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Determination of Laser-Evaporated Uranium Dioxide by Neutron Activation Analysis

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ABSTRACT

Safety analyses of nuclear reactors require information about the loss of fuel which may occur at high temperatures. In this study, the surface of a uranium dioxide target was heated rapidly by a laser. The uranium surface was vaporized into a vacuum. The uranium bearing species condensed on a graphite disk placed in the pathway of the expanding uranium vapor. Scanning electron microscopy and X-ray analysis showed very little droplet ejection directly from the laser target surface. Neutron activation analysis was used to measure the amount of uranium deposited.

The surface temperature was measured by a fast-response automatic optical pyrometer. The maximum surface temperature ranged from 2400 K to 3700K. The Hertz-Langmuir formula, in conjunction with the measured surface temperature transient, was used to calculate the theoretical amount of uranium deposited. There was good agreement between theory and experiment above the melting point of 3120 K. Below the melting point much more uranium was collected than was expected theoretically. This was attributed to oxidation of the surface.

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1. INTRODUCTION

1.1. Background

The analysis of the hypothetical core disassembly accident is a standard part of a reactor safety analysis. This safety analysis requires knowledge of the equation of state of the nuclear fuel at temperatures well above the melting point of 3120 K. However, this is a temperature range where there is limited knowledge of fuel vapor properties.

In 1981 a study was completed¹ which attempted to measure the partial vapor pressures of uranium bearing species over UO_2 . A laser was used to generate a surface temperature excursion on solid UO_2 . This caused various uranium and oxygen bearing species to vaporize and expand into an ultra-high vacuum. A quadrupole mass spectrometer was used to analyze the vapor species as a function of time. The temperature was measured by a fast response optical pyrometer. This information yielded the partial vapor pressures in the jet. Best fits to the experimental results produced a p-T relation that was within the confidence limits recommended by the International Atomic Energy Agency.²

Subsequent analysis showed that an error had been committed during the mass spectrometer calibration. A mistake in the placement of a decimal caused a geometric proportionality constant to be overestimated by two orders of magnitude. Thus, the vapor pressure was too high by the same amount. When corrected, the experimental values were a factor of 100 lower than fairly well accepted literature values.

As part of the continuing 1981 study it was decided to repeat the experiment to resolve the discrepancies in the measured vapor pressure. During the second series of data collection another problem arose. Above 2800 K the mass spectrometer indicated that the amount of the UO_2 species evaporating was independent of temperature (see Fig. 1.1). To check whether the mass spectrometer was saturating, 10% and 40% screens were placed before the mass spectrometer to reduce the molecular density in the ionizer. But still, the UO_2 signal remained independent of temperature.

1.2. Present Work

In this work instead of using a mass spectrometer to measure the blow-off, a 1/8-inch collecting disk was placed in the expansion pathway. Thus, all of the uranium bearing species would simply deposit on it. This, of course, has the disadvantage of losing the time dependence of the evaporation rate and the evaporation rate of the individual species as well.

At 2800 K, the amount of uranium that would deposit on a 1/8-inch disk is very small, less than 100 nanograms. Conventional methods of uranium analysis, such as potentiometry, polarography, colorimetry and visual chromatography are not suitable for this quantity.

1.2.1. Determination of Small Quantities of Uranium

Murali³ compares the sensitivity of the four nuclear techniques employed in the determination of natural uranium.

1.2.1.1. Fission Track

The most sensitive method of measuring uranium is the fission track method. When an ionizing charged fission fragment passes through a dielectric material, the transfer of energy to electrons results in a trail of damaged solid along the particle track. The track can be made visible upon etching in a strong acid or base solution. The entire surface of the material is attacked, but those points at which particle tracks have entered are etched at a faster rate. The tracks can thus be made to form pits on the surface which are large enough to be easily visible through conventional microscopes. The practical sensitivity of this method is restricted by the uranium content of reagents used in dissolving the sample

Fig. 1.1. Mass spectrometer signal.

prior to irradiation. As little as .01 nanograms of uranium can be detected in whole rock samples.

1.2.1.2. Review of Instrumental Neutron Activation Analysis Literature

The next most sensitive method is neutron activation analysis. The sensitivity of this method depends on the interferences produced by the matrix in which the uranium occurs. Radiochemical separation can reduce the interference, but chemical yield determinations, absolute radioactivity measurements, and the necessity to treat a known amount of a standard analogously, renders this method time-consuming and subject to additional errors. What follows is a review of literature on uranium neutron activation analysis without radiochemical isolation.

1.2.1.2.1. Uranium Neutron Activation Analysis with Long Cooling Times

De Wer⁴ measured the intensities of resolved gamma peaks of ^{239}Np relative to the intensity of a high-yield fission product as a rapid means of determining $^{235}\text{U}/^{238}\text{U}$ ratios in small uranium samples by neutron activation analysis. Low energy gamma-spectrometry was done 3 days after irradiation.

Of all the ^{239}Np peaks, the 277 keV photopeak was well separated from the fission products and was used as a measure of the ^{238}U content of an irradiated uranium sample. Unresolved peaks at 106 and 99 keV, from ^{239}Np and the $\text{K}\alpha_1$ X-ray from ^{239}Pu , respectively, were about twenty times more intense than the 277 keV photopeak. In addition, the 99 and 106 keV peaks were essentially devoid of fission product contributions and could also be used to measure ^{238}U .

The most pronounced fission product photopeak, which can be taken as a measure of the ^{235}U content, is the 141 keV photopeak from 6 hour $^{99\text{m}}\text{Tc}$ in transient equilibrium with 67 hour ^{99}Mo . $^{99\text{m}}\text{Tc}$ is also produced directly from fission.

The mean peak-to-background ratio for uranium of natural abundance was 11.6 for the ^{239}Np 277 keV gamma-ray, 3.24 for the ^{239}Np 106 keV gamma-ray, and 6.99 for the 141 keV ^{99}Mo gamma-ray.

1.2.1.2.2. Uranium Neutron Activation Analysis with Intermediate Cooling Times

After 24 hours of cooling, the most easily distinguished photopeaks are: ^{239}Np (105, 278 and

210 keV); 67 hour ^{99}Mo /6.0 hour $^{99\text{m}}\text{Tc}$, 140 keV; 33 hour ^{143}Ce , 290 keV; 20.8 hour ^{133}I , 530 keV; 9.7 hour ^{91}Sr /51 minute $^{91\text{m}}\text{Y}$, 556 keV; 17 hour ^{97}Zr /73 minute $^{97\text{m}}\text{Nb}$, 6584 and 743 keV.⁵ Figure 1.2 shows the γ -ray spectra for U_3O_8 of various enrichments. For natural U_3O_8 , ^{99}Mo is still the largest fission product photopeak. The 105 keV peak of ^{239}Np is 13.84 ± 32 times as large as the 278 keV peak. The activity of the 105 peak is about 20 times that of the 140 keV of ^{99}Mo . The 278 keV peak of ^{239}Np is about 1.4 times as big as the 140 keV peak from ^{99}Mo .

