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MOLYBDENUM COATING OF ThO_2 AND $^{238}PuO_2$ PARTICLES

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ABSTRACT

Both the hydrogen reduction of MoF_6 and $MoCl_5$ were evaluated in a fluid-bed reactor to deposit molybdenum on $^{238}PuO_2$, $^{238}PuO_2$-ThO_2 solid solution, and ThO_2 microspheres and shards. Considerable attack of the ceramic surface by the acid fluoride species was observed. The resulting fluoride impurity significantly increased the neutron emission rate due to the $^{19}F(\alpha,n)^{22}Na$ reaction. The following observations were noted on the MoF_6 system: 1) The fluorine contamination increases with increased surface area of the substrate. 2) The fluorine contamination increases rapidly during the initial moments of the run, then tapers off. 3) There is only a small amount of fluorine residue in the molybdenum coating itself. Likewise $MoCl_5$ and/or HCl attack the substrates' surface. Results of an electron microprobe study show that the chloride residue is associated solely with the ceramic phase.

INTRODUCTION

At Mound Laboratory we are engaged in the production of $^{238}PuO_2$-Mo cermet fuel discs for use in thermoelectric generators. The cermet discs are prepared by coating individual particles of $^{238}PuO_2$ with molybdenum in a fluid-bed reactor by the hydrogen reduction of either MoF_6 or $MoCl_5$. The coated particles are then vacuum hot pressed into the desired configuration. This paper discusses the chemical vapor deposition phase of the program.

Initially our efforts were concerned with coating $^{238}PuO_2$ by the hydrogen reduction of MoF_6 as developed by M. Browning[1] and his associates at Battelle Memorial Institute. However, the resulting fluoride impurity significantly increased the neutron emission rate due to the $^{19}F(\alpha,n)^{22}Na$ reaction. To determine the nature of the fluoride impurity, a study was made using ThO_2 as a nonradioactive substitute.

From the data obtained by coating ThO_2 and $^{238}PuO_2$ using the MoF_6 process, it became evident that the MoF_6 process would not yield a suitable low neutron flux with $^{238}PuO_2$. Thus, it was decided to

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investigate an alternate method of molybdenum deposition. Molybdenum deposition from the hydrogen reduction of $MoCl_5$ was chosen as it required only a minimum of equipment change; and, since the process is well reported in the literature,[2] it should require a minimum of development time. Again initial studies were performed using ThO_2 as the substrate. These studies were then followed using $^{238}PuO_2$ as the substrate.

THE MoF_6 PROCESS

APPARATUS FOR DEPOSITION

The apparatus for the MoF_6-H_2 system is shown in Figure 1. This system is essentially the same as that developed by M. Browning.[1] The reaction chamber consists of a 0.85 in. i.d. (for 100-g batches) or 1.4 in. i.d. (for 200-g batches) Monel tube with a conical section at the base. Directly below the conical section is a block assembly which serves as both a trap and cooling block to minimize deposition at the capillary opening to the conical section. The substrate particles are introduced to the reactor from the feeder at the top through a ½ in. Monel tube which extends well down into the reaction tube. The coated particles are removed by vacuum aspiration. The exhaust gas system consists of a copper wool filter to remove any particulate matter blown over and a scrubber, usually water, to remove HF and any unreacted MoF_6 from the exhaust gas. The MoF_6 flow rate is monitored with a Hastings Mass Flowmeter.

The following are typical conditions used:

H_2 flow	16 ft^3/hr
MoF_6 flow	1.2 g/min
Temperature	650°C
Rate of deposition	0.5 g/min
Batch size	200 g
Particle size	105-177 μm

ThO_2 AS SUBSTRATE

Table 1 is a compilation of the data obtained on the nature of the fluoride attack on the ThO_2 substrate. (See Figure 2.)

From the data in Table 1, it is apparent that the fluoride impurity is greatest in those batches having the largest surface areas (Samples 15 and 19). Sample 18 resulted from a recoating of batch 17. Only a minor increase in the fluoride content was detected even though the molybdenum content was raised from 3.1 to 9.0%. Thus, the fluorine content appears to increase rapidly as the molybdenum is first deposited, then very slowly thereafter. In addition, it implies that there is a small amount of fluorine contamination in the molybdenum coating itself.

