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THE MEASUREMENT OF OXYGEN TO METAL RATIO IN SOLID SOLUTIONS OF URANIUM AND PLUTONIUM DIOXIDES

By
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May 31, 1963

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ABSTRACT

A survey has been made of methods potentially useful for the determination of the oxygen to metal ratio in mixed oxides of uranium and plutonium. A gravimetric method was selected as being the most promising for adaptation in a short period of time. Development of the technique has resulted in a reliable method which meets the requirements for unirradiated mixed oxide fuel samples. The method, based upon an equilibrium weight at 700°C in dry hydrogen, was shown to be capable of measurement of O/(Pu + U) ratios in 20% PuO_2-80% UO_2 pellets with a standard deviation of ± 0.001.

THE MEASUREMENT OF OXYGEN TO METAL RATIO IN SOLID SOLUTIONS OF URANIUM AND PLUTONIUM DIOXIDES

I. INTRODUCTION

Solid solutions of uranium and plutonium dioxides are receiving extensive examinations as fuel for fast ceramic reactors. One of the variables which can affect the fabrication and performance of oxide fuels is the oxygen to metal ratio. It is well known, for example, that some oxygen in excess of the stoichiometric amount can assist in the sintering process for making high density pellets of uranium oxide [1]. This appears to be equally important in the fabrication of mixed oxides of uranium and plutonium. Departures from stoichiometry may have effects on the thermal conductivity, degree of fission gas retention during irradiation, plasticity, and other properties of mixed oxide fuel. There is, further, reason to believe that the compatibility of mixed oxide fuel with the liquid sodium coolant, in the event of fuel element failure, may be a function of the oxygen to metal ratio in the fuel.

It is of interest for the above reasons to be able to determine and to control the O/M ratio of a mixed oxide.

Reported herein are the conclusions derived from a survey of potential methods for the measurement of O/M ratio in mixed oxide and the adaptation of a gravimetric method basically similar to that of Brett and Russell [21] for the measurement of O/M in unirradiated fuel samples.

II. SURVEY OF METHODS

The literature has been surveyed for methods which have been used, or which are potentially useful, in the analysis of mixed plutonium/uranium oxides for the O/M atomic ratio. These various methods are described briefly below and evaluated.

A. Dissolution Methods

A method [2,3] commonly used for the determination of O/U in uranium oxides is that of dissolving the sample in phosphoric acid, performing a coulometric titration of the hexavalent uranium present, oxidizing with ceric sulfate, and titrating the total uranium present. The O/U ratio is determined from the relative peak heights of the two titrations on a current versus time plot using the relation $O/U = 2.0000 + \frac{U\ VI}{U\ total}$. A similar method might be applied to mixed $(Pu, U)O_2$, providing that the mixed oxide could be dissolved in a non-oxidizing acid followed by the determination of an average oxidation number of the solution. The mixed oxide, however, cannot be conveniently dissolved, except by use of hot nitric acid which results in oxidation of PU(III) and U(IV).

Molten salts, however, offer potential means of dissolving the mixed oxides. It has been reported by Lyon and Moore [4] that mixtures of aluminum chloride and potassium chloride, melting near 200°C, are good solvents for the actinide oxides, and do so by converting them to their respective chlorides without changing their valence. The resulting molten salt solution may be examined spectrophotometrically for determination of the species present. Alternatively, the molten salt solution may be frozen, redissolved in an aqueous solution of dilute HCl, and the valence states analyzed by conventional methods.

B. X-Ray Diffraction

Mulford and Ellinger [5] found that the cell constant of the solid solution of uranium-plutonium dioxide was a linear function of the plutonium content, and that the system closely obeyed Vegard's Law.

Drummond and Sinclair [6] showed that the cell parameters of the solid solution could be correlated with its oxygen to metal ratio both above and below the value for stoichiometric dioxide. They concluded that the X-ray method, although less precise than the thermogravimetric method, could yield results more rapidly, providing that the Pu/U ratio was known.

Both X-ray diffraction and X-ray fluorescent techniques are being studied for analysis of unirradiated mixed oxide fuels.

C. Optical and Infrared Spectrometry

There is little information on the optical properties of UO_2 and apparently none on the optical properties of the plutonium-uranium-oxygen system. Ackermann et al [7] have reported on the optical absorption of UO_{2+x} films deposited by sublimation on fused silica, with measurements having been made in the 220 to 800 mμ region. The amount of oxygen in the films was varied by exposing them to an oxygen partial pressure at high temperature. The amount of absorption was shown to vary with excess oxygen, being reduced in the 340 to 480 mμ region and increased in all other regions.

Companion and Winslow [8] made diffuse reflectance measurements on the surfaces of bulk UO_2 and non-stoichiometric uranium dioxide powders. The optical properties were found to be in general agreement with those obtained on thin films. Moreover, the same effects of excess oxygen were observed. In their work a small peak was found near 665 mμ. This was also detected by Gruen [9] who studied the absorption spectra and electrical conductivities of UO_2-ThO_2 solid solutions.

