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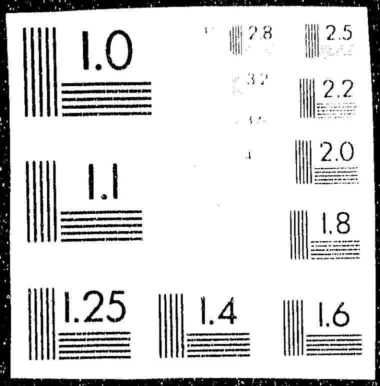

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PALLADIUM DEPOSITED ON KIESELGUHR (Pd/K) FOR THE REPLACEMENT TRITIUM FACILITY (RTF) (U)

by

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WESTINGHOUSE SAVANNAH RIVER COMPANY
INTER-OFFICE MEMORANDUM

January 11, 1990

TO: T. Motyka, 773-A

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

PALLADIUM DEPOSITED ON KIESELGUHR (Pd/K) FOR THE REPLACEMENT TRITIUM FACILITY (RTF) (U)

INTRODUCTION

Palladium deposited on kieselguhr (Pd/K) will be used for several applications in the Replacement Tritium Facility (RTF). [1] The Hydrogen Technology Section (HTS) is responsible for specification development and procurement of the Pd/K that will be used in the RTF. This memorandum describes the production and characterization of Pd/K ordered for the RTF on purchase order AX840942.

SUMMARY

The Pd/K procured for the RTF consists of three batches. All three batches meet the specified particle size distribution that 80 weight percent be between 30 and 50 mesh. One batch contains 53.6% palladium which is less than the specified minimum of 55%. Another batch has a chlorine content of 311 ppm which is slightly in excess of the specified maximum of 250 ppm. These nonconformances are not considered significant since batches will be blended to yield Pd/K for the RTF that meets the chlorine specification and has acceptable palladium content.

Some of the Pd/K procured for the RTF will be heat treated to strengthen the particles against breakdown during use. Heat treating parameters must be determined that will preserve the desired absorption/desorption behavior of the Pd/K.

Development of improved forms and alternatives for Pd/K for future SRS applications has begun.

Derivative Classifier

DISCUSSION

Process for Deposition of Palladium onto Kieselguhr

Ionex Research Corporation performed the deposition of palladium onto the kieselguhr. The kieselguhr was in the form of 30-40 mesh (425-600 micrometers) particles of CHROMOSORB P (AW) , Lot 202, procured from Manville Sales Corporation. The palladium chloride used in the process was procured from D. F. Goldsmith Chemical and Metal Corporation.

The Ionex process has been described previously. [2] An ammoniacal solution containing typically 530 grams of $PdCl_2$ (318 grams of Pd) in 1500 ml of water is mixed with a batch of about 4000 grams (about 10 liters) of kieselguhr. This mixture is stirred to a uniform consistency in teflon-coated bowls, screened through a 10 mesh (2.0 mm) sieve, and dried at 250 ^{o}C using air blowers in a specially designed box. Mixing/drying steps are repeated (about eight times) until the desired amount of palladium has been deposited on the kieselguhr as determined by density measurements. Each batch of Pd/K is then given a primary reduction at about 375 ^{o}C in 8%H_2-92%N_2 to reduce the chlorine level to about 1000 ppm. Several batches are then combined for a final reduction at about 316-371 ^{o}C in pure hydrogen to reduce the chlorine level to less than 250 ppm.

Specifications for RTF Pd/K

Specifications were developed for the RTF Pd/K since it is a Category 1 procurement item.[3]

A palladium content of at least 55 weight percent was specified to achieve the desired capacity for the Thermal Cycling Absorption Process (TCAP). Pd/K produced several years ago for use in the Advanced Hydride Laboratory (AHL) contained 51.2% palladium. These values are near the maximum palladium content that can be produced by the Ionex process without introducing intermediate heat treatments. Palladium contents were determined by hydrogen absorption measurements at SRS.[4]

Chlorine content must be less than 250 ppm to conform to Site Specification No. 5992 for materials that will be in contact with stainless steel in production facilities. Chlorine concentrations were determined by neutron activation analyses at SRS.

The Pd/K must be a free flowing powder with at least 80 weight percent of the particles being between 30 and 50 mesh (300-600 micrometers) to facilitate bed loading without excessive dusting. Particle size distributions were determined by sieve analyses at SRS.

Production of the RTF Pd/K

Ionex produced the RTF Pd/K using the process described previously. After primary reduction, 10 gram samples from each batch were sent to SRS for determination of palladium content. Analyses of the first eight batches (880516 through 880823) shown in Table 1 revealed that all had palladium contents below the specified 55%. SRS requested that Ionex load additional palladium onto the remaining four batches (880920 through 881109) prior to primary reduction in an effort to produce Pd/K with a palladium content of about 56% that could be blended with the other batches to increase the overall palladium content to near the specified 55%. As shown in Table 1, this procedure was successful only for batch 881104 with 56.2% palladium. (Loading of additional palladium onto the Pd/K batches that had been given the primary reduction heating was considered undesirable since the data base for Pd/K at SRS was for material made by the normal Ionex process.) Tap densities of the batches of Pd/K after primary reduction ranged from 0.67 to 0.75 grams/cc.