In additional experiments, extensive (up to 3%) fluorine contamination occurred when ThO_2 particles were treated with either

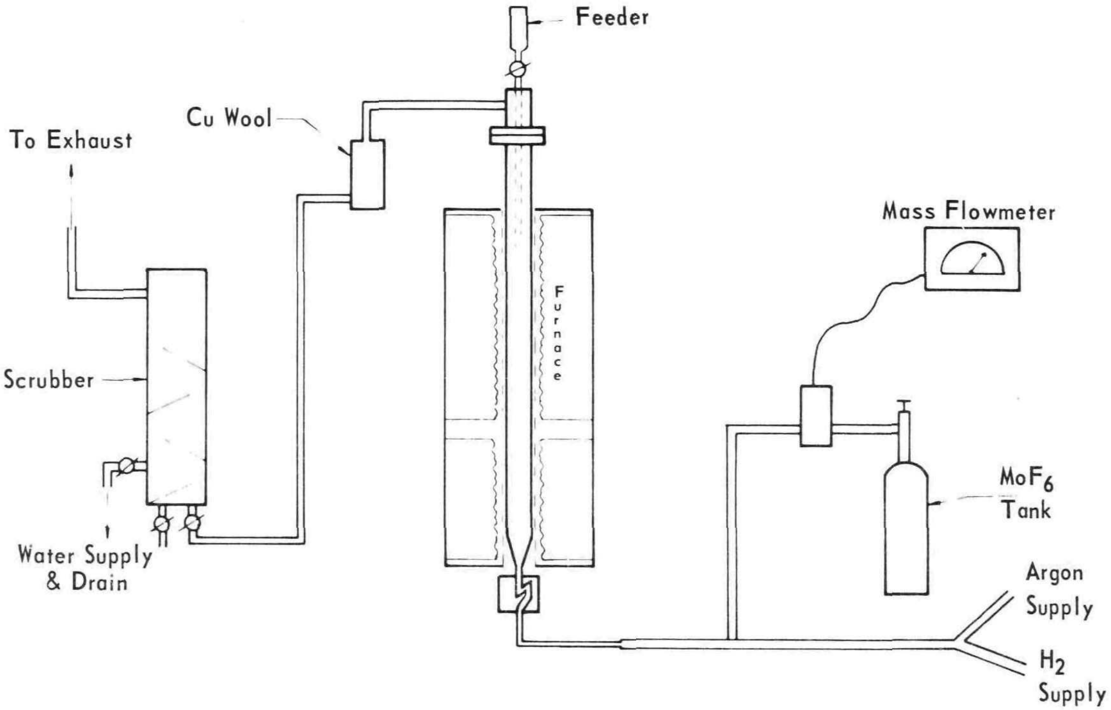


FIGURE 1 - Schematic of chemical vapor deposition apparatus for coating microspheres.