Alter [10] suggested the use of the reflected spectra from UO_2-PuO_2 ceramic fuel pellets as a possible means of measuring the oxygen to metal ratio as well as the Pu/U ratio. This prompted a brief study by the writer to explore these possibilities.

Reflectance spectra versus a magnesium carbonate standard were run for samples of UO_2, UO_{2+x}, U_3O_8, and UO_3 in the wave length range 240 to 750 millimicrons. Although differences in the percent reflectance were observed, as anticipated, no well-defined peaks were found which could serve as a basis for quantitative measurement of oxygen to metal ratio.

Samples were scanned for fluorescence in the 400 to 800 millimicron region when illuminated with 300 to 400 millimicron light. No fluorescence was observed.

Infrared absorption spectra were obtained in the region 2 to 15 microns using the KBr pellet technique. Peaks were observed at 10.7 and 13.6 microns for both U_3O_8 and UO_3, and at 11.6 for UO_3. These peaks were not found in the UO_{2+x} spectrum.

Although these methods did not appear promising for analytical use in the oxygen/metal region of interest in the uranium-oxygen system, it may be of interest to examine the plutonium-containing oxides with these techniques.

D. Magnetic Susceptibility

The magnetic susceptibility studies on the oxides of uranium made by Dawson and Lister [11] and by Arrott and Goldman [12] showed marked variations in the magnetic susceptibility with oxygen/uranium ratio.

Watt [13] has suggested the use of this well-recognized tool for analysis of the PuO_2-UO_2 system.

E. Solid State Coulometric Titrations

Kiukkola [14] has made electromotive force measurements on galvanic cells involving solid electrolytes and an uranium oxide pellet electrode. The emf was determined for pellets of various O/U ratios as a function of temperature.

In addition to these measurements with uranium oxides of predetermined O/U ratios, a few measurements were performed with the solid state coulometric titration technique of Wagner [15, 16]. In these experiments, performed at constant temperature, a current passed through the cell adds, or removes, oxygen, depending upon direction, from the UO_2 electrode. The change in the amount of oxygen x is related to the amount of current passed. Also, the emf required to pass current through the cell is a function of the O/U atomic ratio.

These techniques may be of interest to explore for uranium-plutonium mixed oxides.

F. Reduction and Gas Analysis

Roberts and Harper [17] developed a method in which the oxygen above stoichiometric in UO_2 was estimated directly by measuring the amount of H_2O or CO_2 evolved during complete reduction with H_2 or CO, respectively, at 700°-800°C.

At D.E.R.E. [6] an attempt was made to apply the method to the analysis of uranium-plutonium mixed oxides, but the approach was abandoned because of high blanks and because it could not be applied directly to samples with O/M ratios less than two.

G. Gravimetric Methods

A standard method long used for determining atomic ratios in the uranium-oxygen system has been oxidation to U_3O_8 [18], a conveniently obtained reference state. This method has undergone investigation and refinement by Bright _et al_ [19] and by Stonhill [20].

In the plutonium-uranium-oxygen system, analysis by combustion in air is less convenient than in the uranium-oxygen system. Brett and Russell [21] have observed that in this system the oxidation behavior is anomalous with PuO_2-UO_2 solid solutions taking up less oxygen than would be expected if the oxidation products were U_3O_8 and PuO_2. In more recent work [22, 23] the Harwell workers have observed that oxidation alone may be used to establish a reference point once a given material has been characterized by oxidation and reduction.

The oxidation and reduction technique of Russell et al [21, 22] is based upon the equilibrium weight at 700°C in hydrogen as a convenient reference point. The choice of this temperature for reduction was based upon a compromise between selecting a temperature low enough to prevent reduction of PuO_2 but high enough to reduce hyper-stoichiometric uranium oxide to $UO_{2.00}$.

Drummond et al [6, 24] have reported on a semi-micro thermobalance and technique for analysis of Pu/U mixed oxides. Their method makes use of the weight versus time plot obtained upon reduction in pure hydrogen at 1150°C from a sample which has previously been heated first in argon and then in oxygen at 1000°C. The point on the curve at which the rate of reduction becomes constant is taken as the weight which represents an overall O/M ratio of 2.000.

A microbalance-thermogravimetric technique may well be of value in the analysis of very small samples of mixed oxide fuels, thus possibly permitting analysis of irradiated fuel material without massive shielding, or of samples selected from specific regions within a mixed oxide fuel pellet.

III. THE GRAVIMETRIC METHOD

A macro-gravimetric method was chosen for the determination of oxygen to metal ratio in unirradiated mixed oxide fuel because it appeared to offer the most reliable technique for adaptation to plutonium-containing materials.