1.2.1.2.3. Uranium Neutron Activation Analysis with Short Cooling Times

For cooling periods of one hour, ^{239}U emits a very intense 74 keV photopeak. Unfortunately, this peak also has contributions from ^{134}Te , ^{101}Mo and ^{147}Pr . The peak to background ratio is a very large 43.72.⁶

There is also an intense peak at 147 keV from the fission product ^{131}Te (25 minutes). It is formed from fission and decay of ^{131}Sb (23 minutes). Its peak to background ratio, however, is only .331.

1.2.1.2.4. Uranium Neutron Activation Analysis with Very Short Cooling Times

The gamma-spectra of irradiated uranium samples between 10 and 50 minutes cooling times are rather complex, due to the predominant activities of fission products of very short half-life. Also, the gamma-spectra changes rapidly during this period. Ascribing a peak to a single nuclide becomes unreliable.

1.2.1.3. Delayed Neutrons

This method involves counting the neutrons emitted from nuclei that have been left in a highly excited state by the neutron decay of fission-produced parent nuclei. However, the rate of delayed-neutron emission following irradiation decreases by two orders of magnitude in 2 minutes.⁷ Neutron counting must, therefore, begin within seconds after irradiation, using a neutron moderator and a BF_3 tube detector. The delayed neutron method has the advantage of having very few interferences. The sensitivity is estimated to be 10 nanograms of uranium.

Fig. 1.2. Gamma-ray spectra of NBS Standard Reference Materials with increasing ^{235}U content. A = 5 mg U_3O_8 , 93.27% ^{235}U 1 min irradiation 24 h AEB 40 min count; B = 20 mg U_3O_8 , 10.007% ^{235}U 5 min irradiation 24 h AEB 40 min count; C = 20 mg U_3O_8 , 2.10% ^{235}U 5 min irradiation 24 h AEB 40 min count; D = 20 mg U_3O_8 , 0.72% ^{235}U 5 min irradiation 24 h AEB 40 min count.

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1.2.1.4. Passive Gamma-Ray Spectroscopy

The least sensitive method of uranium analysis is done by simply counting the natural radioactivity emitted by uranium. ^{235}U emits an intense peak at 185.72 keV^8 and can be used to determine the uranium present.

1.2.2. Method Chosen

Since this experiment will be concerned with nanogram quantities of uranium, the fission track method would seem ideal. However, it was decided that individual track counting would be tedious and very time consuming. Automatic counting systems are available, but involve a sizable investment in cost and complicated experimental procedures.

The delayed-neutron method was rejected because a BF_3 neutron detector was not available.

Passive gamma-ray analysis, although very easy, has low sensitivity. For the conditions of this experiment it was estimated that the minimum detectable activity would correspond to $5 \mu\text{g}$ of uranium. This limit was mainly due to a high background level from uranium in surrounding building materials.

Since the Department of Nuclear Engineering has a TRIGA Mark III reactor, neutron activation analysis was chosen.

In general, the most satisfying types of analysis are those that are most rapid. Not only does this reduce the inventory of samples, but it allows immediate redirection of effort should a problem arise during the early stages of experimentation. Hence, neutron activation with minimum cooling time would be best.

Activation with 10 minute cooling time is clearly undesirable, due to the complex, rapidly changing spectra.

Cooling for only one hour and counting ^{235}U involves some radiation exposure considerations. Experience showed that for the irradiation times used, the irradiated uranium was reading $200 \frac{\text{millirem}}{\text{hour}}$ at 30 cm. Some post-irradiation handling is required to remove the irradiated uranium from the reactor and place it before a detector. Since this had to be done numerous times, a longer cooling period

would have to be tolerated.

A cooling period of 17-24 hours was chosen since by this time the radiation levels had decayed to 30 $\frac{\text{millirem}}{\text{hour}}$ on contact. According to reference 5, the most intense peaks occur at 105 and 278 keV. The ^{239}Np peak at 278 keV was used to determine the amount of uranium on specimens exposed to material vaporized by the laser. As little as 5 nanograms of uranium was detected using this peak.

2. EXPERIMENTAL

2.1. Apparatus

2.1.1. General Overview

The laser system target vacuum chamber, optical pyrometer and data recording device are shown in Figure 2.1. The collector assembly (Figure 2.2) is mounted inside the target vacuum chamber.

2.1.1.1. Target Vacuum Chamber

The target vacuum chamber is pumped by a diffusion pump with a liquid nitrogen cold trap. When the gate valve to the pump is open during laser shots the background pressure is 10^{-7} Torr. A glass window is used to sight the target from the optical pyrometer for surface temperature measurements. A quartz window provides the entrance for the laser beam.

The UO_2 target (one centimeter in diameter, one millimeter thick and natural uranium) fits inside a molybdenum holder. A rotary feed-through is used to mount the electron bombardment heater and the target holder. A heated tungsten filament emits electrons which heat the back face of the target by conduction to 1500K. This is sufficiently above the ductile-brittle transition temperature (DBTT)⁹ to preclude thermal stresses exceeding the fracture stress and causing the UO_2 target to shatter during rapid laser heating. The electron bombardment heater holding the UO_2 target is aligned by shooting a continuous He-Ne CW gas laser through the rear end of the Nd-glass laser, the laser rod, optical components and hitting the center of the UO_2 target.

The collector assembly is fastened to a ten-inch flange on top of the target chamber. The collector assembly consists of a 16 inch rod, flange attachment, graphite disk holder and it's cover plate (see Figure 2.2). The graphite disk is 1.27 cm in diameter and .16 cm thick. The disk holder and cover plate are made of copper. The holder and plate are held together by screws made of the dissimilar metal stainless steel. This prevents galling at high temperatures. The collector and target disks are parallel and coaxial.

Fig. 2.1 Apparatus setup.

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Fig. 2.2. Collector Assembly

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2.1.1.2. Laser

The laser is a Lasermatrix Model 936-G4-21. The laser uses a neodymium-doped glass rod, 15.24 cm long and 1.27 cm in diameter, with planar front and rear reflectors. The system delivers multimode laser pulses nearly 750 μ second wide. The maximum laser output is 50 Joules per pulse. No correcting or focusing lens are used. The laser spot covers a radius of approximately 0.375 cm of the UO_2 target area. The laser beam is partially split to measure laser power and pulse shape by a MgO diffuser-Korad KD-1 photodiode arrangement (see Figure 2.1). The photodiode signal is pre-calibrated with respect to the total energy of the laser beam using a Korad KJ-1 calorimeter. The photodiode signal is transmitted to a wave form recorder (Biomation 1015) which gives the laser energy and the power history for each shot.

2.1.1.3. Optical Pyrometer

The UO_2 surface temperature is measured by a PYRO "PHOTOMATIC" 1 Automatic Optical Pyrometer manufactured by the Pyrometer Instrument Company, Inc. of Northdale, New Jersey. The instrument is divided into two units. The optical system has the photomultiplier tube, high voltage power supply and pre-amplifier¹⁰. The optical system is mounted on a very precisely adjustable vernier gear and tripod. The electronic package contains the direct reading temperature indicating meter, scale range indicating lights, control knobs, a recorder jack and a controller jack.