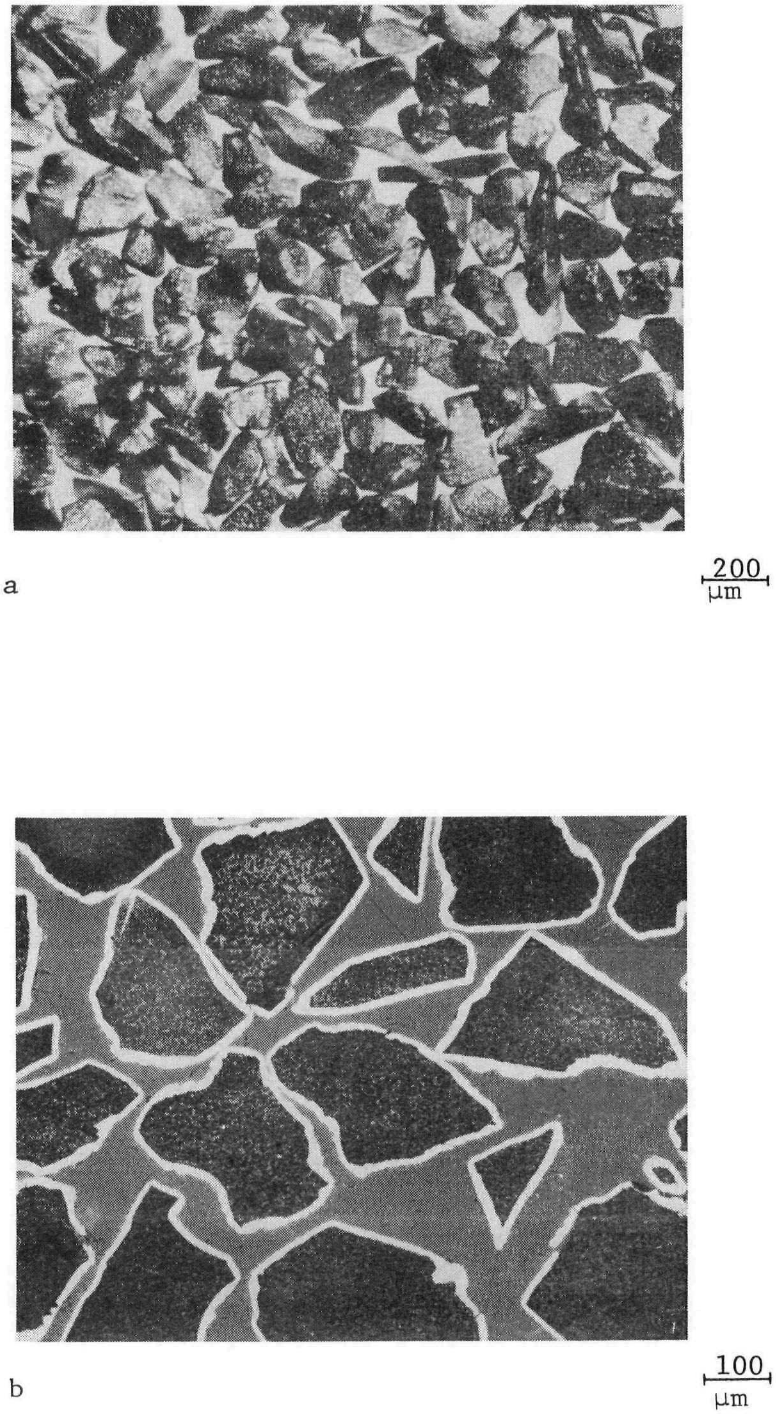


FIGURE 2 - Molybdenum coated thoria particles.

Table 1

FLUORIDE ANALYSIS DATA - ThO_2 SUBSTRATE

Sample Number	Particle Shape of Substrate	Batch Size (g)	Diameter (μm)	Mo (wt %)	F (wt %)
1	irregular	102	105-177	18.5	2.1
2	irregular	101	105-177	20.4	2.0
3	irregular	99	105-177	20.5	1.3
4	irregular	100	105-177	26.4	1.0
5	irregular	52	105-177	17.0	1.3
6	irregular	32	105-177	23.2	0.8
7	irregular	62	105-177	24.5	0.9
8	irregular	45	105-177	26.0	1.3
9	irregular	46	105-177	32.4	0.8
10	irregular	104	105-177	16.2	2.4
11	spherical	200	149-177	11.7	0.8
12	irregular	95	105-177	11.9	1.4
13	spherical	200	149-177	15.6	0.4
14	irregular	101	105-177	12.8	1.0
15	irregular	98	53-105	22.7	4.7
16	irregular	86	105-177	7.2	0.8
17	irregular	48	105-177	3.1	0.7
18	irregular	45	105-177	9.0	0.8
19	irregular	62	53-105	14.9	4.0

MoF_6-Ar or HF-H_2 gas mixtures in the fluid bed maintained at 600°C. These observations suggest that the major source of the fluorine contamination results from fluorination of the surface of the thoria particles possibly by the following reactions:

$$2\ MoF_{6(g)} + 3\ ThO_{2(s)} \xrightarrow{600°C} 3\ ThF_{4(s)} + 2\ MoO_{3(s)},$$

$$4\ HF_{(g)} + ThO_{2(s)} \xrightarrow{600°C} ThF_{4(s)} + 2\ H_2O_{(g)}.$$

Other reactions such as the formation of various molybdenum or thorium oxyfluoride species may also occur. As was indicated above, the molybdenum coating also contains some fluorine contamination. Uniform distribution of a small amount of fluorine throughout the ThO_2 is a possibility but is not likely.

$^{238}PuO_2$ AS SUBSTRATE

Numerous batches of $^{238}PuO_2$ have been coated. The coatings all appear uniform, dense, and continuous. The neutron flux was monitored during all of the initial runs. Figure 3 illustrates the increase in neutron flux observed for different types of feed material. The total neutron emission was measured and is presented in Table 2.

Photomicrographs of cross-sections of samples corresponding to the above batches listed in Table 2 are presented in Figure 4.

