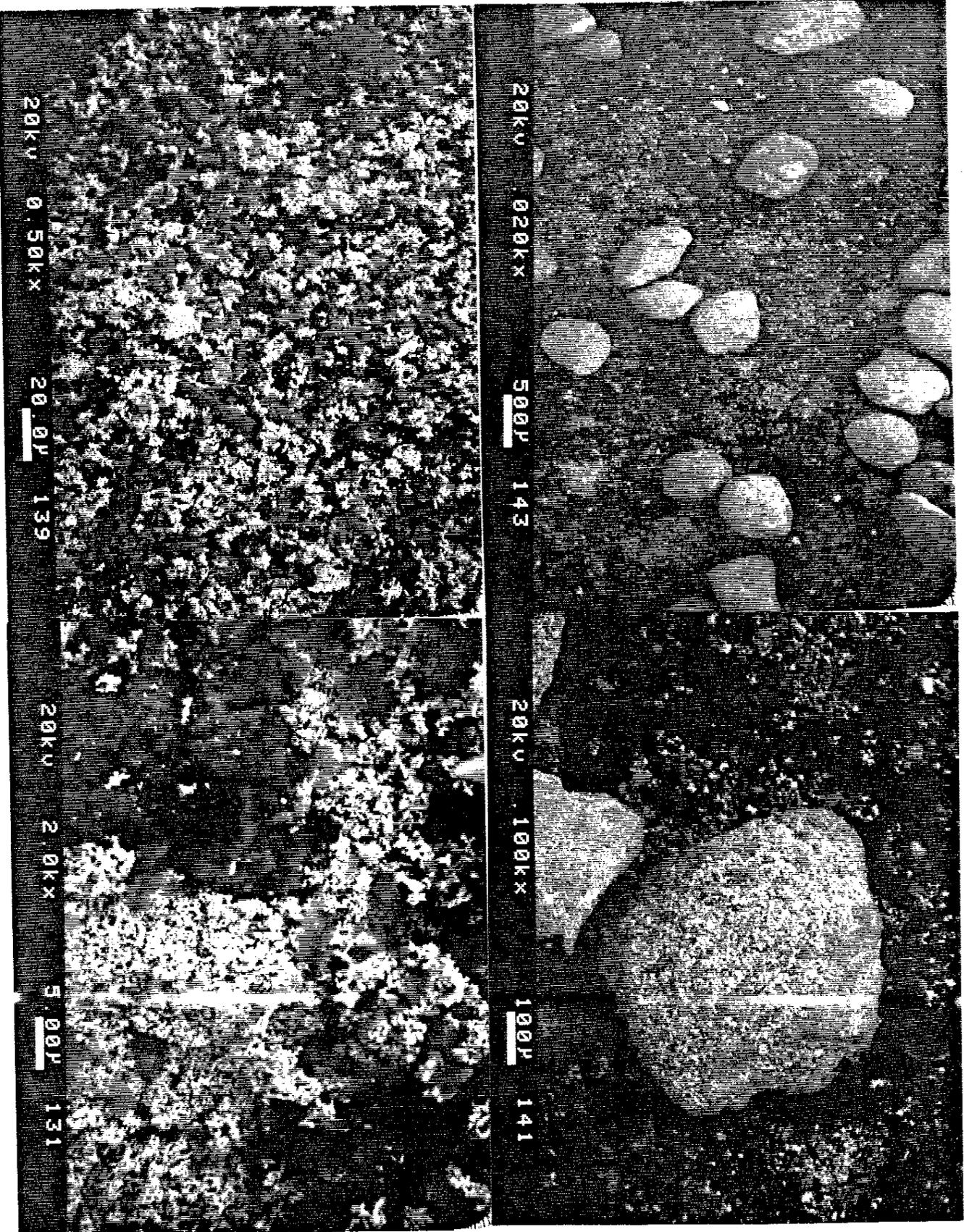


Figure 7 SEM of cross-sectioned particles of as-received and 1100°C heat-treated RTF Pd/k (Batch 890113A1)