The pyrometer has three modes of operation, two of which will be described.

The pyrometer was calibrated in both modes up to 3100 K, using a black-body (graphite hole) at the NASA Ames Research Laboratory.

The automatic mode was used for reading the initial temperature of the preheated target surface. A fixed fraction of light per unit area per unit solid angle from the target is compared by a photodetector to a fixed fraction of light coming from a standard tungsten reference lamp. The current through this internal reference lamp is adjusted by an electronic null balance system until the lamp and target are emitting the same amount of radiation. The lamp current is thus a measure of the target surface temperature and is indicated on a meter on the electronic control unit of the pyrometer.

In the transient mode the pyrometer acts as an optical system coupled to a photomultiplier and the instrumental time constant is of the order of nanoseconds. This makes it suitable for following the transient target surface temperature, which varies within a couple of milliseconds during laser pulsing. The anode of the photomultiplier is coupled to the waveform recorder via a pre-amplifier. The recorded signal, volts versus time, is converted to temperature versus time, using the pyrometer calibration, for each laser shot.

2.1.1.4. Transient Waveform Recorder

The Biomation Model 1015 records the signals from the laser power diode and optical pyrometer simultaneously. The fastest sampling rate is $10\mu\text{s}$ per sample. The recorder has the ability to record the leading base line before the rise of the two signals. This reduces systematic errors by providing a definite starting point of the transient.

The resistance and capacitance of the transient recorder and long interconnecting cables cause appreciable RC distortion in the raw output current from the photodiode and photomultiplier. Electrical corrections were made to prevent this. The photodiode current is terminated by the Biomation's normal $1\text{ M}\Omega$ resistor with an additional $50\ \Omega$ added in parallel to reduce the overall effective resistance and RC time constant. The photomultiplier, which generates weak currents, can't produce enough voltage across a $50\ \Omega$ resistor to be adequately measured. It requires a current-to-voltage preamplifier to transmit a voltage signal to the waveform recorder. The pre-amplifier is located as close to optical unit of the pyrometer as possible. The final output of the waveform recorder is volts versus time for the laser pulse and the surface temperature.

2.1.2. Counting Apparatus

The gamma-ray counting apparatus is composed of two parts: (1) the photon detector system and (2) the associated computer/electronics.

The gamma-ray detector system consists of the following:

1. semiconductor element
2. cryostat
3. liquid nitrogen dewar
4. low noise charge-sensitive preamplifier
5. high-voltage filter.

The semiconductor detector element is a single crystal of p-type high-purity germanium (HPGe) with a lithium-diffused outer contact. The single crystal, Model No. GEM-15-15180, was grown by EG&G ORTEC and has a closed-end coaxial configuration. The full width at half maximum is 1.62 keV for the 1.33 MeV gamma ray of Co-60. The crystal dimensions are 51 mm in diameter and 40 mm in length. The distance from the outside of the aluminum end cap to the first intrinsic region of the crystal is 5 mm.¹¹

The computer/electronics consists of the following:¹²

1. Cooled Preamplifier
2. Linear Amplifier (with pileup detection/live time correction circuitry)
3. LSI 11/23 Microprocessor.

The relevant operating system that runs on the LSI 11/23 computer is NAA, which stands for neutron activation analysis. It has the capabilities of a data acquisition machine and also has the ability to call the program that directly handles the data with a computer.

The particular code that does peak fitting is known as *RAYGUN* and was developed at Los Alamos National Laboratory for mass production neutron activation analysis. The program is a union of *GAMANAL* and *GRPANAL*, written at the Lawrence Livermore Laboratory.¹³ The code fits peaks by first determining the background under a peak. It then fits the top of the peak to a Gaussian and adds a single exponential tail. An overall fitting error is reported for each peak found.

2.2. Collector Material

In order to be able to detect a small amount of a radioactive element, its gamma peaks must be significantly higher than the background, which arises mainly from the Compton scattering of higher energy gamma rays. The Compton continuum is very prominent in Ge(Li) detectors. To reduce this continuum, higher energy gamma rays should be eliminated as much as possible. With irradiated uranium most of the continuum comes from fission products and activation of the collector material.

The contribution from fission products is unavoidable, but the collector material can be chosen such that it has a very low neutron absorption cross section.

Graphite has a low absorption cross section and can withstand the heating due to thermal radiation from the laser-illuminated spot on the nearby UO_2 target. A 0.16 cm thick, 1.27 cm diameter disc of nuclear-grade graphite contains about 136 nanograms of uranium as an impurity. Less than this was expected to deposit on the collector, thus a more pure form of graphite was needed for low temperature laser shots. The Ultra-Carbon Corporation of Bay City, Michigan makes a very pure form of graphite. They guarantee the total impurity content to be less than 4.5 ppm. By chemical analysis the impurities were identified as silicon, iron, magnesium, copper and aluminum. The chemical analysis was performed by the supplier. An attempt was made to do a quantitative impurity comparison of the chemical analysis with the neutron activation analysis to verify the experimental method used herein (see section 2.2.1). Activation analysis in this laboratory of this graphite detected ^{64}Cu , ^{24}Na , ^{38}Cl , ^{41}Ar , ^{56}Mn and ^{187}W . Figure 2.3 shows the gamma spectrum 99.1 minutes after a one hour irradiation at $2.25 \times 10^{12} \frac{\text{neutrons}}{\text{cm}^2 \text{ s}}$.

No uranium or fission products were detected. More importantly, no photopeaks were observed near the 277.60 keV peak of ^{239}Np (see Figure 2.4). Thus, this ultra-pure graphite collector was not expected to produce any interferences during post-irradiation spectroscopy.

The annihilation peak had a half-life of 12.2 hours and was produced mostly by 12.8 hour ^{64}Cu .

The activity of ^{24}Na and ^{38}Cl shows that they came from roughly equal amounts of natural sodium and natural chlorine. This indicates the source of ^{24}Na and ^{38}Cl is sodium chloride. Sodium chloride occurs in human perspiration. It is likely that handling techniques at the factory contaminated this otherwise very pure graphite.

The ^{41}Ar comes from air in the rotary specimen rack where the graphite is irradiated. During reactor operation the ^{40}Ar in the air absorbs neutrons to produce 1.83-hr ^{41}Ar , which decays by emitting a 1293.60 keV photon. The ^{41}Ar leaks out into the reactor room and is detected. The ^{41}Ar concentration in the reactor room is about $10^{-6} \mu\text{Ci/cc}$.¹⁴

Fig. 2.3. Gamma spectrum of blank Ultra-Carbon graphite disk.

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Fig. 2.4. Low energy gamma spectrum of blank Ultra-Carbon graphite disk.

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Tungsten, Copper and manganese were the only intrinsic impurities detected by activation analysis.