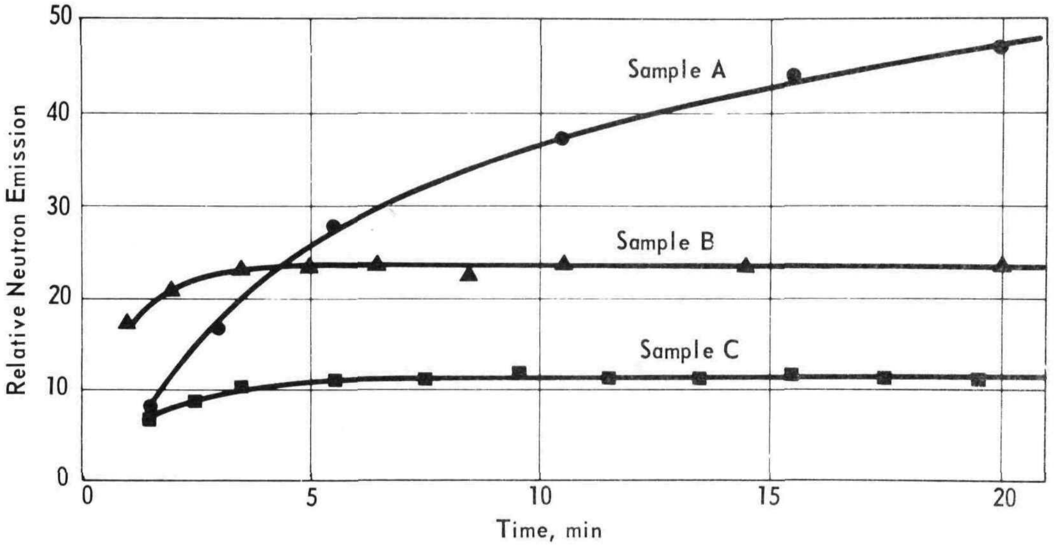


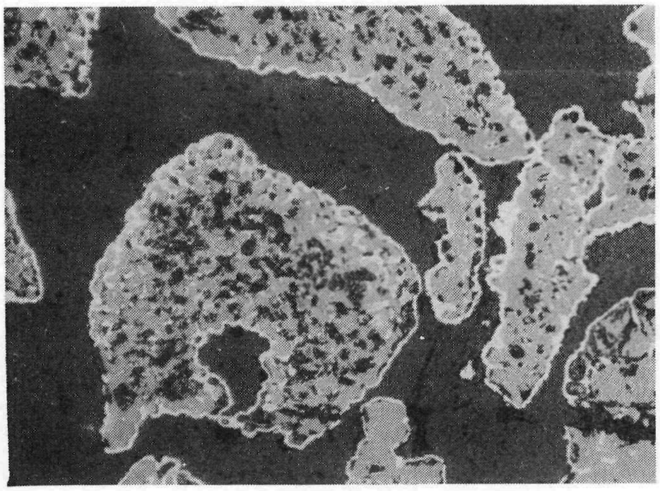
FIGURE 3 - Neutron flux as a function of time during molybdenum deposition from MoF_6.

Table 2

FLUORIDE CONTAMINATION AND NEUTRON EMISSION OF PuO_2 PARTICLES AND PuO_2-ThO_2 SOLID SOLUTION PARTICLES AS A FUNCTION OF SUBSTRATE POROSITY

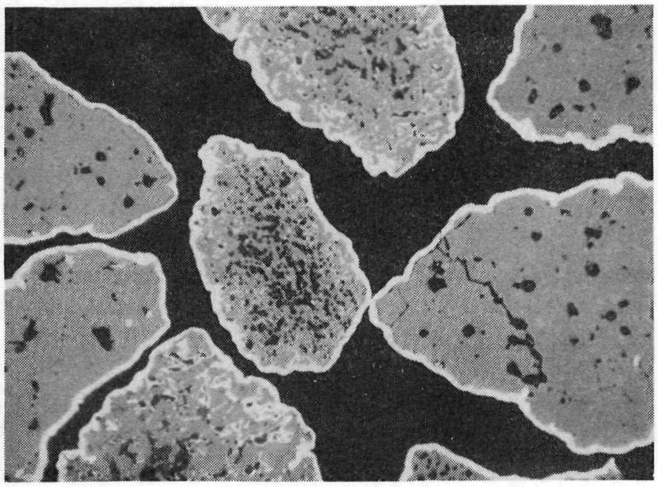
Sample	Substrate[a]	Mo (wt %)	F^- (wt %)	Neutron Emission Before Coating (n/sec/g)[b]	Neutron Emission After Coating (n/sec/g)[b]	Factor Increase in Total Neutron Emission
A	$^{238}PuO_2$ Particles (105-177 μm)	16.8	2.55	1.9×10^4	3.4×10^5	17.9
B	$^{238}PuO_2$ solid solution particles (105-177 μm)	17.9	0.56	1.9×10^4	9.0×10^4	4.7
C	$^{238}PuO_2$-ThO_2 solid solution (105-177 μm)	14.4	0.20	2.2×10^4	5.1×10^4	2.3