After primary reduction, the RTF Pd/K was combined into three large batches as indicated in Table 1 for final reduction at 316 °C for 6-7 hours in hydrogen. Neutron activation analyses at SRS revealed chlorine concentrations of 2633, 640 and 600 ppm for final reduction batches 890113, 890116 and 890118, respectively. Subsequent analyses of the primary reduction batches showed that the unusually high chlorine level of 2633 ppm in batch 890113 was caused by the extremely high level of chlorine (21546 ppm) in one of the four primary reduction batches. Apparently something went wrong with the processing of batch 880707. (It bears noting that this batch number identifies material that was being processed during the Fourth of July holiday period when working conditions may not have been normal.)

The three batches of RTF Pd/K were each given an additional eight hours of final reduction heating at 316-371 °C in pure hydrogen with periodic purges with nitrogen for 15 minutes every 2-3 hours to reduce the chlorine concentrations. Previous development had shown such treatment to be effective in removing chlorine.[5] As shown in Table 1 for batches 890113A, 890116A and 890118A, chlorine levels were decreased to 2351, 364 and 410 ppm, respectively. However, the lowest levels still did not meet the specified maximum of 250 ppm.

Although the Pd/K particles were becoming more fragile, heating at 316-371 °C in hydrogen with periodic nitrogen purges for 15 minutes every 3-4 hours was continued in efforts to reduce the chlorine levels to below 250 ppm. These treatments proved successful for batches 890116A1 and 890118A1 where 13.5 and 11.5 hours of additional heating reduced chlorine levels to 202 and 180 ppm, respectively. Heating for an additional 22.5 hours reduced the chlorine in batch 890113A1 to 311 ppm which is only slightly above the specified maximum.

All three final reduction batches of the RTF Pd/K had the same value for tap density of 0.75 grams/cc.

Physical Properties of the RTF Pd/K

Physical properties of the RTF Pd/K are compared with the specifications in Table 2.

The RTF Pd/K was ordered by volume rather than by weight. Because of densification during final reduction, the volume of Pd/K received was slightly less than the volume that was ordered. This shortage should not be a problem since the volume ordered was in excess of RTF needs.

Particle size distributions of the three final reduction batches of RTF Pd/K are shown in Figure 1. Specifications required that at least 80 weight percent of the particles must be between 30 and 50 mesh (300-600 micrometers). As shown in Table 2, all three final reduction batches meet this specification although batch 890113A1, the one that received the longest heat treatment to remove chlorine, is barely acceptable. This specification may not be critical since further particle breakdown is expected during handling and cycling in hydrogen. If needed, the Pd/K can be sieved to remove fine particles. Because of the excess material ordered, sieving should leave adequate Pd/K for RTF needs.

Two of the three final reduction batches, 890113A1 and 890118A1, meet the specified minimum for palladium content of 55 weight percent. The low value of 53.6% for batch 890116A1 will result in a 2.5% reduction of Pd/K bed capacity if it is used by itself and a 0.9% reduction if it is blended with the other two batches. Such reductions in capacity are not considered significant.

Batches 890116A1 and 890118A1 meet the specification of no more than 250 ppm of chlorine. Batch 890113A1 with a chlorine content of 311 ppm cannot be used by itself. It must be blended with either batch 890118A1 or both batches 890116A1 and 890118A1 to produce Pd/K with an overall chlorine content less that 250 ppm that will be acceptable under Site Specification No. 5992.

Structures of the RTF Pd/K

Samples of particles from the three batches of Pd/K made for the RTF were mounted in plastic, ground, polished and examined with a scanning electron microscope (SEM) using backscattered electrons to reveal the distributions of palladium with the kieselguhr particles. The palladium is the bright phase in these SEM images shown in Figures 2, 4 and 6. The same specimens were examined with another SEM equipped with an energy dispersive x-ray analyzer that allows mapping of elemental distributions. Figures 3, 5 and 7 show the maps for palladium, silicon and aluminum along with the corresponding SEM images.

The SEM revealed nonuniform distributions of palladium throughout the particles for all three batches of RTF Pd/K. Highest concentrations of palladium occurred within 100 micrometers of particle surfaces. Areas with high palladium concentrations along with areas with essentially no palladium occurred within the particles. Similar distributions of palladium were observed for Pd/K made for the Advanced Hydride Laboratory by Ionex Research Corporation using essentially the same process [6].

Breakdown of Pd/K During Use

Two types of Pd/K particle breakdown have been identified that could occur during use in the RTF.

Breakdown of Pd/K particles during absorption and desorption of hydrogen was reported previously.[6] The region near the surfaces of Pd/K particles containing a high concentration of palladium became detached from the inner region with a much lower concentration of palladium. Examinations revealed that regions with high concentrations of palladium were much less dense and probably had less structural strength than regions with low palladium concentrations. Breakdown is attributed to fracture caused by repeated stressing of the interface between regions with high and low concentrations of palladium during cyclic absorption and desorption of hydrogen. This type of breakdown would be expected to increase with the number of cycles with the palladium becoming more concentrated in smaller particles. Examination of Pd/K (similar to the RTF Pd/K) that was cycled 9000 times showed that the region containing a high concentration of palladium had been completely removed from the surfaces of the largest particles.[7] Most of the particles containing high concentrations of palladium were smaller than the 300 micrometer lower limit of the RTF Pd/K specification.