2.2.1. Quantitative Impurity Comparison

By comparing the impurity content from both methods, it is possible to determine if the neutron activation analysis, used herein, is in gross error. Except for copper the elements detected by chemical analysis were not detected by activation analysis. At first glance the chemical analysis and activation analysis do not agree very well. However, the sensitivity for one element may be very high for one method and very low for the other, thereby leading to this apparent discrepancy.

For neutron activation analysis the sensitivity will depend on isotopic abundance A_0 , absorption cross section $\sigma_{0 \rightarrow 1}$, neutron flux Φ , half-life λ_1 , cooling time t_c and irradiation time t_{irr} . The disintegration rate $N_1 \lambda_1$ of a radioactive nuclide present after a cooling time t_c is

$$N_1 \lambda_1 = A_0 N \sigma_{0 \rightarrow 1} \Phi (1 - e^{-\lambda_1 t_{irr}}) e^{-\lambda_1 t_c}$$

where N is the number of atoms of the natural element. Most disintegrating nuclides emit gamma-rays of various energies. Near the threshold of detectability only the gamma-rays with the largest branching ratio R will produce a photopeak above background. Thus $\frac{N_1 \lambda_1 R}{\Phi N}$ is a measure of the disintegration rate of the strongest gamma-ray per unit flux per impurity atom. The higher this number the higher the sensitivity to neutron activation analysis.

Table 2.1 compares the sensitivity of various activated isotopes from the most common impurities in graphite using an irradiation time of 1 hour and cooling time of 1 hour (per reactor regulation) and the absorption cross section for thermal energies.^{15 16 17} $\frac{N_1 \lambda_1 R}{\Phi N}$ is expressed in units of cm^2 . Some activation products do not emit gamma-rays or if they do they are of a very low energy. In this case "no gammas" is indicated in the table.

Table 2.1

Sensitivity of Some Nuclides to Neutron Activation Analysis

Activated Nuclide	$\frac{N_1 \lambda_1 R}{\Phi N_0} \times 10^{-26}$	Activated Nuclide	$\frac{N_1 R}{\Phi N_0} \times 10^{-26}$
⁵¹ Ti	.07	⁵¹ Cr	.70
⁶⁴ Cu	630	⁵³ Cr	<.01
⁶⁶ Cu	<.01	⁵⁶ Mn	24000
¹⁸¹ W	<.01	²⁴ Na	59
¹⁸⁵ W	<.01	³⁸ Cl	86
^{185m} W	<.01	³⁶ Cl	<.01
¹⁸⁷ W	982	^{38m} Cl	<.01
⁹⁹ Mo	289	³¹ Si	.004
¹⁰¹ Mo	2	⁵⁵ Fe	no gammas
⁶⁵ Zn	.22	⁵⁹ Fe	.01
^{69m} Zn	6.3	⁴¹ Ca	no gammas
⁶⁹ Zn	<.01	⁴³ Ca	no gammas
^{71m} Zn	.06	⁴⁷ Ca	<.01
⁷¹ Zn	<.01	⁴⁹ Ca	.2
²⁸ Al	.00002	²⁷ Mg	.4
⁹³ Zr	no gammas	¹² B	no gammas
⁹⁵ Zr	.02	⁵⁹ Ni	no gammas
⁹⁷ Zr	.23	⁶³ Ni	no gammas
⁵² V	.07	⁶⁵ Ni	6.0
²⁰⁵ Pb	no gammas	²³⁹ U	2200
²⁰⁹ Pb	no gammas		

Using data from Table 2.1, Table 2.2 compares the impurity content as detected by the two methods. The impurity content by activation analysis was measured in this study and the impurity content by chemical analysis was provided by the supplier. For neutron activation analysis if an impurity isn't detected the minimum detectable amount is quoted instead. ³⁸Al is not detectable after one hour due to its short 2.28 minute half-life. The counting efficiency used is given in Figure 2.5. The two disks of graphite contain 1.615×10^{22} atoms of carbon.

The results are fairly consistent, thus verifying the neutron activation analysis method used. The sensitivity of the neutron activation analysis could have been improved by using multiple irradiations of different times and judiciously choosing prudent cooling times.

Fig. 2.5. Detector efficiency vs. gamma-ray energy. Source-detector distance is 2.72 cm.

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Table 2.2

Impurity Content of Ultra-Carbon Graphite (ppm)

Element	Activation	Chemistry
Mo	<.05	none detected
Ti	<480	none detected
Cu	.2	1
Zn	<4	none detected
Al	not detectable	1
Zr	<140	none detected
Cr	<30	none detected
Mn	.002	none detected
Na	4	
Cl	5	
Si	<10 ⁴	.5
Fe	<2100	1
Ca	<38	none detected
Mg	<87	1
Ni	<5	none detected
V	<340	none detected
W	.019	none detected
U	<.016	

2.3. Standard

As a standard, a measured volume of solution containing uranium was deposited on graphite discs identical to those used in the experiment. This standard was irradiated along with the graphite that had been exposed to the UO_2 target during laser pulsing. They were placed very close together during irradiation in order to receive the same neutron flux.

The standard solution was prepared by placing .0284 grams of natural UO_2 in a solution of 10 M nitric acid and .02 M hydrofluoric acid. The solution was then heated to 70 C until the UO_2 dissolved, usually in about 30 to 40 minutes. Using distilled water, the solution was diluted to 500 ml.

A volume of 0.2 ml of this standard solution was pipetted onto a graphite disc; a second disc was similarly prepared. Both solutions were evaporated to dryness under a heat lamp to produce a uniform deposition of uranium. The two discs were then sandwiched together at the uranium-coated faces to prevent loss of uranium by abrasion. Lastly, the standard discs were placed in polyethylene bags for irradiation. The total amount of uranium (not UO_2) on the pair of standard discs was 20 μg . This produced 100,000 counts above background in the 277.60 keV peak after 1 hour of irradiation at

2.25×10^{12} neutrons per sq. cm per second, 21 hours of cooling and 24 minutes counting. This was sufficiently above the background to provide good statistics.

2.4. Experimental Procedure

The experiments are performed in the following manner:

- (1) Place the graphite disc in the collector assembly.
- (2) Insert the collector assembly through the 10-inch flange of the target vacuum chamber and rotate to previously-marked positions to ensure exact geometric replication.
- (3) Mount the UO_2 target on the electron bombardment heater and install in the target chamber.
- (4) Evacuate the target chamber.
- (5) Align the target with the He-Ne laser as described in Section 2.1.1.1.
- (6) Turn on the Nd laser power supply and set the voltage of the capacitor banks for the desired temperature.
- (7) Align and focus the optical pyrometer on the target.
- (8) Preheat the target with the electron bombardment heater. Measure the target temperature with the auto mode of the optical pyrometer. Stabilize the temperature at 1500 K, which is the initial specimen temperature for temperature transient calculations.
- (9) Set the optical pyrometer to the transient operating mode.
- (10) Connect the photodiode and optical pyrometer to the transient waveform recorder.
- (11) "Arm" the transient recorder in the "Ready" mode for data recording.
- (12) Fire the Nd-glass laser. Part of UO_2 blow-off will deposit on the collector.
- (13) The transient recorder should record two signals for the experiment (temperature and laser power) and stop recording after receiving a pre-set delayed triggering signal.
- (14) Turn off the electron bombardment heater and wait 15 minutes.
- (15) Open target chamber and remove graphite collector from the collector assembly.