A. Equipment and Procedures

The apparatus assembled for the gravimetric determination of oxygen to metal ratio consisted of a substitution weighing analytical balance, an Ainsworth Type 10 with weigh-below attachment, a combustion furnace, a 750 watt Hevi Duty Model 70T with 1-1/4" diameter and 12" length chamber, and a pyrometer-controller, General Electric Model HP-32, for controlling the furnace. (Figure 1).

The balance was mounted on the top of the glove box with a small pan suspended by a wire extending into a Plexiglass chamber attached to the top panel of the glove box. This chamber was closed off during the weighing operation to prevent a flow of air through the small hole which would affect the reading of the balance.

A furnace tube of Vycor glass was used. A thermocouple installed at the mid-point of the furnace length, and between the tube and the element, was used to control the temperature. The temperature within the sample boat placed directly above this thermocouple was found not to vary more than ± 5°C from the set temperature while the furnace was holding at 700°C by the single point controller.

Argon and 6% hydrogen-94% helium gases were supplied through Victrometer flow meters, and were passed through a magnesium perchlorate column, before entering the furnace tube. The exit gas from the tube was passed through a filter flask containing glass wool to reduce the possibility of air diffusing backward into the system. For the oxidation cycle, the furnace tube was left open to the air atmosphere of the glove box.

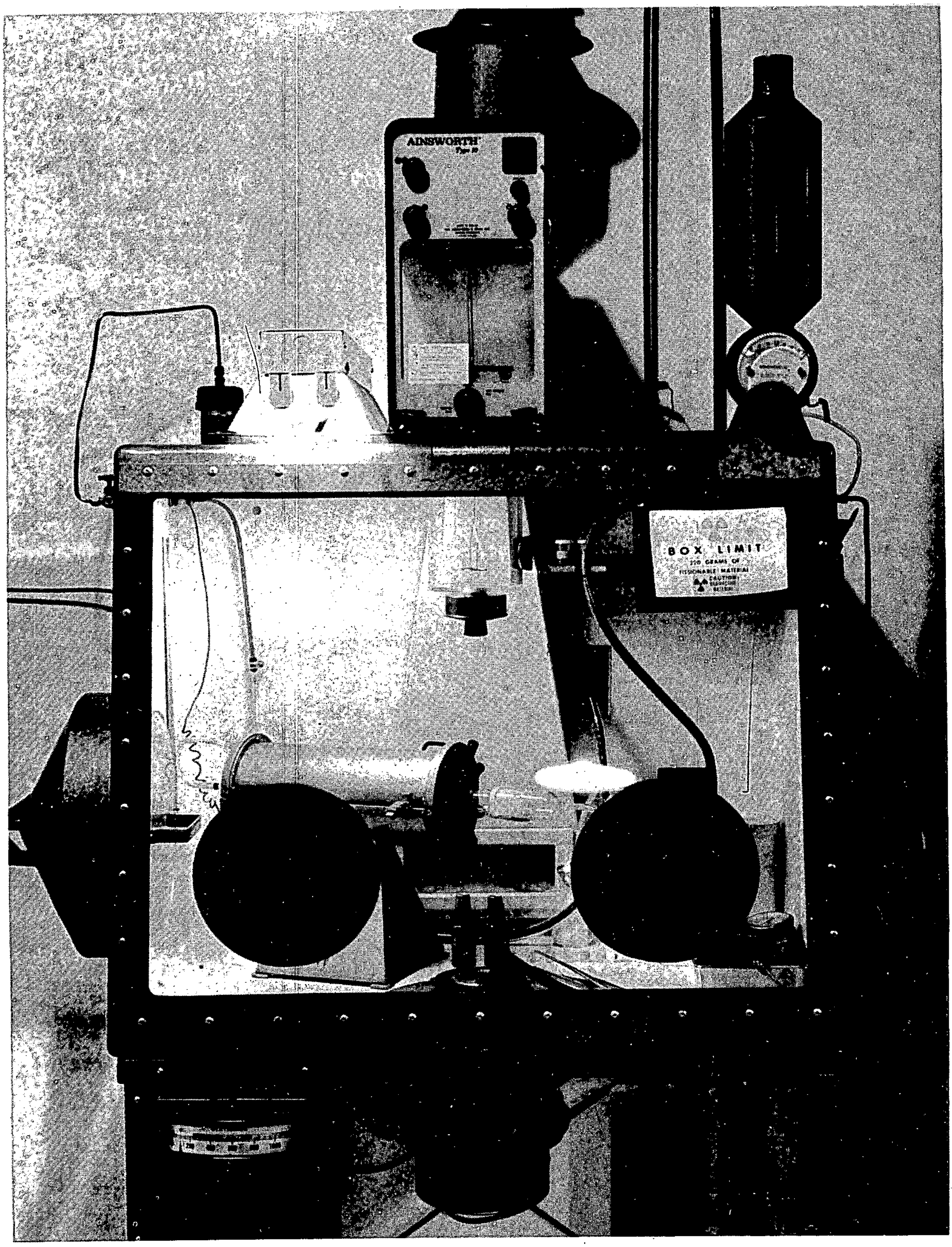

Figure 1. GLOVE BOX AND APPARATUS

Used in the gravimetric oxygen to metal determinations on mixed PuO_2 - UO_2 oxides

Samples were placed in either aluminum oxide or platinum boats. Since sintered pellet samples of 20% PuO_2-80% UO_2 composition were found not to decrepitate upon oxidation and reduction, these were transferred with forceps directly to the pan of the balance for weighing. Powder samples, on the other hand, were run in platinum boats which were found not to change weight in the atmospheres used.