[a] $^{238}PuO_2$-ThO_2 was 10% ThO_2.
[b] Per gram of ^{238}Pu.



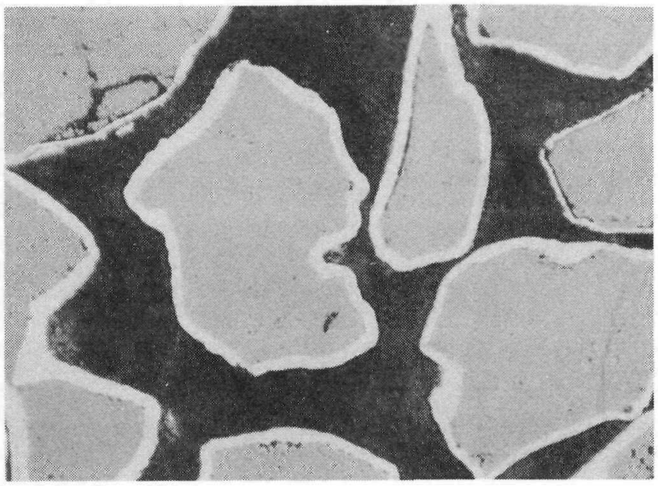
Sample A
$^{238}PuO_2$

100 μm



Sample B
$^{238}PuO_2$-ThO_2
Solid Solution

100 μm



Sample C
$^{238}PuO_2$-ThO_2
Solid Solution

100 μm

FIGURE 4 - Cross-section of molybdenum coated (MoF_6 process) particles.

Note that some of the data presented in Table 2 were obtained on $^{238}PuO_2$-10% ThO_2 solid solution particles; however the same results have been observed in numerous $^{238}PuO_2$ runs.

From the results of the ThO_2 and $^{238}PuO_2$ or $^{238}PuO_2$-10% ThO_2 solid solution experiments, it appears that the comparatively large fluoride contamination is primarily due to surface attack of substrate by HF and MoF_6. The reaction of HF with PuO_2 in the presence of H_2 to form PuF_3 is reported in the literature.[3]

The greater the surface area, including surface connected porosity, per unit weight, the greater is the amount of fluoride contamination in the coated product. Photomicrographs of cross-sections (Figure 4A, 4B) show clearly that H_2 and MoF_6 will penetrate porous material thereby maximizing the surface area available for molybdenum deposition. A comparison of these photomicrographs with the residual fluoride (Table 2) contamination in these samples clearly illustrate that fluorination also increases with increased particle porosity (surface area). Very porous material, such as Sample A, has such a large area of fluorination and molybdenum deposition that the neutron flux increased throughout the entire run.

THE $MoCl_5$-H_2 PROCESS

APPARATUS FOR DEPOSITION

The apparatus for the $MoCl_5$-H_2 process is illustrated in Figure 5. This system is essentially the same as the one used in the hexafluoride process. The main differences arise because $MoCl_5$ is much less volatile (m.p. 194°C). This fact necessitates the addition of a vaporizer to volatilize the $MoCl_5$, and all $MoCl_5$ lines must be kept above 200°C to prevent condensation.

Considerable time was spent on the development of the vaporizer. Schneider and Schonwald[2] developed a process for coating UO_2 and ZrO_2 spheres in a fluid bed by the hydrogen reduction of $MoCl_5$. They used a quartz system charging the vaporizer with only a given amount for a particular run and then running for as long as necessary to transfer that amount through the fluid-bed reactor. Schneider and Schonwald[2] allowed approximately 50% of their total hydrogen flow (120 liters/hr) to pass through the vaporizer to carry the $MoCl_5$ to the fluid-bed. Since our interest was concerned with the development of a production system, we decided to use a large metallic vaporizer which could be charged with up to 2-3 lb of $MoCl_5$. However, when using hydrogen as a carrier gas, we found that, although the rate of $MoCl_5$ transfer was satisfactory for the initial one or two runs, the rate fell off drastically thereafter. Upon close examination we found that all the $MoCl_5$ remaining in the vaporizer had been reduced to the red, much less volatile $MoCl_3$. Upon substituting argon as the carrier gas, we found that we could make numerous runs from a 2 or 3 lb charging of the vaporizer.