- (16) Place the exposed side against an identical graphite disc and heat seal the pair in a polyethylene bag.
- (17) Dissolve any deposited uranium on the collector assembly by immersing in a solution of acetic, phosphoric and nitric acids.
- (18) Repeat steps 1 thru 17 for different laser energies.
- (19) Place standard and collector graphite discs in the reactor and irradiate.
- (20) After cooling, place graphite in plexiglass holders.
- (21) Place holders in front of Ge(Li) detector in numbered slots and count.

3. THEORY

3.1. Vaporization Rate

The rate of evaporation in a vacuum can be calculated from the kinetic theory of gases when vapor pressure is known. Langmuir¹⁸ has shown that the vapor pressure p of a substance is related to its rate of evaporation per unit area per unit time $\dot{m}$ in a vacuum by the following relation:

$$\dot{m} = p \sqrt{\frac{M}{2\pi RT_s}} \quad (1a)$$

where M is the molecular weight of the vapor, R is the gas constant and T_s is the surface temperature. Many theoretical investigations^{19 20 21} have shown that 18% of the forward vaporization flux back-scatters to the surface when the flow above the vaporizing surface departs from free molecular flow. For uranium dioxide, this occurs when the peak temperature of the surface during the pulse is above about 2700 K.²² Thus, for $T_{s,max} > 2700$ K:

$$\dot{m} = 82p \sqrt{\frac{M}{2\pi RT_s}} \quad (1b)$$

During a laser shot the vapor pressure and temperature of the uranium dioxide target are functions of time. If Langmuir's equation is integrated over time and laser target area, the total amount of uranium dioxide evaporated can be theoretically calculated. However, only a fraction $F_{1 \rightarrow 2}$ of this total amount will actually deposit on the graphite collector and be detected.

3.1.1. Configuration Factor

The fraction of the blow off that will deposit on the collector can be determined by the use of a configuration factor. The configuration factor for an emitting surface A_1 to a receiving surface A_2 , written $F_{1 \rightarrow 2}$, is herein defined as the fraction of the total molecular flux leaving A_1 (i.e., $\dot{m}A_1$) that is incident upon A_2 . It depends on the geometry of the two surfaces (Figure 3.1) and the angular distribution of the emitted molecules $I(\theta)$.

Consider differential areas dA_1 and dA_2 on the emitting and collecting surfaces, respectively. The solid angle (in steradians) subtended at dA_2 from dA_1 is the area of dA_2 projected on the plane normal

Fig. 3.1. Geometry of the vaporizing and collecting surfaces.

to ρ divided by ρ^2 or $d\Omega = \frac{dA_2 \cos u}{\rho^2}$. The rate at which molecules are emitted from dA_1 into a unit solid angle at ρ at an angle u is $I(u)dA_1 = \frac{\dot{m} \cos u dA_1}{\pi}$ molecules/s-st. The configuration factor $F_{1 \rightarrow 2}$ is the integral of $I(u)d\Omega dA_1$ taken over the area of the surface then divided by $\dot{m}A_1$:

$$F_{1 \rightarrow 2} = \frac{1}{\pi A_1} \int dA_1 \int dA_2 \frac{\cos^2 u}{\rho^2}$$

For diffuse surfaces the emission varies as the cosine of the angle from the surface normal. A surface emitting in this fashion is said to obey Lambert's Cosine Law. In radiative heat transfer a blackbody is always a diffuse surface. Thus the configuration factors used in thermal radiation exchange between two blackbodies can be directly applied to the present case because the UO_2 target is a diffuse emitter. The first research into configuration factors for commonly used elements of the geometry found in engineering structures was conducted by the National Advisory Committee For Aeronautics.¹³ For the case of parallel, directly opposed, plane circular disks (Fig. 3.1) the configuration factor is:

$$F_{1 \rightarrow 2} = \frac{1}{2} (x - \sqrt{x^2 - 4E^2 D^2}) \quad (2)$$

where

$$x = 1 + (1 + E^2) D^2$$

$$E = \frac{R_2}{d}$$

and

$$D = \frac{d}{R_1}$$

The geometric factor for the transient shots is based on the following dimensions:

$$R_1 = .375 \text{ cm}$$

$$R_2 = .622 \text{ cm}$$

$$d = 2.86 \text{ cm}$$

Using these quantities Eq. (2) gives:

$$F_{1 \rightarrow 2} = .0446$$

For steady state heating where the entire UO_2 surface is heated by the E-B heater, the configuration factor is based on the following:

$$\begin{aligned}R_1 &= .45 \text{ cm} \\R_2 &= .622 \text{ cm} \\d &= 2.86 \text{ cm}\end{aligned}$$

The steady state configuration factor is slightly smaller:

$$F_{1 \rightarrow 2} = .0443$$

3.1.1.1. Comparing Theory and the Experiments of Tsai

Tsai²⁴ attempted to measure the directional distribution $I(\nu)$ by collecting the ejected uranium with arrays of disks placed in a semicircular fashion around the target. For maximum surface temperatures around 4500 to 4800 K the angular distribution was approximated by a $\cos^n \theta$ distribution, where n was found to lie between 1 and 2. For the case of $n=1$ the surface obeys the Cosine Law, thus justifying the use of the configuration factor for radiation heat transfer in the preceding analysis.

For Tsai's geometry the theoretical configuration factor is $F_{1 \rightarrow 2} = .0069$. In one series of 5 pulses, Tsai collected 60.39 μg out of an estimated 8800 μg emitted. The second series of laser shots he collected 33.75 μg out of an estimated 4200 μg . Assuming that every atom of the vapor which strikes the collector condenses, the experimental configuration factors are .0069 and .0080 respectively. The value of the theoretical configuration factor based on a diffuse surface is thus between these two experimental values. Thus, the error introduced by using Lamberts form of the emitting mass flux $\dot{m}$ is assumed to be too small (in comparison with other errors) to warrant the complications introduced by the use of a non-Lambertian distribution.

3.2. Expected Uranium Collected

3.2.1. Transient Laser Shots

Based upon Eq. (1) the theoretical amount of uranium collected during transient heating of the target (for $T_{s, \text{max}} > 2700 \text{ K}$) is calculated from

$$m_{\text{theory}} = \frac{238}{270} .82 F_{1 \rightarrow 2} A_1 \sqrt{\frac{M}{2\pi R}} \int \frac{P(t) dt}{\sqrt{T_s(t)}} \quad (3a)$$

where

$$M = \frac{270 \text{ g}}{\text{gmole}}$$

$$A_1 = 0.000442 \text{ m}^2$$

$$R = \frac{8.3143 \text{ J}}{\text{gmole-K}} = \frac{8314 \text{ g-m}^2}{\text{s}^2\text{-gmole-K}}$$

Hence

$$m_{\text{theory}} = 10.4 \int \frac{p(t)dt}{\sqrt{T_s(t)}} \quad (3b)$$

The vapor pressure $p(t)$ in Eq. (3b) is expressed in atm, m_{theory} in μg of uranium and t in seconds. The temperature is assumed to be uniform over the laser spot A_1 . In calculating m_{theory} , the experimentally determined surface temperature transient, $T_s(t)$, was used in the integral of Eq. 3. Note the vapor pressure p is a function of time t via $T_s(t)$ and the p-T relationship. Individual shots are characterized by the setting of the capacitor of the laser power supply as well as the maximum observed surface temperature produced by the shot.