Following a furnace treatment in the inert or reducing atmosphere, it was, of course, necessary to cool the samples to room temperature in this atmosphere before weighing to prevent reoxidation in air. The furnace tube was, therefore, equipped with a wire hook which could be used to withdraw the sample boat into the cold region of the tube in order to cool the sample quite rapidly without shutting off the furnace.

B. Preliminary Experiments

In adopting a method similar to that of Brett and Russell [21] it was necessary to go through the proof of the method in our system. This was necessary (1) because of the use of 6% H_2-94% He gas rather than pure hydrogen for reasons of safety, and (2) because knowledge of the kinetics of oxidation or reduction in the materials to be analyzed was lacking.

The first stage of the development was to study the oxidation and reduction behaviors of the individual oxides.

1. Oxidation-Reduction of Uranium Dioxide

Uranium dioxide pellets of the same diameter as the mixed oxide pellets were available. Samples from this batch were reported to have an O/U ratio of 2.0063 ± 0.0003, having been analyzed by the phosphoric-acid-dissolution- and electro-metric-titration method.

Uranium dioxide pellets from this batch were first equilibrated at 700°C in 6% H_2-94% He gas taken directly from the cylinders for several hours, cooled under this gas, and weighed periodically. No weight reduction could be observed.

A magnesium perchlorate column was then added to the system to dry the reduction gas. A reduction of weight of the UO_2 pellets was then observed from which an O/U ratio in the original samples was calculated as 2.006 ± 0.001. This value was confirmed by oxidizing the samples in air at 850°C to U_3O_8.

The water content of the hydrogen-helium gas taken directly from the cylinders was found by analysis to vary from 200 to 800 ppm. It was not apparent whether reduction of UO_2 was incomplete in this "wet" hydrogen-helium, or whether the samples were picking up weight by surface absorption of moisture from the gas after cooling.

2. Oxidation and Reduction of Plutonium Dioxide

Plutonium dioxide pellets were prepared from oxide derived from plutonium (IV) oxalate and were pressed and sintered in the Plutonium Laboratory sintering furnace under standard conditions in use for the sintering of mixed oxide pellets.

Two pellets from this batch were weighed in the "as-sintered" condition, and then were heated in air at 900°C until a constant weight was obtained. The composition after this oxidation could reasonably be assumed to be $PuO_{2.000}$. The calculations of the O/Pu ratios in the as-sintered pellets from this reference composition gave values of 1.850 and 1.855.

The next step was to determine whether an equilibrium weight obtained at 700°C in dry H_2-He gas could be obtained with PuO_2 from which to calculate the oxygen stoichiometry.

Plutonium oxide pellets were therefore treated as follows: An initial weight was obtained after heating in dry argon at 100°C for 1/2 hour. The samples were heated to 750°C in air and held for one hour, and then heated in 6% H_2-94% He gas at 700°C. The samples were cooled and weighed periodically. No loss in weight was observed during six hours of treatment in the reducing atmosphere. Calculation of the O/Pu ratio for the original sample, based upon the equilibrium weight at 700°C in H_2-He taken as stoichiometric gave a value of 1.850 ± 0.001 for the two samples. This composition obtained upon reduction was shown to be $PuO_{2.000}$ by subsequently igniting in air at 900°C without change of weight.

3. Gravimetric Behavior of Mixed Oxides

The gravimetric procedure was next applied to mixed oxide pellets. In order to observe the kinetics of the oxidation and reduction reactions, an experiment was designed in which four similar pellets, from the same powder batch and sintered under similar conditions, were used. (It would have been preferable to section a single pellet into at least four pieces, except that the sample size would then have been too small for good precision.)

The four samples were first heated in dry argon at 100°C to constant weight. Then they were oxidized individually for various times at 750°C in air (Table I). Finally they were reduced simultaneously, being withdrawn for weighing at regular intervals. The data for three of the pellet samples are plotted as ΔW versus time in Figure 2. Using the constant weights obtained upon reduction, the initial O/M ratios were determined for the samples. These numbers gave an arithmetic mean value of 1.986 with a standard deviation of 0.001.