Recently, a second type of breakdown of Pd/K particles was recognized to occur when particles are vigorously agitated by passage of gas onto and off of a bed.[7] Such breakdown is attributed to abrasion of particle surfaces as they hit together and can be controlled somewhat by limiting the gas flow rate. Since Pd/K particle surfaces contain high concentrations of palladium, such breakdown will lead to an increasing portion of the palladium in fine particles. The suspected low structural strength of the regions with high palladium concentrations may also be a contributing factor in particle breakdown. Heating Pd/K at 1100°C for one-half hour in air has been shown to strengthen Pd/K against breakdown by causing the submicrometer size palladium particles in the regions with high palladium concentrations to sinter together and grow.[8] Palladium particles up to 20 micrometers in size have been detected in heat treated Pd/K. Particles this large may alter the helium retention and absorption/desorption behavior of the Pd/K.

Both types of particle breakdown could occur to varying degrees during use of the as-received Pd/K in the RTF.

CONCLUSIONS

Because the chlorine content of 311 ppm of RTF Pd/K batch 890113A1 exceeds the specification limit of 250 ppm, it must be blended with either batch 890118A1 or both batches 890116A1 and 890118A1 to produce an overall chlorine concentration less than 250 ppm before it is used in the RTF.

For use in the RTF, all three batches of the Pd/K should probably be blended to yield material with an overall uniform palladium content of 54.5 weight percent. Although this value is lower than the specified minimum of 55.0 %, the reduction in capacity of the RTF Pd/K beds will not be significant.

Before the RTF Pd/K is used, decisions must be made on how to control particle breakdown.

FUTURE STUDIES

Since the immediate goal is to use the large quantity Pd/K made for the RTF, initial development efforts should be directed at reducing particle breakdown to an acceptable level. While heating at 1100 ^{o}C has been shown to be effective in strengthening Pd/K particles against breakdown, the effects of palladium grain growth caused by such heating on helium retention and hydrogen absorption/desorption behavior must be determined. Heating conditions for the RTF Pd/K need to be optimized for reduced breakdown and preservation of desired behavior. Facilities for heating large quantities of Pd/K need to be identified. It is likely that the heating used to strengthen the Pd/K particles will also reduce the residual chlorine content below 250 ppm. If this reduction in chlorine content occurs, blending of the batches of Pd/K will not be necessary but this needs to be confirmed.

Efforts are underway to produce an improved form of Pd/K for future use in the RTF or other tritium processing applications at SRS. Depositing palladium on kieselguhr by soaking the particles in a saturated tetraamminepalladium (II) nitrate solution yields a uniform distribution of palladium and does not create regions of low structural strength. Also, chlorine concentrations are below the specified maximum of 250 ppm.

Deposition of palladium on porous support materials with higher strength than kieselguhr is also being investigated.

ACKNOWLEDGEMENTS

Palladium contents of the Pd/K batches were determined by R. T. Walters.[4] Joyce Hunter determined the particle size distributions. Gordon Lien and Glenda Fulmer performed the neutron activation analyses to determine chlorine concentrations. Frank Odom prepared the polished Pd/K particles for SEM examinations by Ann Holston. Dan Steedly recorded the elemental distributions by x-ray mapping.

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TABLE I. PRODUCTION OF RTF Pd/K

FINAL REDUCTION				INITIAL REDUCTION			
LOT #	Pd (%)	Cl(ppm)	Tap Dens.	LOT #	Pd(%)	Cl(ppm)	Tap Dens.
890113	-	2633	-	880516	54.5	840	0.75
890113A	-	2351	0.75	880620	53.3	1491	0.68
890113A1	54.9	311	0.75	880628	53.6	1256	0.68
				880707	51.9	21546	0.71
				AVG	53.3	6283	0.71
890116	-	640	0.70	880725	52.7	760	0.70
890116A	-	364	0.73	880803	53.2	535	0.67
890116A1	53.6	202	0.75	880815	51.9	1069	0.70
				880823	52.1	984	0.68
				AVG	52.5	837	0.69
890118	-	600	0.73	880920	54.0	774	0.68
890118A	-	410	0.75	881028	54.8	1131	0.72
890118A1	55.0	180	0.75	881104	56.2	842	0.70
				881109	54.5	1406	0.69
				AVG	54.9	1038	0.70

TABLE II. PROPERTIES OF RTF Pd/K

PROPERTY	SPECIFICATION	Pd/K BATCHES 890113A1	890116A1	890118A1
Particle Size-Weight Percent 30-50 mesh (300-600 microns)	80 minimum	80.7	88.1	85.2
Palladium Content (Weight Percent)	55 Minimum	54.9	53.6	55.0
Chlorine Content (ppm)	250 Maximum	311	202	180
Tap Density	None	0.75	0.75	0.75