The p-T relation used in the integral, for temperatures above the melting point, is the one proposed by Breitung²⁵ based on in-pile heating techniques.

$$\log p = 24.79 - \frac{29605}{T_s} - 4.76 \log T_s \quad (4a)$$

It includes a factor of 2 uncertainty band. For temperatures below the melting point a slightly modified version of the equation of Tetenbaum and Hunt is used.^{26, 27}

$$\log p = \frac{-31,284}{T_s} + 8.768 \quad (4b)$$

The vapor pressures in Eq. 4 are expressed in atm.

Figure 2, 3.3 and 3.4 show the trace of the temperature as function of time parametric in voltage across the laser's capacitor banks.

A total of 12 laser shots were fired. Table 3.1 shows the theoretical calculation for uranium deposited on the collector.

Fig. 3.2 Surface Temperature versus Time.

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Fig. 3.3. Surface Temperature versus Time.

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Fig. 3.4. Surface Temperature versus Time.

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Table 3.1

Theoretical Uranium Deposited

Shot No.	Capacitor kV	$T_{s,max}$ (K)	uranium(ng)
1	4.50	2379	2.89
2	4.50	2462	13.2
3	5.00	2666	67.4
4	5.50	2906	629
5	5.50	2938	736
6	6.00	3130	3650
7	6.50	3213	5980
8	6.50	3303	8360
9	7.00	3513	21,800
10	7.50	3666	28,500
11	8.00	3554	24,800
12	8.00	3648	29,500

3.2.2. Steady State Evaporization Test

For steady state calculations the surface area is $A_s = .0000636 \text{ m}^2$. The theoretical amount collected is given by

$$m_{theory} = \frac{18.1 p t}{\sqrt{T_s}}$$

where p is expressed in atm, m_{theory} in μg and t in seconds. The electron-bombardment heater was run for 2 hours 46 minutes at 1788K. The theoretical uranium deposition was 7990 nanograms.

4. DATA ANALYSIS

4.1. Calculation of Laser Deposited Uranium

The experimental amount of uranium deposited on the collector m_{exp} is calculated by dividing the ^{239}Np 277.60 keV gamma-rays per second emitted from the collector $RN_{exp}\lambda$ by the gamma-rays per second emitted from the standard $RN_{std}\lambda$ and multiplying by the amount of uranium deposited on the standard:

$$m_{exp} = m_{std} \frac{RN_{exp}\lambda}{RN_{std}\lambda}$$

where R is the gamma-ray branching ratio (.141) and λ is the decay constant of ^{239}Np ($\frac{0.294}{\text{days}}$). Most days counting times were 24 minutes each for the standard and collector. No corrections were made for the decay of 2.355 day ^{239}Np during the 48 minute count time.

The gamma spectrum of both collector and standard showing the ^{239}Np peaks is plotted in Figure 4.1 for a 5.50 kV shot. The top line is the spectrum of the standard. The bottom line is the spectrum of the collector. The irradiation was 1 hour at $2.25 \times 10^{12} \frac{\text{neutrons}}{\text{s-cm}^2}$. Cooling time was 21 hours and count time was 24 minutes for each. The amount deposited on the standard was $m_{std} = 20.028 \text{ ng U}$. From the counts in the 277.60 keV ^{239}Np γ -ray peak and the detector efficiency (0.062), the amount collected is:

$$m_{exp} = 20.028 \text{ ngU} \frac{210.9 \frac{\text{gams}}{\text{sec}}}{1220 \frac{\text{gams}}{\text{sec}}}$$

$$m_{exp} = 3463 \text{ ngU}$$

A second count yielded 3439 ng U. The average is 3451 ng U.

The laser-evaporated uranium deposits in a nearly cosine distribution. However, the uranium deposited on the standard by pipettes and heat lamps deposits uniformly. To verify that this source geometry difference does not effect the counting efficiency, both the standard and collector were placed far enough away (17 cm) such that they could be considered point sources. Then they were moved closer to verify that $\frac{RN_{exp}\lambda}{RN_{std}\lambda}$ remained constant. This ratio remained constant, within 3%, when the sources

Fig. 4.1. Low energy gamma spectrum of the irradiated collector (lower trace) for shot no. 4 and standard (upper trace) showing the ^{239}Np peaks. The 277.60 keV ^{239}Np γ -ray was used in determining the amount of UO_2 deposited.

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were 0.8 cm or 17 cm from the detector element.

4.4. Error Analysis

4.2.1. Uranium on Standard

All the standard disks had 0.4 ml of standard solution evaporated onto them from a pipette. The fractional standard deviation $\frac{\sigma_n}{\bar{x}}$ in ^{239}Np count rate from the same 0.4 ml was about 6.5%. The flux variation across the irradiation capsule is a few percent, but the collector and standard were always placed close together.

There is a photopeak fitting error associated with each count. However, this was usually less than 1%.

4.2.2. Configuration Factor

The uncertainty in the configuration factor is based on the measurements of laser target area, exposed collector area and target-to-collector distance. Table 4.1 gives the nominal values and uncertainty in measured distances.

Table 4.1
Configuration Factor Uncertainty

$$\begin{aligned} R_1 &= .375 \pm .04 \text{ cm} \\ R_2 &= .62 \pm .03 \text{ cm} \\ d &= 2.86 \pm .32 \text{ cm} \\ F_{1 \rightarrow 2} &= .0446 \pm .0139 \end{aligned}$$

4.2.3. Surface Temperature

The uncertainty in measurement of the transient temperature is estimated to be 50 K. This uncertainty does not include optical absorption of the light emanating from the laser-irradiated spot by the UO_2 vapor cloud. This has never been addressed experimentally. A 30% reduction in the light intensity reaching the pyrometer could result in a 10% reduction in surface temperature.

The uncertainty in steady state temperature is estimated to be 20 K.

This causes an uncertainty in vapor pressure. Table 4.2 shows the uncertainty in the integral of equation 3 and in the corresponding steady-state quantity.