A similar experiment was performed using pulverized mixed oxide made by crushing four similar pellets in a mortar, and dividing this into two samples. One sample was oxidized to constant weight (obtained after two hours, and found to correspond to O/M = 2.340) and then weighed at intervals during the reduction. Constant weight after reduction was reached in

TABLE I

DATA FROM THE OXIDATION AND REDUCTION OF MIXED OXIDE PELLETS

Sample Number	B-7-52	B-7-94	B-7-128	B-7-135
Initial Weight (g)	1.6089	1.6233	1.5955	1.6134
Wt. after heating in argon 1 hr. at 110°C (g)	1.6088	1.6233	1.5955	1.6135
Time of oxidation at 750°C in air	5 min.	30 min.	60 min.	80 min.
Weight after oxidation (g)	1.6210	1.6459*	1.6173	1.6443
Weight after reduction 30 min.	1.6148	1.6328	1.6097	1.6372
Weight after reduction 60 min.	1.6107	1.6268	1.6041	1.6297
Weight after reduction 90 min.	1.6098	1.6249	1.6010	1.6245
Weight after reduction 150 min.	1.6098	1.6249	1.5972	1.6150
Weight after reduction 270 min.	1.6098	1.6249	1.5970	1.6149
Weight after reduction 360 min.	1.6097	1.6250	1.5967	1.6146
Calculated O/M after oxidation	2.118	2.218	2.215	2.315
Calculated O/M of original sample	1.989	1.983	1.987	1.985

*Sample B-7-94 was inadvertently broken in half following oxidation.

