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of Molybdenum-Coated
Plutonium Dioxide Particles***

D. E. Etter and R. L. Deaton

June 2, 1972

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A Simple Method for the Determination of the Molybdenum Concentration of Molybdenum- Coated Plutonium Dioxide Particles

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ABSTRACT

A simple technique for the determination of the molybdenum content of molybdenum-coated plutonium dioxide particles has been devised. This technique utilizes the oxidation of molybdenum metal and the decomposition of a plutonium-molybdenum-oxygen ternary complex to determine the molybdenum content.

INTRODUCTION

A cermet composed of molybdenum and plutonium dioxide (PMC) is used as a heat source material for SNAP (Systems for Nuclear Auxilliary Power) applications.

Since the molybdenum concentration has a definite effect on the power density and physical characteristics of the fuel material it must be accurately determined prior to hot pressing into the desired shape. The prepressed material consists of $^{239}\text{PuO}_2$ particles (105 to 250 μm) which are coated by the chemical reduction of MoCl_5 by hydrogen in a fluid bed.

In the past the molybdenum concentration has been determined by a wet chemical method which requires a minimum of 3 hr to complete. The inherent corrosive nature of this method makes it undesirable for routine analysis in a stainless steel glovebox. As a result a method was developed which requires no acids or bases, but instead utilizes the inherent oxidation characteristics of molybdenum.

At temperatures above 725°C, catastrophic oxidation of molybdenum and rapid volatilization of MoO_3 has been shown to occur.¹ These distinctive qualities are very favorable to the simple technique of oxidizing the molybdenum coating, volatilizing the MoO_3 , and subsequently calculating the molybdenum concentration from the sample weight loss.

EXPERIMENTAL

Initial studies were carried out using a thermogravimetric analysis apparatus previously described.² This technique was employed in an attempt to follow the oxidation and volatilization that occurred during heating.

A 16-mg sample of molybdenum-coated plutonium dioxide was heated at 3°C/min up to 910°C, in air. The resulting thermogram, Figure 1, exhibited a weight gain from 490°C to about 710°C. The weight remained constant until 740°C, at which point a rapid loss began and continued to 810°C. At this temperature the rate of weight loss decreased noticeably, but continued until 910°C was reached after which time no further loss was observed.

FIGURE 1 - TGA thermogram of molybdenum-coated PuO_2 .

Originally attempts were made to calculate the molybdenum concentration from the weight gain at 710°C, assuming that it was oxidized to MoO_3 and no volatilization occurred. In every analysis the weight gain was insufficient to account for the known quantity of molybdenum. It was then assumed the probable cause of this error was the competing reactions of oxidation and volatilization occurring simultaneously. Efforts were made to volatilize the molybdenum by raising the temperature to 825°C and holding until no further weight loss was observed. The concentration of molybdenum was then calculated from the weight loss. This technique resulted in insufficient weight loss to account for the known quantity of molybdenum.

In an effort to explain these anomalies, metallographic and electron microprobe examinations were made of the heated materials. The results exhibited the presence of an intermediate phase. Figures 2 and 3 are photographs of electron microprobe line scans for plutonium and molybdenum of a sample heated in air at 710°C for 30 min. The horizontal line on the photos is the exact location of the scan, while the vertical peaks depict the intensity of the plutonium and molybdenum in Figures 2 and 3, respectively.

The darker region which shows no plutonium and a high molybdenum concentration is very likely MoO_3 . The intermediate region exhibits the presence of both plutonium and molybdenum, whereas the grey portion depicts a high concentration of plutonium and no molybdenum. These results can be compared to identical line scans of

FIGURE 2 - A line scan for plutonium of a molybdenum-coated PuO_2 particle (13 wt % Mo) heated at 710°C for 30 min in air.

FIGURE 3 - A line scan for molybdenum of the same particle shown in Figure 2.

FIGURE 4 - A line scan for plutonium of an unheated molybdenum-coated PuO_2 particle (13 wt % Mo).

FIGURE 5 - A line scan for molybdenum of the same particle shown in Figure 4.

unheated material shown in Figures 4 and 5. The dark grey area is unoxidized molybdenum and, as expected, exhibits a high molybdenum concentration and the absence of plutonium. The lighter grey portion depicts the reverse element concentration. Virtually no intermediate phase is present. These results suggest that the intermediate phase is a ternary complex of Pu-Mo-O. This reaction would prevent all of the molybdenum from forming MoO_3 under the previously described conditions and as a result account for the insufficient weight gain for correct calculation of known quantity of molybdenum. This incomplete formation of MoO_3 would also effect the calculation of the molybdenum concentration from weight loss due to vaporization.