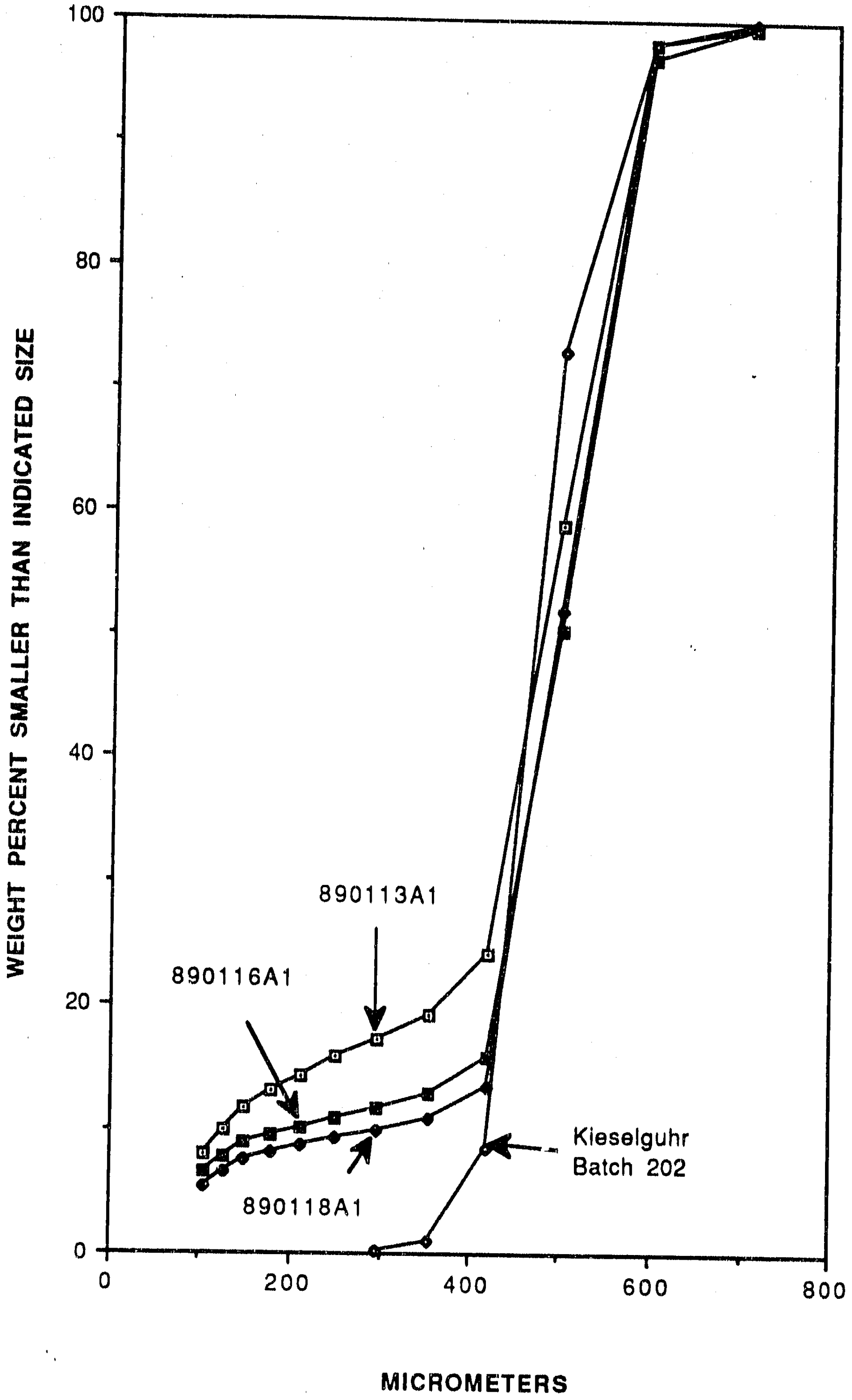

FIGURE 1. Particle Size Distributions for RTF Pd/K and Kieselguhr Batch 202

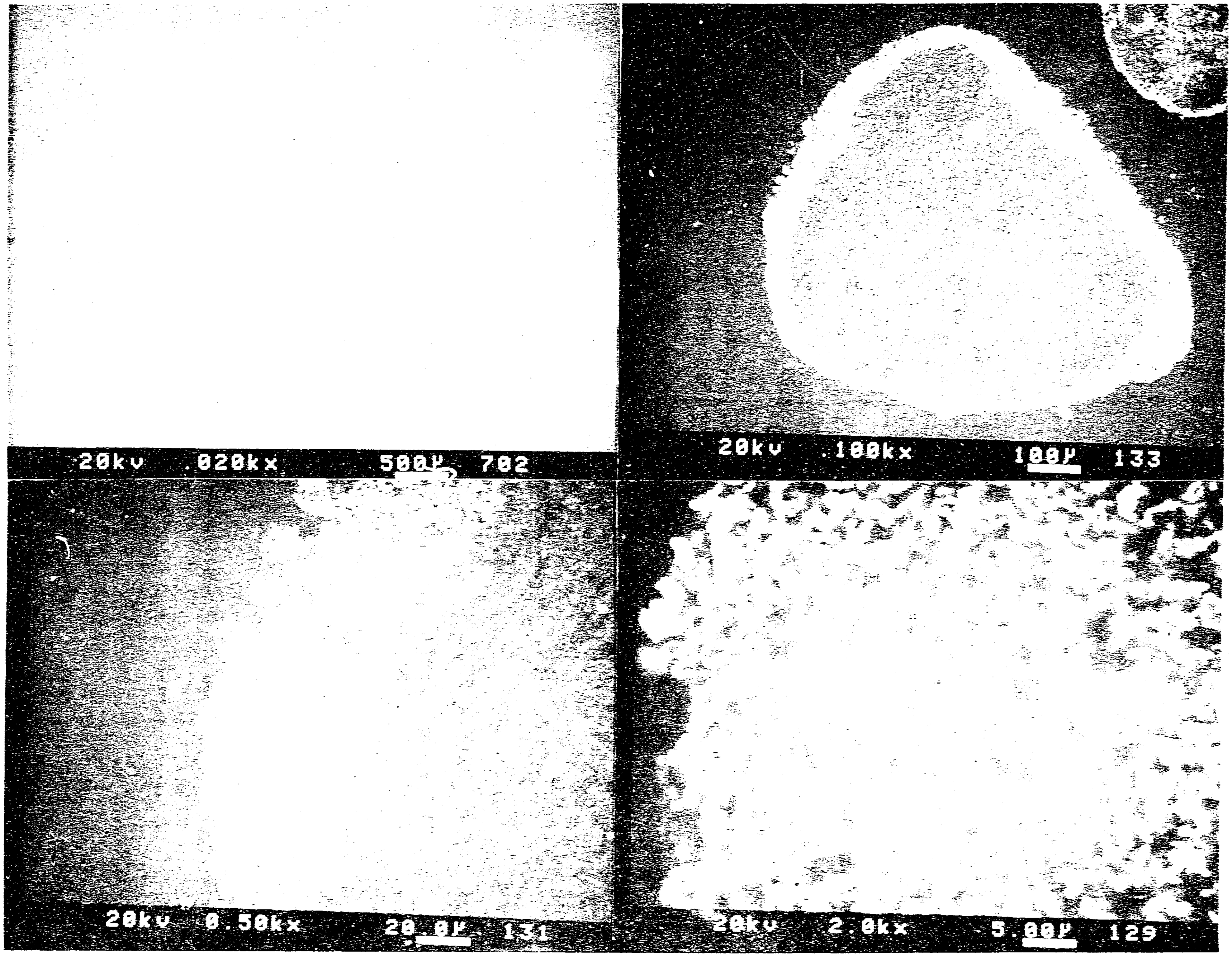

FIGURE 2. SEM BSE Images of Polished