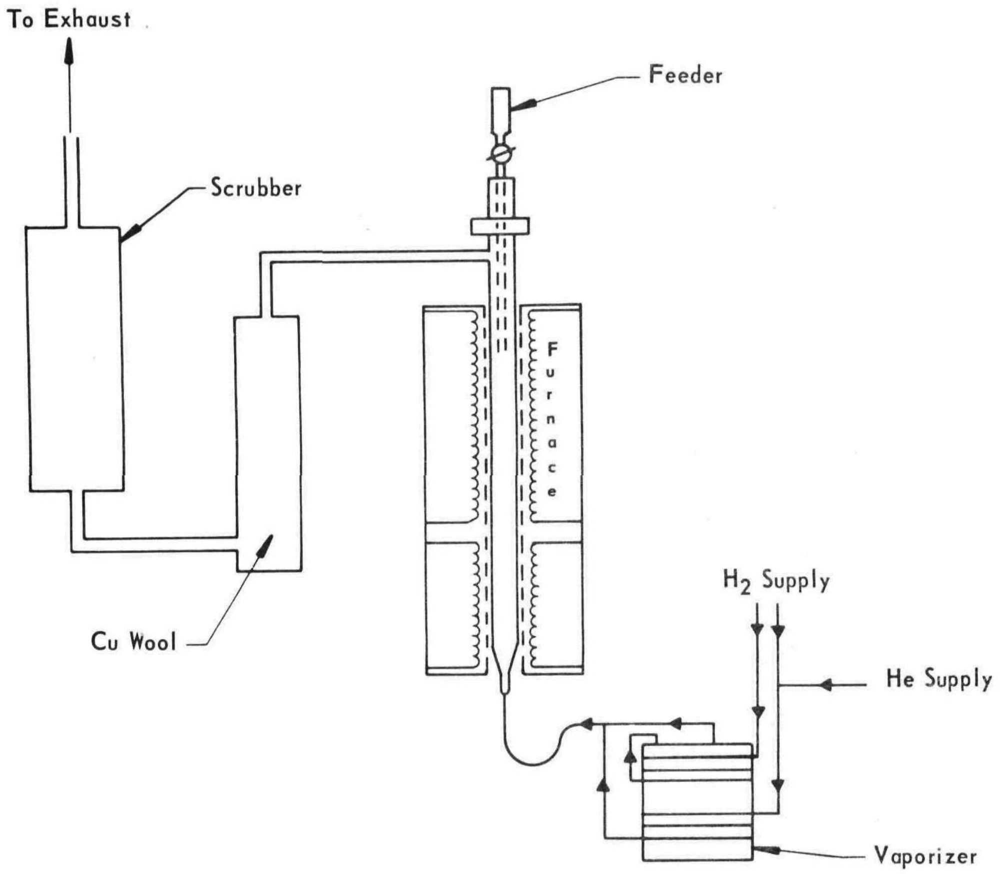


FIGURE 5 - Schematic of $MoCl_5$ chemical vapor deposition system.

The vaporizer is approximately 5 in. in diameter by 6 in. high (inside measurements). Our initial vaporizer was made of nickel-plated copper and is still in use after over one year's service. For convenience in handling the $MoCl_5$, a stainless steel beaker is used to hold the $MoCl_5$ charge inside the vaporizer.

The fluid-bed reactor is made of 1.4 in. i.d. Monel pipe and is routinely used to coat 200-230 g batches at deposition rates up to 0.7 g/min.

The following conditions are typical for a given run:

Weight of substrate PuO_2	200 g
Temperature of fluid bed	700°C
Temperature of vaporizer	220°C
Hydrogen flow through fluid bed	12 ft^3/hr
Ar flow through vaporizer	4 ft^3/hr
Size of particles	105-177 μm
Rate of deposition	0.5 g/min
Efficiency	>80%

ThO_2 AS SUBSTRATE

The results obtained are presented in Table 3.