Further investigation showed that this ternary phase was readily decomposed at temperatures above 925°C under vacuum or air, since all the molybdenum could be accounted for by weight loss determinations in samples heated to this temperature. In addition to this no evidence of the ternary complex in the remaining PuO_2 was found by metallographic examination.

With this background data in mind, a simple oxidation-vaporization apparatus, shown in Figure 6, was designed and fabricated for this technique. It consists of a quartz vacuum chamber, which houses a suspended platinum sample pan. The chamber is heated by a resistance furnace and can be evacuated or purged with oxygen as desired. A flowmeter is used to monitor a flow rate in the 300 to 400 ml/min range. The sample temperature is measured by a chromel-alumel thermocouple located in proximity to the

sample pan.

The analysis involved weighing the sample pan, adding the sample, reweighing, then introducing the pan into the quartz vacuum chamber. The oxygen flow was adjusted to about 400 ml/min, and the sample temperature was raised to between 950-980°C. The length of heating was dependent upon sample size (maximum of 500 mg); 1 hr was found to be sufficient for a 200 to 300 mg specimen. After 1 hr, the chamber was evacuated with a roughing pump to a pressure of about 10 mm of Hg for 5 min, and the sample was reweighed. This was repeated until no further weight loss occurred. A time parameter can be established for the selected sample weight.

FIGURE 6 - Oxidation-vaporization apparatus.

Data shown in Table 1 compare the results of this technique with those of the wet chemistry method. The maximum disagreement is 0.9 wt % molybdenum for 11 determinations. This technique does have the shortcoming that any volatile impurities present will be calculated as molybdenum. However, the particles are normally heat treated to 700 to 800°C in hydrogen atmosphere after coating and are examined metallographically. Otherwise the maximum error is the weighing accuracy which has a limit of ± 0.4 mg.

The data in Table 2 show calorimetry values for plutonium-238 before and after analysis. These determinations were made to check for possible loss of plutonium during the decomposition of the previously discussed Pu-Mo-O phase. It is obvious from the results that no loss occurred.

Table 1

A DATA COMPARISON OF THE OXIDATION-
VAPORIZATION AND THE WET CHEMISTRY METHODS
FOR THE DETERMINATION OF MOLYBDENUM CONCENTRATION

Batch No.	Molybdenum Concentration by	
	Oxidation-Vaporization (wt % Molybdenum)	Wet Chemistry (wt % Molybdenum $\pm 0.5\%$)
PC1-191, 192	17.1	17.3
PC1-196-L	13.9	14.1
PC1-191-L	25.5	25.5
PC1-195, 196-S	11.9	11.6
PC1-195, 196-S	11.8	11.6
PC1-91, 94-R-5	14.8	14.9
PC1-195, 196-S-E2	21.3	20.9
PC1-195, 196-S-E2	21.2	20.9
PC1-195, 196-S-E2	21.2	20.9
PC1-195, 196-S-E2	21.0	20.9
PC1-195, 196-S-E2	21.1	20.9

Table 2

A COMPARISON OF CALORIMETER DATA BEFORE
AND AFTER ANALYSIS

Batch No.	Plutonium-238 Content	
	Before Heating (W/g $\pm 0.3\%$)	After Heating (W/g $\pm 0.3\%$)
195-196-S-1	0.3086	0.3091
195-196-S-2	0.3071	0.3082
195-196-S-3	0.3087	0.3097
195-196-S-4	0.3076	0.3086

CONCLUSION

This method has desirable features that are amenable to routine analysis in a stainless steel glovebox, namely:

- a) no requirement of corrosive acids or bases,
- b) it is a relatively rapid analysis, requiring about 1 hr,
- c) during most of the analysis the apparatus can be unattended,
- d) the apparatus is simple and economical to fabricate.

Since no coated standards were available, the method accuracy was compared only to the results obtained by the previously mentioned wet chemistry technique. The accuracy is believed to be affected mainly by the volatile impurities and the weighing accuracy, which in this work is estimated to be $\pm 1\%$.

During the course of this investigation a reaction was discovered between the molybdenum coating and the PuO_2 when they were heated in air at 710°C . Metallographic and electron microprobe examinations revealed the presence of both molybdenum and plutonium in this phase. This strongly suggests a Pu-Mo-O ternary complex. This is not surprising since other group IV/actinide complexes have been reported in the literature.³

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