Particles from RTF Pd/K Batch 890113A1

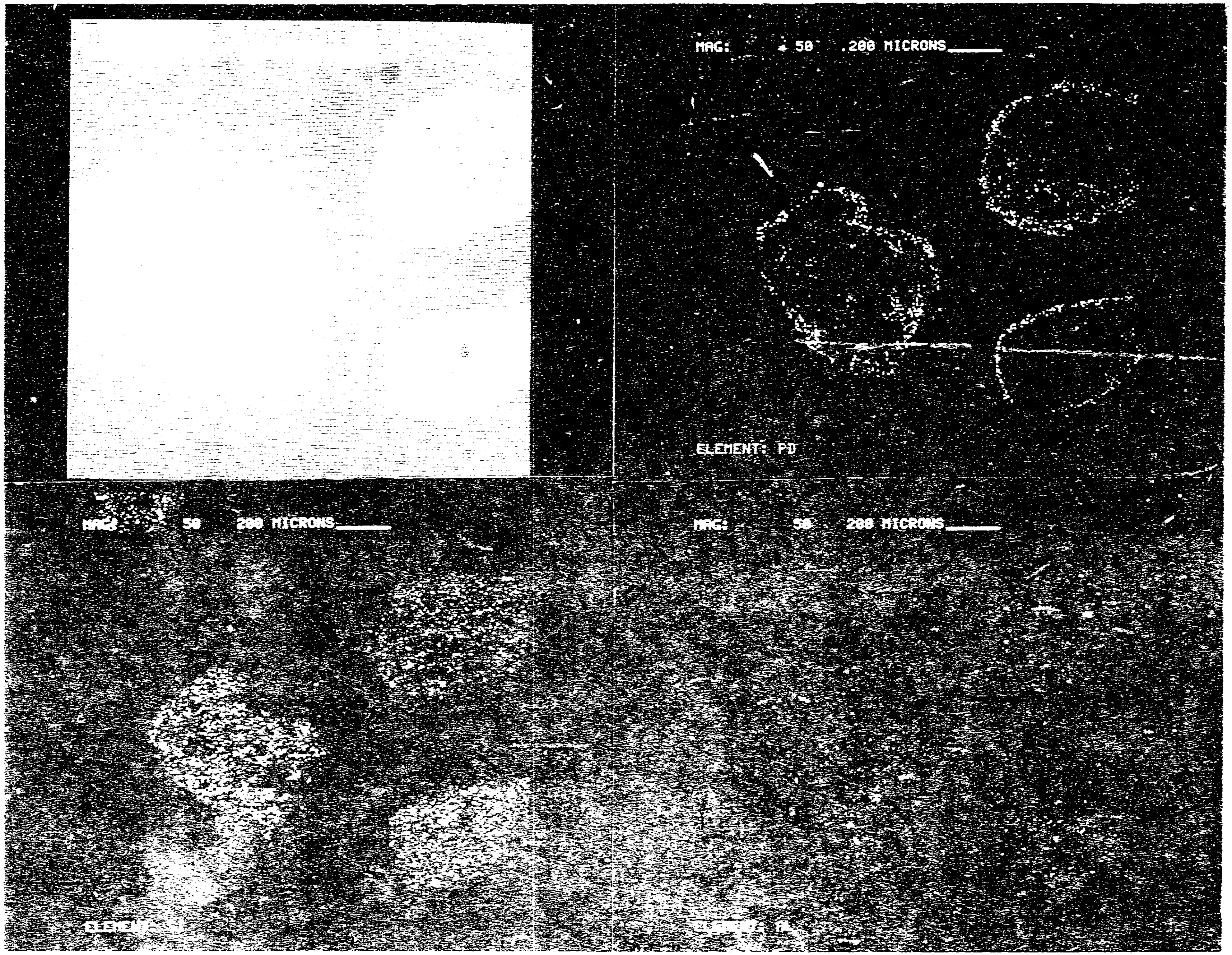

FIGURE 3. SEM Image and Palladium, Silicon and Aluminum Maps for Polished Particles from RTF Pd/K Batch 890113A1