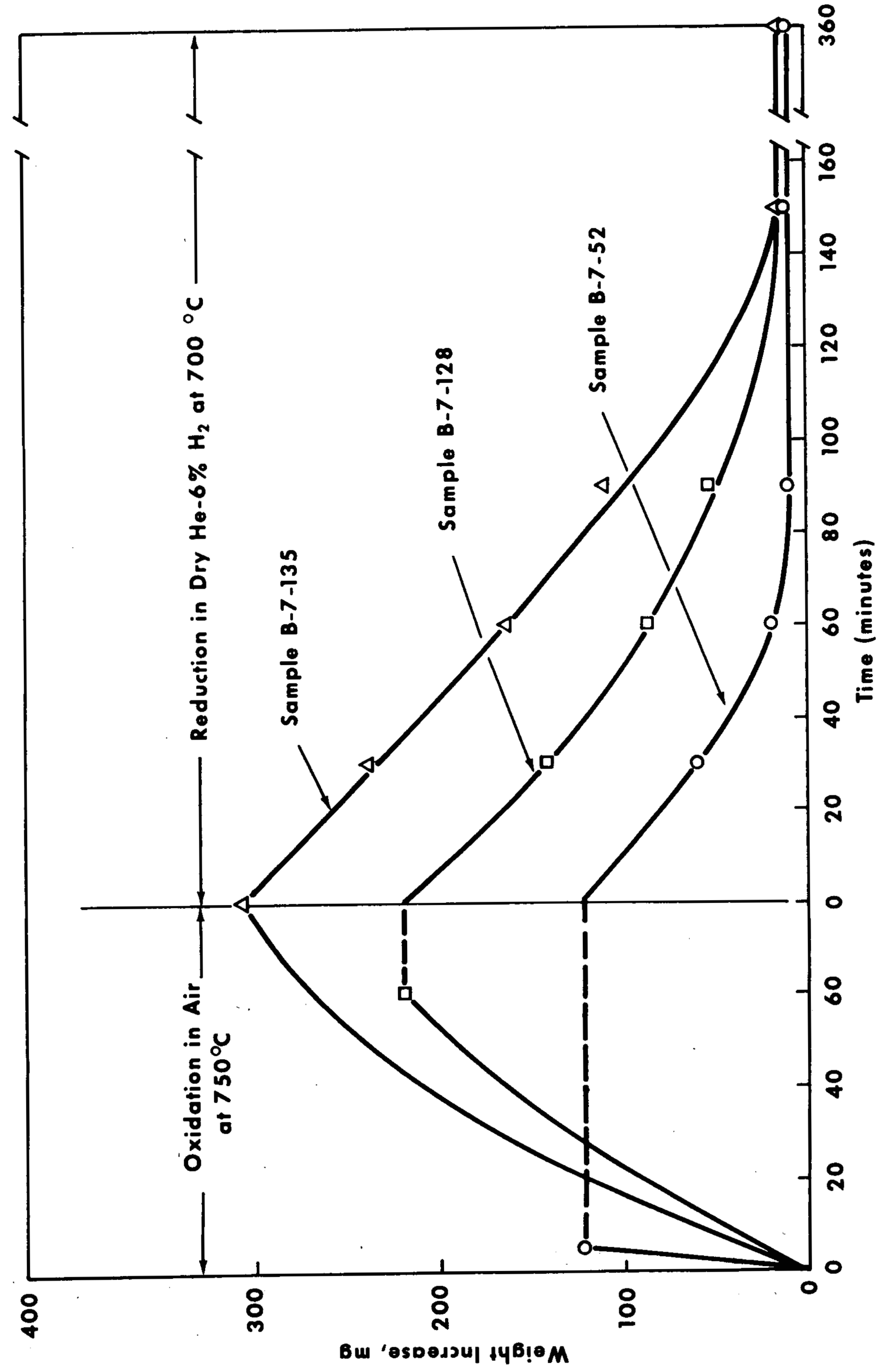

Figure 2. OXIDATION AND REDUCTION OF UO_2-20% PuO_2 MIXED OXIDE PELLETS

approximately four hours (refer to Figure 3). The O/M ratio of the sample calculated from this weight was 1.972. The second powdered sample was analyzed by oxidizing for a period of only 15 minutes (to O/M = 2.321) followed by reduction to constant weight in three hours. A value of 1.973 was obtained for the original material, in excellent agreement with that obtained on the other part of the sample.

It was concluded from these experiments that the extent to which the mixed oxide is oxidized is of no importance, providing that the sample is hyper-stoichiometric before the reduction step. Knowledge of the times required for reduction of powder and pellet samples permitted the adoption of a standard procedure for the analyses.

C. Analytical Procedure

Based upon the foregoing experiments to establish the technique, a standard analytical procedure was established for routine O/M measurements. The procedure is as follows:

1. The sample is heated in dry argon gas at 110°C until a constant weight is obtained. In the case of a sintered pellet sample, the weight loss upon drying will ordinarily be very slight or nil. However, in the case of an active powder sample, there may be a significant weight loss which is due to absorbed moisture and gases. Care must be taken not to remove a powder sample from the inert atmosphere without cooling to room temperature. The dry weight of the sample is taken as the true weight of oxide, W_1.

2. The sample is heated in air (furnace tube open) to 750°C. This weight is recorded only as a record of the extent of oxygen pick-up. Samples may be removed from the furnace while hot.