Table 4.2

$$\text{Uncertainty of } I = \int \frac{p(t)dt}{\sqrt{T(t)}}$$

Shot No.	Laser kV	$T_{s,max}$ (K)	$I \pm \sigma_I$ ($\times 10^{-9} \frac{\text{atm-sec}}{\text{K}^{1/2}}$)
1	4.50	2379	.2278 $\pm$.1568
2	4.50	2462	1.039 $\pm$.65
3	5.00	2666	5.317 $\pm$ 2.875
4	5.50	2906	61.32 $\pm$ 27.42
5	5.50	2938	70.76 $\pm$ 30.92
6	6.00	3130	350.5 $\pm$ 101.3
7	6.50	3213	574.9 $\pm$ 155.9
8	6.50	3303	804.3 $\pm$ 211.5
9	7.00	3513	2100 $\pm$ 484
10	7.50	3666	2736 $\pm$ 574
11	8.00	3554	2382 $\pm$ 530
12	8.00	3648	2837 $\pm$ 599
steady state		1788	441.2 $\pm$ 204.6

4.2.4. Error Assessment

The theoretical amount of uranium collected, from equation 3, is

$$m_{theory} \propto F_{1 \rightarrow 2} A_1 I$$

If the errors are statistically independent then they can be added according to

$$\left(\frac{\sigma_m}{m_{theory}}\right)^2 = \left(\frac{\sigma_F}{F_{1 \rightarrow 2}}\right)^2 + \left(\frac{\sigma_A}{A_1}\right)^2 + \left(\frac{\sigma_I}{I}\right)^2$$

where

$$\sigma_F = .0139$$

$$F_{1 \rightarrow 2} = .0446$$

$$\sigma_A = .00009 \text{ m}^2$$

$$A_1 = .000044 \text{ m}^2$$

The values for σ_I and I are from Table 4.2. Table 4.3 gives the fractional error associated with the theoretical amount of uranium deposited on the collector.

Table 4.3

Fractional Error of m_{theory}

Shot No.	Capacitor kV	$T_{s,max}$ (K)	$\frac{\sigma_m}{m_{theory}}$
1	4.50	2379	.78
2	4.50	2462	.73
3	5.00	2666	.66
4	5.50	2906	.58
5	5.50	2938	.57
6	6.00	3130	.47
7	6.50	3213	.46
8	6.50	3303	.46
9	7.00	3513	.44
10	7.50	3666	.43
11	8.00	3648	.43
12	8.00	3554	.43
steady state		1788	.46

5. RESULTS AND DISCUSSION

5.1. Results

Table 5.1 compares the theoretical (m_{theory}) and experimental (m_{exp}) amounts of uranium deposited on the collector disk.

Table 5.1

Theoretical and Experimental Uranium Deposition

Shot No.	Capacitor kV	$T_{j,max}$ (K)	$m_{theory} \pm \sigma_m$ (ng)	$m_{exp} \pm 6.5\%$ (ng)
1	4.50	2379	2.89 ± 2.3	108 ± 7
2	4.50	2462	13.2 ± 9.6	566 ± 37
3	5.00	2666	67.4 ± 44	674 ± 44
4	5.50	2906	629 ± 370	3315 ± 215
5	5.50	2938	736 ± 420	3348 ± 218
6	6.00	3130	3650 ± 1700	6844 ± 445
7	6.50	3213	5980 ± 2800	8503 ± 553
8	6.50	3303	8360 ± 3800	$15,273 \pm 993$
9	7.00	3513	$21,800 \pm 9600$	$23,010 \pm 1496$
10	7.50	3666	$28,500 \pm 12,000$	$31,150 \pm 2025$
11	8.00	3554	$24,800 \pm 11,000$	$32,734 \pm 2128$
12	8.00	3648	$29,500 \pm 13,000$	$34,713 \pm 2256$
steady state		1788	7990 ± 3700	$10,317 \pm 671$

Table 5.1 is depicted graphically in Figure 5.1. The error in $T_{j,max}$ for both m_{theory} and m_{exp} is ± 50 K.

Below 3200 K there is serious disagreement between the experimental and theoretical values. However, the agreement between theory and experiment for shots in which the peak surface temperature exceeded the melting point is excellent.

5.2. Discussion

5.2.1. Contamination Effects

It was postulated that the molybdenum crucible, which holds the uranium dioxide target, had solidified-molten uranium on it from previous laser shots and this was being heated by the laser. In addition, part of the laser beam does reflect from the surface of the target and strike the walls of the target vacuum chamber. Uranium coated on the walls from long operation could thus be heated this way.

Fig. 5.1. Mass of uranium collected versus Peak Surface Temperature.

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To verify that this was not a source of uranium contamination, the uranium dioxide target was replaced with a graphite disk and two 6.00 kV laser shots were fired. This resulted in 8 ng of uranium depositing on the collector. Clearly, this did not explain the large differences at low temperatures. This experiment also verified that the post-shot handling techniques did not contaminate the graphite. These handling techniques involve removing the uranium coated collector assembly from the target vacuum chamber and then carefully (with sterile vinyl gloves) removing the graphite from the collector assembly.

5.2.2. Vapor Pressure Dependence on Stoichiometry

The vapor in equilibrium with UO_{2x} does not consist simply of UO_2 molecules, but is a complex mixture of various species, including O, O_2 , U, UO , UO_2 and UO_3 molecules. Equation 3 assumes congruent vaporization. More correctly, the partial vapor pressure of all the uranium bearing species should be summed:

$$m_{\text{theory}} = 10.4 \sum_n \int \frac{p_n(t) dt}{\sqrt{\frac{M_n}{270} T_r(t)}}$$

where n represents all the uranium bearing species and M_n is the atomic weight.

The partial vapor pressures vary with x and T , as can be seen in Figure 5.2, taken from Storms.²⁸ The p - T relation from Tetenbaum and Hunt used for the temperature range below 3120 K in equation 3 of chapter 3 is the "total pressure of uranium-bearing species above stoichiometric uranium." Positive deviation from exact stoichiometry changes the vapor pressure substantially. Furthermore, the process of vaporization itself changes the oxygen-to-uranium ratio of the condensed phase. No single mixture of gases is an adequate approximation because the composition of the vapor will be sensitive to the extent of vaporization of the target i.e. low energy versus high energy laser shots. To be precise, account should be taken of the complex nature of the vapor in calculations of vapor properties.

The effect of non-congruent vaporization can be estimated as follows. The initial composition of the UO_2 specimen comes close to exact stoichiometry. Because UO_3 is the preferentially vaporizing species at this composition, heating causes a reduction in the surface O/U ratio. The

Fig. 5.2. A comparison between the partial pressures and the total pressure over various compositions of UO_{2-x} at 2000 K.

best thermochemical information on solid hypostoichiometric urania is that of Storms. He shows that the UO_2 partial pressure is independent of stoichiometry. In addition, for the small extent of sub-stoichiometry at the surface expected for laser shots which do not result in melting, UO_2 is the principle vapor species. The total pressure obtained by summing the partial pressures of the uranium bearing species is not significantly lower than that given by Tetenbaum and Hunt. This can be seen by comparing p given by Eq. (4b) at 2000 K (which is 1.4×10^{-7} atm) with the values of the total vapor pressure from Storm's plot (Figure. 5.2). The difference is no larger than 40%. Consequently the large discrepancies observed for the lower-energy shots can not be attributed to laser-induced hypostoichiometry of the evaporating surface.