Table 3

$MoCl_5$: DEPOSITION DATA[a]

Sample Number	Batch Size (g)	Mo (wt %)	Cl (wt %)
1	48	0.38	0.20
2	52	1.56	0.23
3	52	3.42	0.29
4	63	6.70	0.29
5	75	6.31	0.27
6	85	7.28	0.25
7	71	15.4	0.21

[a] Substrate consisted of 105-177 μm irregularly shaped ThO_2 particles.

It is significant to note that although the amount of molybdenum varies from 0.38 to 15.4%, the amount of chlorine impurity is relatively constant. The quality of the deposited molybdenum is comparable with that obtained from MoF_6. However, due to the lack of a convenient monitoring device for the $MoCl_5$ flow, considerable difficulty occurs in control of the deposition rate.

$^{238}PuO_2$ AS SUBSTRATE

Over the past year numerous 200-g batches of $^{238}PuO_2$ have been coated with 15 to 20% molybdenum using the apparatus and techniques described. The neutron flux was measured before and after almost all runs and, as expected, did not change at all. Samples from the initial runs were analyzed for chloride residue. All of these initial runs contained less than 0.2% chlorine. No significant reaction zone could be detected between the coating and substrate in photomicrographs of cross-sections from these batches (Figure 6).

However, once this process went into production, there appeared from time to time a few samples containing a definite third phase (Figure 7). Initially the composition of this third phase was not immediately apparent as it could be either a partially reduced molybdenum chloride, a plutonium chloride species, or some Pu-Mo mixed species. Electron microprobe studies soon resolved the matter. As can be seen from Figure 8, the chloride is solely in the plutonium-rich phase. No molybdenum is found in the chloride or third-phase region. This is not surprising since PuO_2 is known to react with HCl in the presence of hydrogen to form $PuCl_3$ at

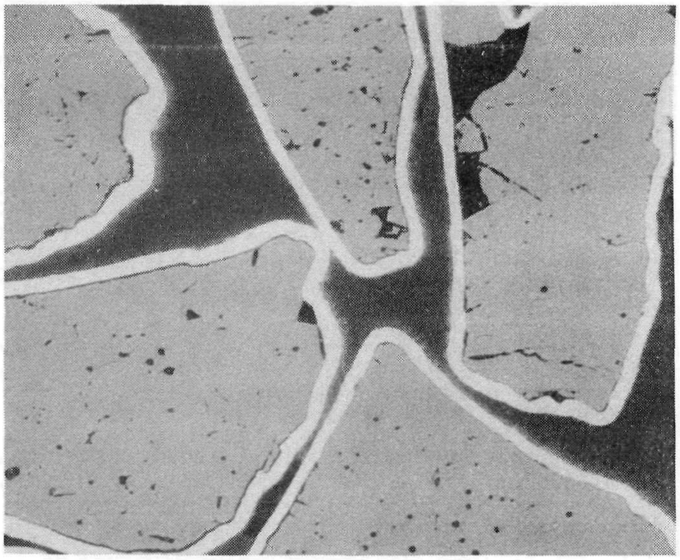


FIGURE 6 - Cross-section of Mo coated $^{238}PuO_2$ by $MoCl_5$ -H_2 process.

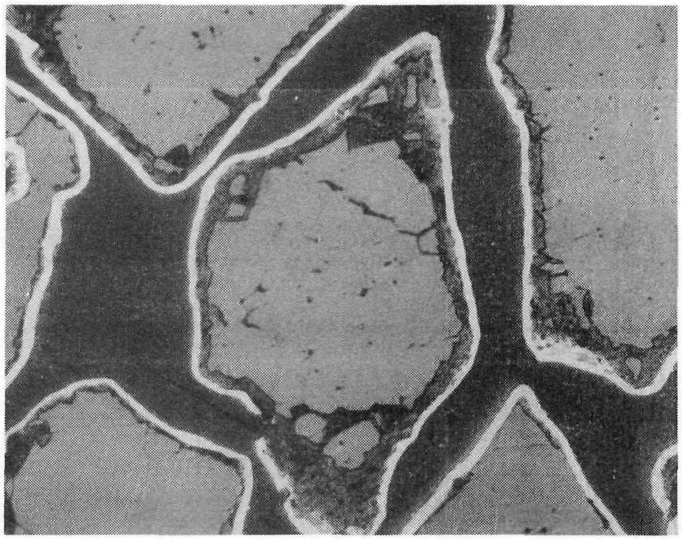


FIGURE 7 - Cross-section of Mo coated $^{238}PuO_2$ showing large reaction zone. $MoCl_5$ -H_5 process.