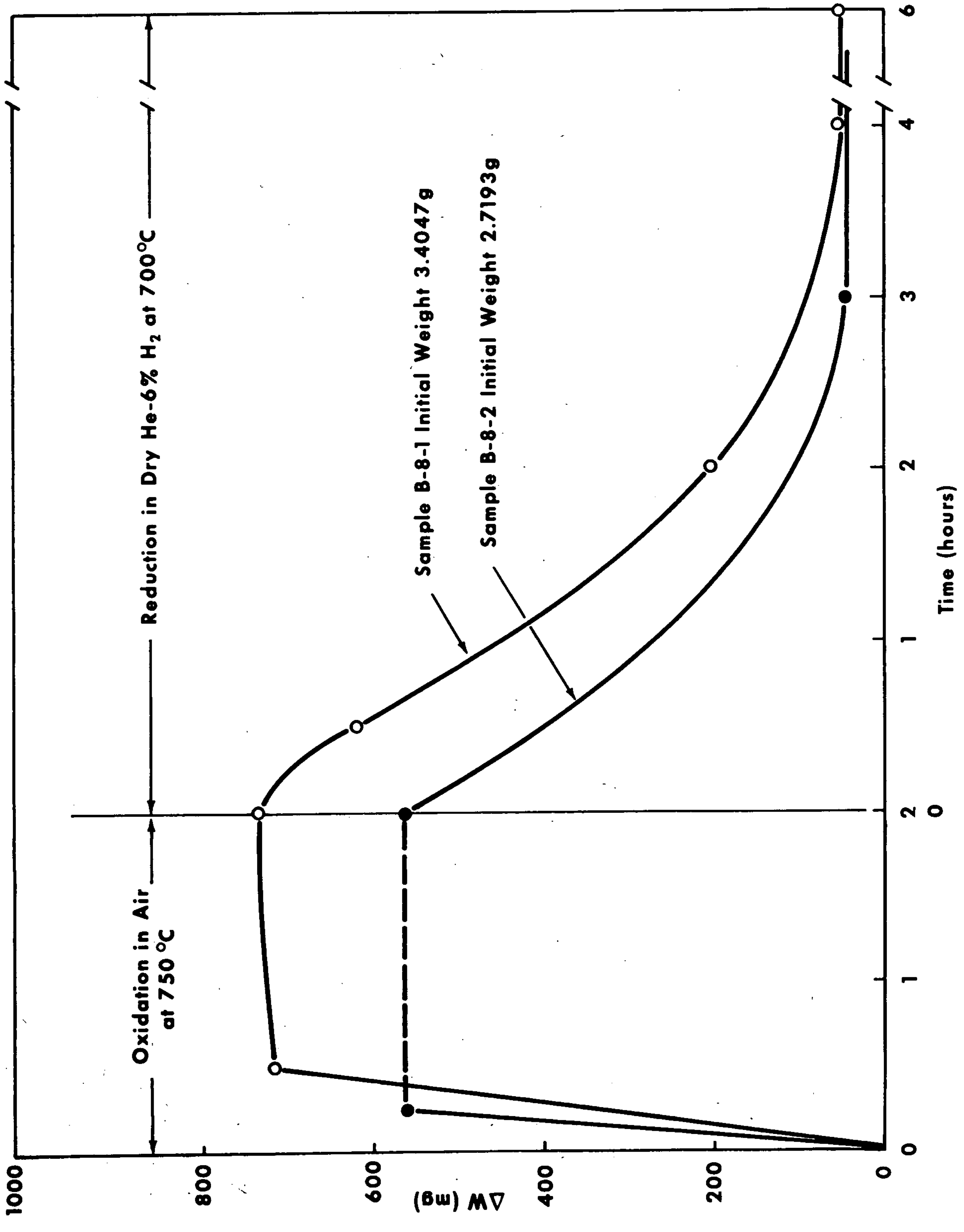

Figure 3. OXIDATION AND REDUCTION OF UO_2-20% PuO_2 MIXED OXIDE GRANULES

3. The sample is heated in a 5 cfh flow of dry 6% hydrogen-94% helium mixture with the furnace controller set at 700°C for 2-1/2 hours at temperature. The boat containing the samples is withdrawn to the cooling zone and cooled under the reducing gas to near room temperature before weighing. (Powder samples must be completely cooled to prevent oxidation when exposed to air.)

4. The reduction at 700°C is repeated for additional periods of two hours until it has been observed that a constant weight has been obtained within the limit of weighing sensitivity.

5. The O/M ratio is calculated for each sample as

$$O/M = 2.000 - \frac{M}{16}\left[\frac{W_3 - W_1}{W_3}\right]$$

where W_3 is the equilibrium weight upon reduction at 700°C, W_1 is the dry weight, and M is the average molecular weight of the oxide mixture. For a powder sample, W_3 and W_1 are gross weights of sample plus boat, and an additional weight, W_t, the tare weight is included,

$$O/M = 2.000 - \frac{M}{16}\left[\frac{W_3 - W_1}{W_3 - W_t}\right]$$

D. Results and Discussion

The oxygen/metal ratio has been determined by the gravimetric method on representative samples of all mixed oxide fuel loaded into irradiation capsules for the various tasks within the Fast Ceramic Reactor Program. In addition, this characterization of mixed oxides has served as an evaluation of the fabrication processes. In the latter application, the O/M values on ceramic powders have been useful in correlation with sintering behavior. Also, the O/M values on sintered mixed oxides have been essential in the development of conditions for control of stoichiometry during sintering.

Table II gives typical values from the analyses of various mixed oxide pellets and from urania and plutonia sintered under similar conditions. Table III gives typical values obtained upon mixed oxide powders prior to sintering.

TABLE II

OXYGEN TO METAL RATIOS AS DETERMINED IN UNIRRADIATED FCR FUEL SAMPLES

Batch Number	Pellet Numbers	Composition	Sintering Atmosphere	Average O/M Ratio
B-2	94, 89	UO_2-20% PuO_2	He-6% H_2 as received	1.982 ± 0.009
B-3	4, 96	UO_2-20.6% PuO_2	"	1.980 ± 0.012
B-4	116, 117	UO_2-28.1% PuO_2	"	1.979 ± 0.006
B-5	51, 76	UO_2-19.9% PuO_2	"	1.991 ± 0.005
B-6	45, 79	UO_2-22.5% PuO_2	"	1.972 ± 0.019
B-7	84, 157-162 incl.	UO_2-19.7% PuO_2	"	1.978 ± 0.010
B-7	52, 94, 128, 135	UO_2-19.7% PuO_2	"	1.986 ± 0.001
B-8	(Six pellets not identified)	UO_2-19.9% PuO_2	"	1.972 ± 0.001
B-8	137 - 140 incl.	UO_2-20% PuO_2	He-6% H_2 with H_2O addition	1.998 ± 0.001
B-9	134, 137	UO_2-20% PuO_2	"	2.000 ± 0.001
U-5	7	UO_2	He-6% H_2 as received	2.007
P-2	3	PuO_2	"	1.850
B-21	2, 3	UO_2-20% PuO_2	He-6% H_2 with H_2O addition	1.999 ± 0.001
B-21	32, 33	UO_2-20% PuO_2	"	1.996 ± 0.001
B-21	42, 43	UO_2-20% PuO_2	"	1.997 ± 0.001
B-21	93, 94	UO_2-20% PuO_2	"	1.998 ± 0.001
B-22	67, 68, 69, 70	UO_2-20% PuO_2	He-6% H_2 3 hrs dry gas 1 hr wet gas	1.998 ± 0.001

TABLE III

OXYGEN TO METAL RATIOS AS DETERMINED IN CERAMIC GRADE MIXED OXIDE POWDERS

Sample	O/M Ratio	Notes
B-8	2.180	(a)
B-8-A	2.110	(a) (c)
B-9	2.182	(a)
B-20	2.182	(a)
B-21	2.098	(a)
B-22	2.365	(b)
B-22-A	2.084	(a) (c)
B-23	2.146	(a)
B-24	2.122	(a)

NOTES:

(a) Good ceramic powders which sintered to high density.