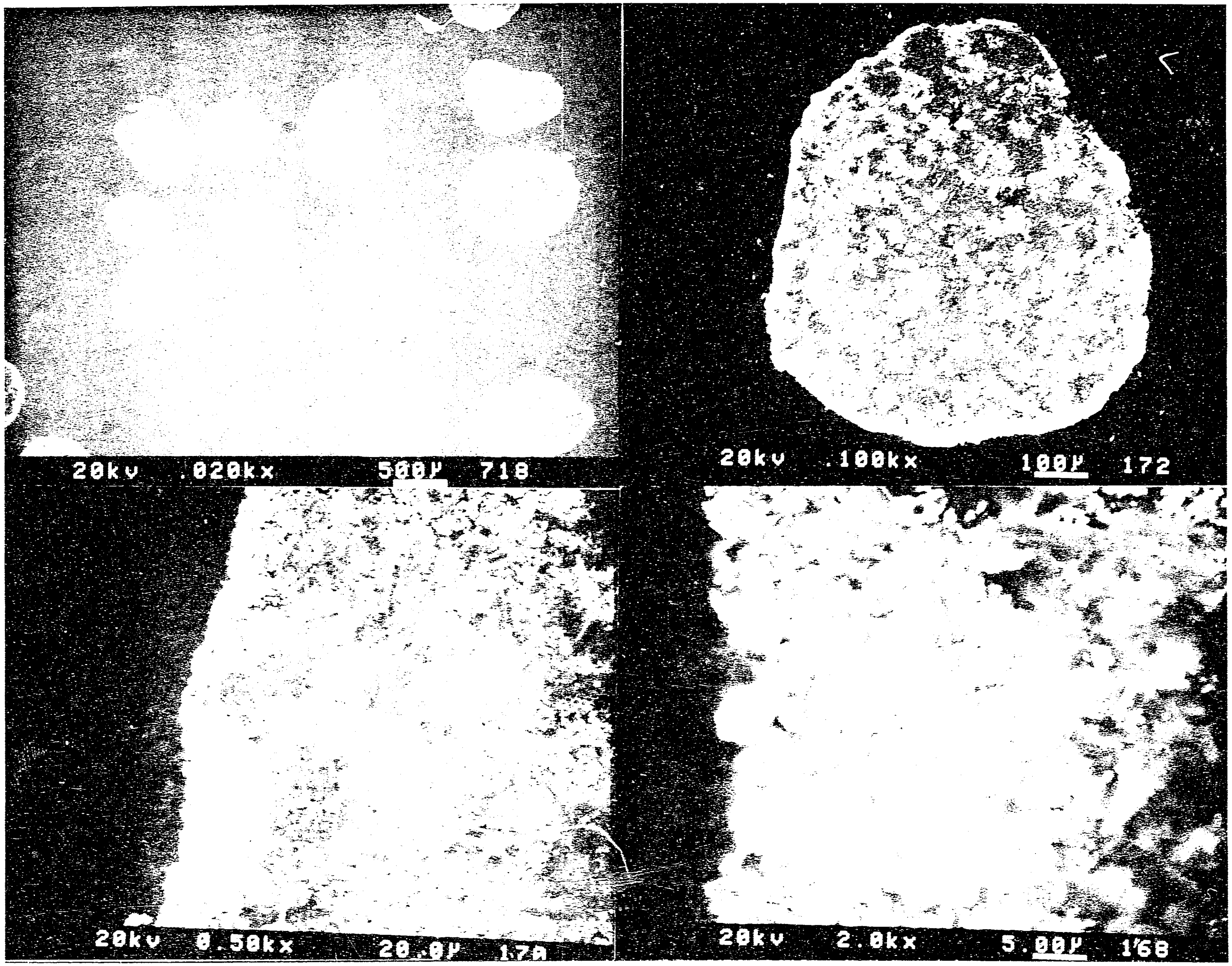

FIGURE 4. SEM BSE Images of Polished Particles from RTF Pd/K Batch 890116A1

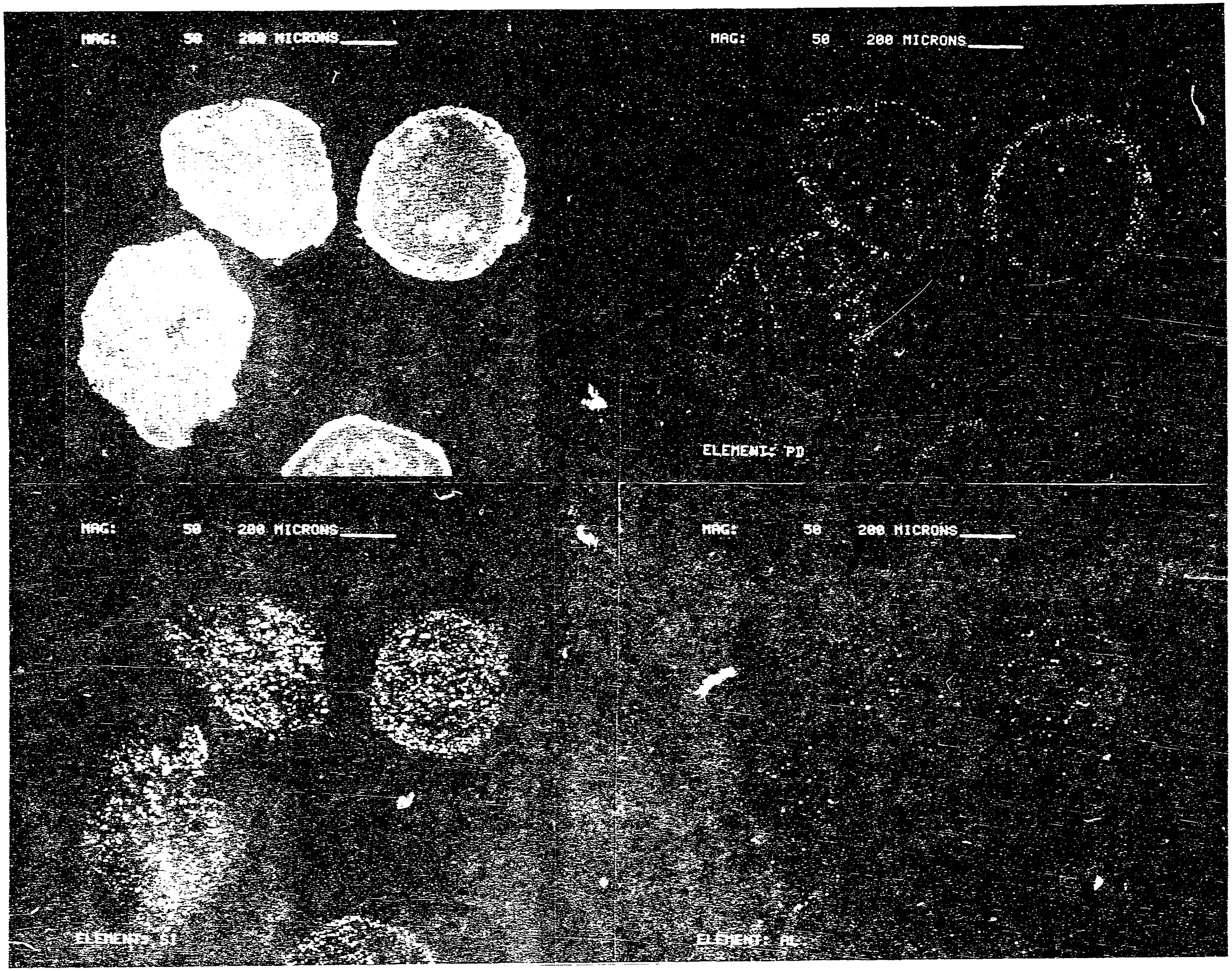

FIGURE 5. SEM Image and Palladium. Silicon and Aluminum Maps for Polished Particles from RTF Pd/K Batch 890116A1