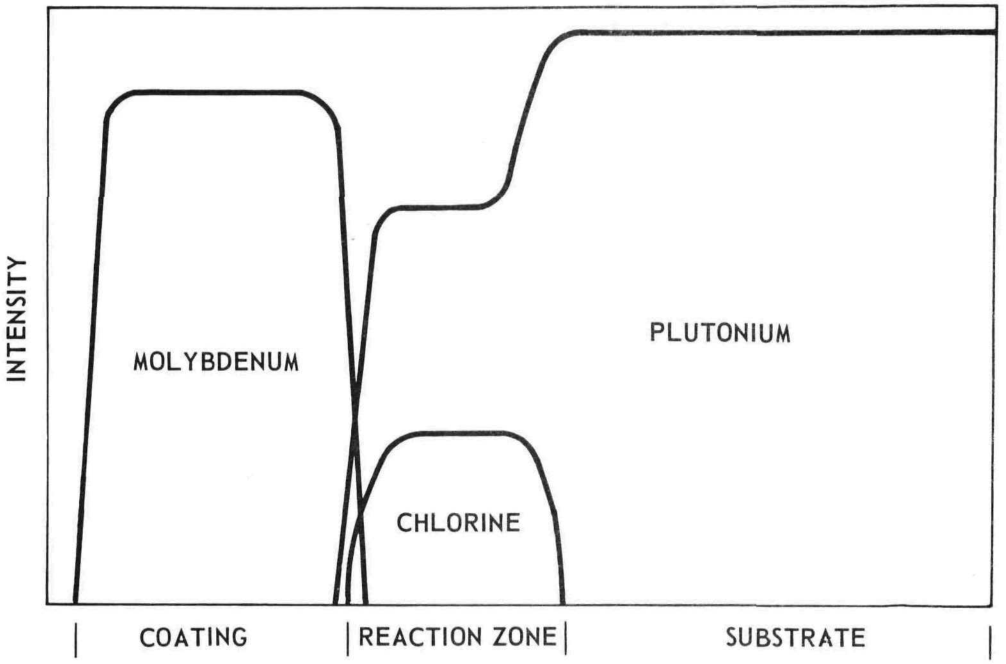


FIGURE 8 - Compilation of electron microprobe results showing relative positions of the elements.

700°C. We must emphasize that Figure 8 is not quantitative in illustrating the relative amounts of the three elements, but is presented to clearly show the regions where the elements are located with respect to the three phases (substrate, reaction zone, and coating).

Resolution of the conditions that cause the reaction and thus its control remain equivocal. The high chloride residue has occurred in samples from all ranges of deposition rates and temperatures. Although it cannot be satisfactorily shown, there appears to be a greater incidence of occurrence at high deposition temperatures. The problem is complicated by its intermittant occurrence.

REFERENCES

1. M. POBERESKIN, Midyear Report on Development for Fabrication of Composite Fuel Form of PuO_2-238, BMI-1831 (Battelle Memorial Institute, Columbus, Ohio), March 11, 1968, 100 pp.

2. H. SCHNEIDER and D. SCHONWALD, The Deposition of Molybdenum on ZrO_2 and UO_2 Spheres from the Gas Phase, MLM-1508(TR) (May 8, 1968), 22 pp. [translated from Die Abscheidung von Molybdän auf ZrO_2 - und UO_2 - Kugeln aus der Gasphase, KFK-555, Gesellschaft Fur Kernforschung m.b.H., Karlsruhe, West Germany (January, 1967), 19 pp.].

3. M. N. MYERS, Thermal Decomposition of Plutonium (IV) Oxalate and Hydrofluorination of Plutonium (IV) Oxalate and Oxide, USAEC Report HW-45128, Hanford Atomic Products Operation, General Electric Co., August 1, 1956.

4. B. M. ABRAHAM, B. B. BRODY, N. R. DAVIDSON, F. HAGEMANN, I. KARLE, J. J. KATZ, and M. J. WOLF, "Preparation and Properties of Plutonium Chlorides and Oxychlorides," in G. T. Seaborg, J. J. Katz, and W. M. Manning (Eds.), The Transuranium Elements, National Nuclear Energy Series, IV, 14B, pp. 740-758, McGraw-Hill Book Co., Inc., New York, 1949.