(b) This material sintered poorly; apparently spontaneous oxidation occurred after its preparation.

(c) These powders were sampled after recycling through the reduction step.

IV. CONCLUSIONS

The macro-gravimetric method for measuring the oxygen to metal atomic ratio in solid solutions of uranium and plutonium dioxides is both convenient and sufficiently accurate for use (1) as an aid in the control of the fabrication process for these materials, and (2) as an important tool in the characterization of these fuel materials prior to irradiation in reactors.

The basic finding of Brett and Russell — that the solid solution mixed oxides can be reduced to the stoichiometric reference state at 700°C — has been confirmed and extended to use of the helium-6% hydrogen gas system.

REFERENCES

1. Belle, J., Ed.: Uranium Dioxide: Properties and Nuclear Applications, Naval Reactors, Division of Reactor Development, USAEC.

2. Booman, G. L., Holbrook, W. B., and Rein, J. E.: "Coulometric Determination of Uranium (VI) at Controlled Potential", Anal. Chem. 29, 219 (1957).

3. Stromatt, R. W., and Connally, R. E.: "Determination of the Stoichiometry of Uranium Dioxide by Controlled Potential Coulometry", Anal. Chem. Vol. 33, No. 3 (1961).

4. Lyon, W. L. and Moore, R. H.: "Distribution of the Actinide Elements in the Molten System: $KCl-AlCl_3-Al$", HW-59147 (1959).

5. Mulford, R. N. R. and Ellinger, F. H.: J.A.C.S. 80, 2023 (1958).

6. Drummond, J. L. and Sinclair, V. M.: "Some Aspects of the Measurement of the Oxygen to Metal Ratio in Solid Solutions of Uranium and Plutonium Dioxides". Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology. Gatlinburg, Tennessee (October 1962).

7. Ackermann, R. J., Thorn, R. J., and Winslow, G. H.: "Visible and Ultraviolet Absorption Properties of Uranium Dioxide Films". J. Optical Soc. Am. 49, 11 (1959).

8. Companion, A., and Winslow, G. H.: "Diffuse Reflective Measurements on Bulk Uranium Dioxide", J. Optical Soc. Am. 50, 1043-1045 (1960).

9. Gruen, D. M.: "Absorption Spectra and Electrical Conductivities of UO_2-ThO_2 Solid Solutions", J. Am. Chem. Soc. 76, 2117-2120 (1954).

10. Alter, H. W.: Vallecitos Atomic Laboratory Memo Report, October 18, 1962.

11. Dawson, J. K. and Lister, M. W.: "Magneto-Chemistry of the Heaviest Elements. I. Sensitive Magnetic Susceptibility Balance for Small Samples", J. Chem. Soc., 2177-2181 (1950).

12. Arrott, A. and Goldman, J. E.: "Magnetic Analysis of the Uranium-Oxygen System", Phys. Rev. 108, 948-953 (1957).

13. Watt, G. W.: Personal communication (1962).

14. Kiukkola, K.: "High Temperature Electrochemical Study of Uranium Oxides in the $UO_2-U_3O_8$ Region". Acta Chemica Scandinavica 16, No. 2 (1962).

15. Wagner, C. J.: Phys. Chem. 21, 1819 (1953).

16. Kiukkola, K. and Wagner, C. J.: Electrochem. Soc. 104, 379 (1957).

17. Roberts, L. E. J. and Harper, E. A.: "The Determination of Oxygen in Uranium Oxides". AERE C/R 885 (1952).

18. Rodden, C. J.: Analytical Chemistry of the Manhattan Project. 1st Ed. McGraw-Hill Book Co., Inc., New York (1950).

19. Bright, N. F. H. et al: "The Determination of Oxygen-Uranium Atomic Ratio in Non-Stoichiometric Uranium Dioxide, and Other Oxides of Uranium". Canada Dept. of Mines and Technical Surveys, Report MD207 (1956).

20. Stonhill, L. G.: "The Determination of Atomic Ratios in the Uranium-Oxygen System by a Thermogravimetric Method". Can. J. Chem. 37 (1959).

21. Brett, N. H. and Russell, L. E.: "The Sintering Behaviour and Stability of $(PuU)O_2$ Solid Solutions". AERE-R-3900 (1962).

22. Russell, L. E.: Personal communication (February 5, 1963).

23. Brett, N. H. and Fox, A. C.: AERE-R-3937 (1963).

24. Drummond, J. L. and Chapman, H.: "A Semi-Micro Thermobalance for Plutonium Compounds". UKEA TRG Report 466 (D).