5.2.3. Possible Effects of Surface Non-Stoichiometry Due to Atmospheric Oxidation

The uranium dioxide pellets were exposed to atmospheric air for days prior to being placed in the target vacuum chamber. Due to oxidation a thin surface layer could have become hyperstoichiometric. If this oxygen-rich region were thin enough, the high temperature shots would burn through it and vaporize principally the underlying nominally-stoichiometric uranium dioxide substrate. The low-temperature laser shots, however, would heat only the hyperstoichiometric surface layer.

There is an increase in the total pressure of uranium-bearing species over UO_{2+x} compared to that over $\text{UO}_{2.00}$. This could result in more uranium vaporization than expected in the low energy shots where only the high-vapor-pressure UO_{2+x} layer is affected by the laser pulse.

An experiment to test this possibility consisted of a 8.00 kV laser shot, with the collector retracted behind a shield; followed in 42 seconds by a 5.00 kV laser pulse with the shield removed and the collector exposed to the blow-off. The first laser pulse was intended to burn off the hyperstoichiometric outer layer, if any, and leave the bulk stoichiometric UO_2 exposed to the second low-temperature pulse. An 8.00 kV shot vaporizes approximately 2 μm of the target. To prove that the shielded collector was not contaminated by the initial cleaning pulse, an 8.00 kV laser shot was fired with the collector retracted. Only 5 ng was collected.

The quantity of uranium collected in the second low-energy shot with the unshielded collector was

only 30% less than that collected in the test without pretreatment of the surface. For a typical 5.00 kV shot $\frac{\sigma_m}{m_{theory}}=67.6\%$ and $\frac{m_{exp}}{m_{theory}}=10$. The 30% reduction is small compared to the accuracy of this work and certainly does not explain the order of magnitude discrepancy with theory.

The 5.00 kV shot is calculated to vaporize only the top 5 monolayers of the UO_2 surface. With a backpressure of 5×10^{-7} Torr there are enough water molecules striking the UO_2 target (if all stick and decompose) to cover the surface with 10^{16} oxygen atoms/cm² (10 monolayers) in 42 seconds. The adsorbed oxygen can then diffuse into the bulk and, given enough time, the near-surface stoichiometry and thus the uranium-bearing vapor pressure will increase.

The diffusivity of oxygen in UO_{2+x} has been reviewed by Breitung.²⁹ At 1500 K the diffusivity D is $2.5 \times 10^{-5} \frac{cm^2}{s}$. The diffusion penetration depth from a surface source is $\sim \sqrt{Dt}$. Thus in 42 seconds, surface oxygen could penetrate $\sim 320 \mu m$ into the oxide, provided that the surface reaction by which adsorbed oxygen is incorporated into the bulk as ions is not rate-limiting. For example, suppose the $10^{16} \frac{\text{oxygen atoms}}{cm^2}$ supplied by water vapor impinging on the surface are distributed uniformly over the first 1000 UO_2 monolayers. This would increase the O/U ratio from 2.000 to 2.015. With this initial O/U ratio the same temperature transient will evaporate 6 times as much uranium. Thus it is possible that even though this test was designed to remove an oxidized surface layer, oxidation nonetheless reoccurred and increased the amount of uranium evaporated. In addition, the rough unpolished surface of the target could have increased the effective surface area A_1 . This effect is important when only a few monolayers of UO_2 are evaporated.

5.2.4. Specimen Hyperstoichiometry

In contrast to the hypostoichiometric region, at low temperatures (2000 K) the total vapor pressure increases abruptly over a very narrow composition range from $UO_{2.00}$ to $UO_{2.01}$ (see Fig. 5.2). This very steep change in vapor pressure with composition makes any evaluation in the hyperstoichiometric side region near $UO_{2.00}$ very difficult at low temperatures. This marked change is the probable cause of differences in measured pressures reported for nominal UO_2 at low temperatures. As the melting point

(3120 K) is approached the vapor pressure variation with composition becomes more gradual. If the target is only slightly hyperstoichiometric (even after the surface cleaning pulse) this could explain why more uranium is collected below the melting temperature and why the theoretical amount is collected above the melting temperature.

5.2.5. SEM Analysis

A test was done to determine whether the vapor blowoff consisted solely of molecular vapor or also contained a condensed phase. The latter form could arise from liquid droplet ejection directly from the melt or explosive ejection at the surface from rapid expansion of gases in the pores.

For this test the graphite collector was replaced with highly-polished semiconductor-grade silicon wafers. The silicon surface is essentially featureless under a scanning electron microscope (SEM) and small particles on the surface can be identified easily.

A 7.00 kv $T_{s,max} = 3500K$ laser shot was fired and the silicon collector was analyzed by SEM. Most of the silicon wafer remained featureless. In a couple of isolated areas surface agglomerates were present (Figure 5.3). Their sizes ranged from 1 μm to 6 μm in diameter. Elemental X-ray analysis on these particles showed them to be composed of uranium. A high estimate of the amount of uranium on the disk shown in Fig. 5.3. is 6 ng. A typical 7.00 kV laser shot will evaporate 30,000 ng of uranium dioxide. Thus, the very small mass associated with the agglomerates does not effect the interpretation of the evaporation process as solely molecular.

Figure 5.4 shows the uranium target after an 8.00 kV laser shot ($T_{s,max} = 3600 K$). The left hand part of this target was shielded from the laser by the target holder. This unaffected region appears rough because the target was not polished. The smooth area to the right had melted, and verifies the pyrometer reading that the surface temperature had clearly exceeded the melting point (3120 K).

10 μm

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Fig. 5.3. Uranium condensed phases on silicon wafer substrate after 7.0 kV shot

Fig. 5.4. UO₂ Target after 8.0 kV laser shot showing laser-melted region to the right and unaffected region to the left.

6. CONCLUSION

The purpose of this experiment was to determine if the absolute amount of UO_2 vaporizing from a laser-heated target corresponds to the amount predicted by the Hertz-Langmuir formula, with a gas dynamic correction applied for surface temperatures above 2700 K (Fig. 1.1).

The results of the neutron activation experiments presented here confirm the validity of the Hertz-Langmuir formula for laser pulses in which the UO_2 surface temperature exceeded the melting point. For surface temperatures lower than the melting point, the quantity of UO_2 collected exceeded the Hertz-Langmuir predictions by as much as a factor of 40. The best explanation for this discrepancy is slight hyperstoichiometry, either of the surface layer or of the entire specimen bulk, which greatly increases the UO_3 vapor pressure. However, a steady state vaporization test at low temperature vaporized a quantity of uranium entirely consistent with the prediction of the Hertz-Langmuir formula.

A possible reason for the discrepancy between the mass spectrometer results for $T_{s,\text{max}} > 3120$ K and the free-molecular vaporization theory is the extensive condensation of the uranium oxides to produce "polymers" which would not be detected by the mass spectrometer used in these measurements. Such species would be deposited on the collectors in the present experiment, however, and lead to good agreement between the data and prediction.

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