**Figure 8 SEM of as-received RTF Pd/k after drop test (particles smaller than 300μm were removed before SEM)**

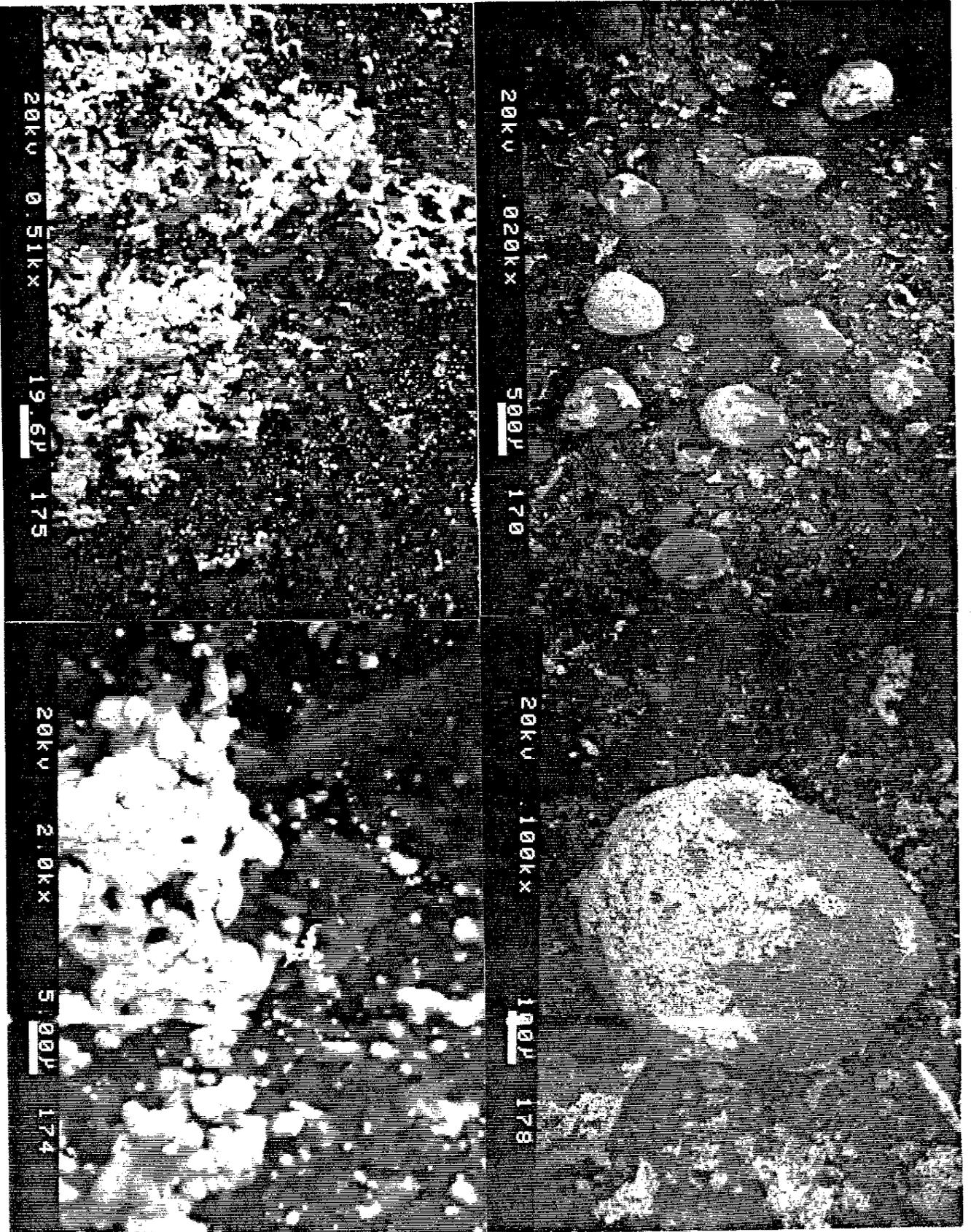


Figure 9 SEM of 1100°C heat-treated RTF Pd/k after drop test

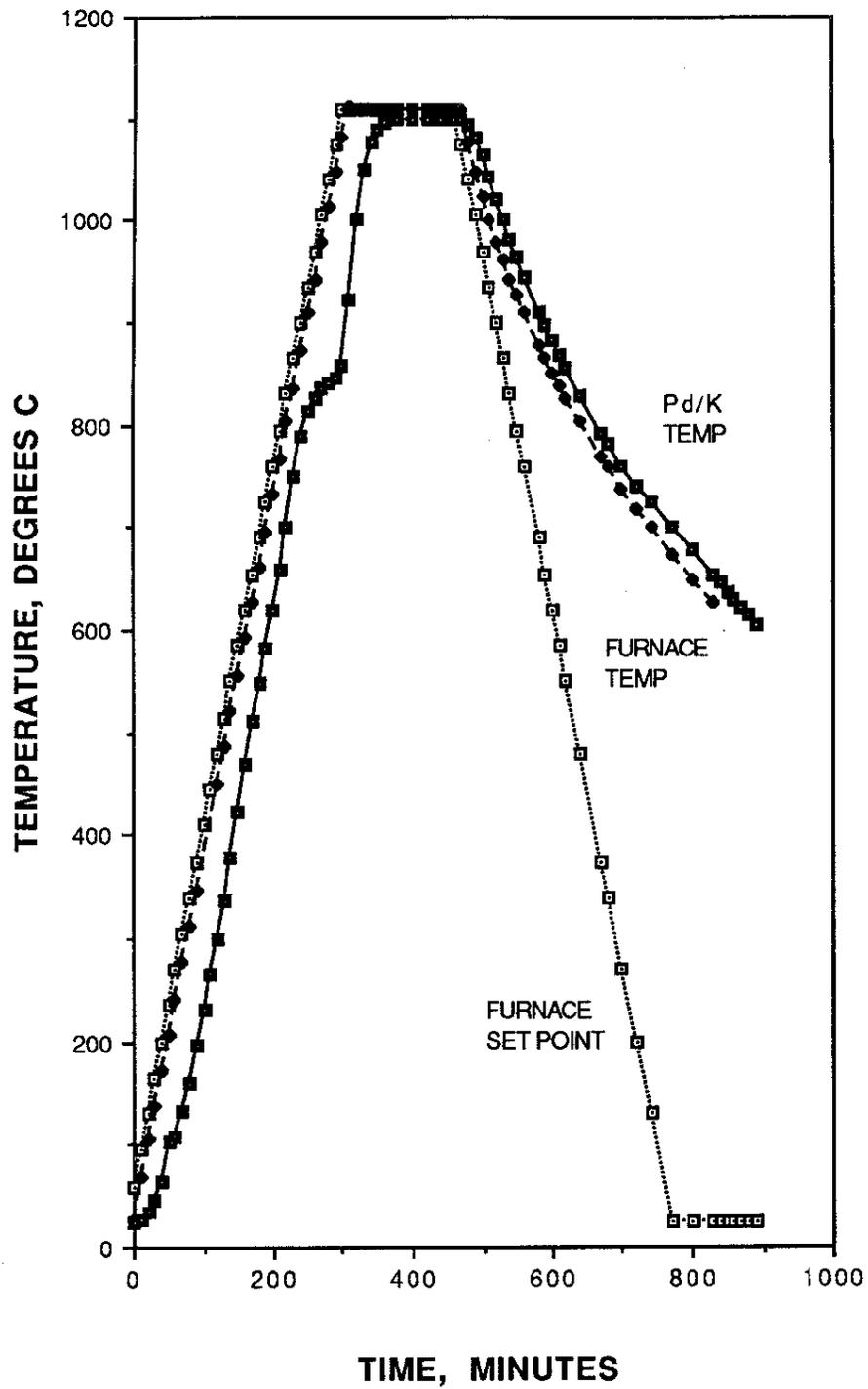
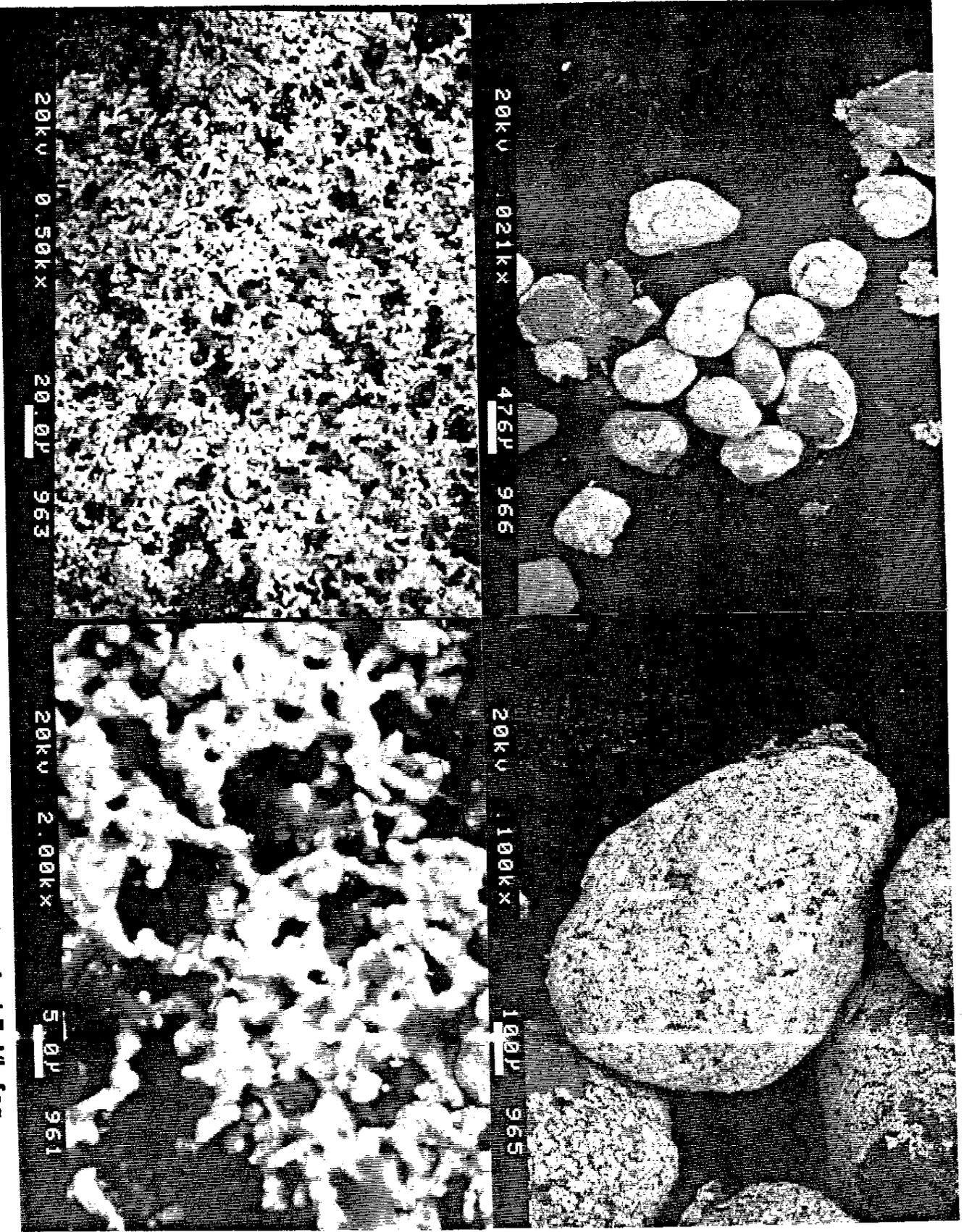


Figure 10

Temperature-time profile for 1100°C heat treatment of a large batch of Pd/k (900619)



**Figure 11** SEM of particles of 1100°C heat-treated, sieved and blended P J/K for RTF and 232-H TCAP units

I would appreciate it if you would complete and return this Customer Response Form so I will know if my work is helping you.

Thank you,

Clanton Mosley

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TO: W. C. Mosley, 773-A, C-157, 725-2404

FROM: \_\_\_\_\_  
Name Location Date

**CUSTOMER RESPONSE**

Pd/K FOR RTF AND 232-H TCAP UNITS (U)  
WSRC-TR-90-554

1. Was the information in this report useful to you?  
 Yes  No
2. Was it understandable?  
 Yes  No
3. Was it complete?  
 Yes  No
4. Do you need any more information on this subject?  
 Yes  No
5. Do you have suggestions for further work?  
 Yes  No

If answers to 4 and/or 5 are yes, please list below or on back.