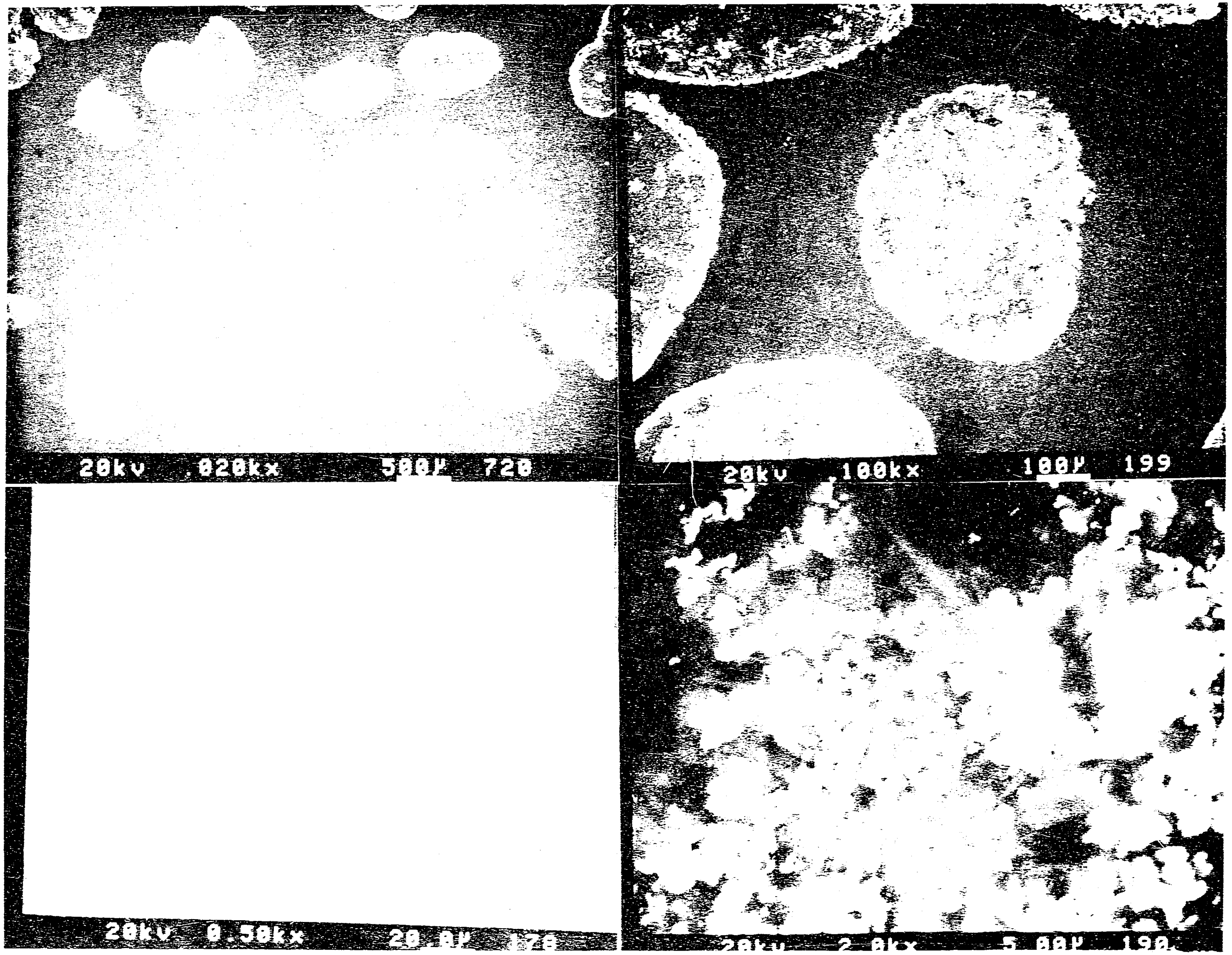

FIGURE 6. SEM BSE Images of Polished Particles from RTF Pd/K Batch 890118A1

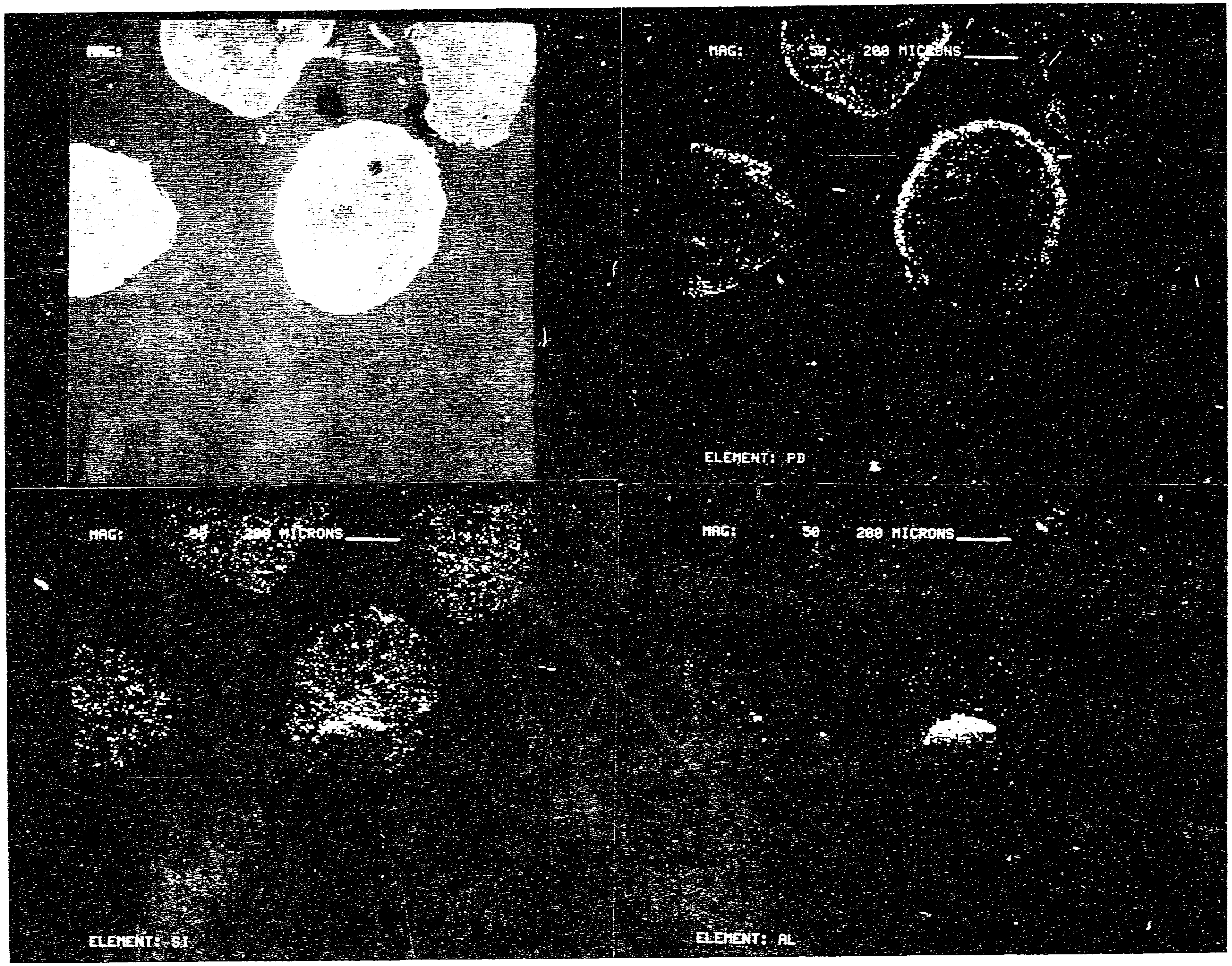

FIGURE 7. SEM Image and Palladium, Silicon and Aluminum Maps for Polished Particles from RTF Pd/K Batch 890118A1

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